

ASD-TDR-63-160

63-34
TR 62-460.7

403 810

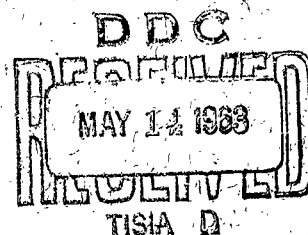
CATALOGED BY ASTIA
AS AD NO. 403810
HIGH TEMPERATURE OXIDATION-RESISTANT COATINGS
FOR TANTALUM BASE ALLOYS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-160

February 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force System Command
Wright-Patterson Air Force Base, Ohio

Project No. 7312, Task No. 731201



(Prepared under Contract No. AF 33(657)-7339 by the
General Telephone & Electronics Laboratories, Inc.,
Bayside, New York; L. Sama, Author.)

ASD-TDR-63-160

TR 62-460.7

OXIDATION RESISTANT COATINGS FOR
TANTALUM ALLOYS AND OTHER METALS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-160
February 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force System Command
Wright-Patterson Air Force Base, Ohio

Project No. 7312, Task No. 731201

(Prepared under Contract No. AF 33(657)-7339
by the General Telephone & Electronics Laboratories,
Inc., Bayside, New York; L. Sama, Author.)

FOREWORD

This is a final report prepared by the GT&E Laboratories under USAF Contract No. AF 33(657)-7339. This contract was initiated under Project No. 7312, Task No. 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 covers work conducted from 1 November 1961 to 30 November 1962.

Acknowledgment is made to Dr. R.H. Powers for performing the reduced pressure oxidation test evaluation and to B. Reznik for the mechanical test evaluation. The x-ray analyses and electron probe work were performed by P. Lublin. Coating work and other test evaluations were made by G.T. Pepino, Jr., D. Melone, and O. Haines, and metallography by H. Woods.

ABSTRACT

The effect of coating composition on structural changes and oxidation behavior was studied using a Sn-Al spray-slurry system with tantalum, tantalum alloys, columbium, tungsten and molybdenum. In tests conducted at 3000°F it was found that increased oxidation protection was most significantly related to the thickness of the tin-rich phase at the surface. The use of refractory metal powder additives plus excess aluminum to form aluminide particles served best to increase the thickness of this phase. Coating composition was optimized and an extensive evaluation was carried out with Ta-10%W, Ta-30%Cb-7.5%V, and Cb-5%Zr. In oxidation tests at 1100° to over 3000°F protective life was significantly affected by substrate composition, coating thickness and thermal cycling. Tensile and stress rupture data were obtained on coated samples at 2000 to 3000°F and correlated fairly well with data in the literature for uncoated material. Preliminary studies were made of coating stability at air pressures in the micron to millimeter range. Oxidation and diffusion effects were explored by metallographic electron probe and x-ray analysis. A brief study of Ta-10Hf-5W in contact with Al_2O_3 at elevated temperatures showed that this alloy was unstable in contrast to pure tantalum, Ta-10W, and Ta-30Cb-7.5V, which were quite stable.

Oxidation data were obtained for several tantalum alloys coated with Ti-Si. A diluent system was sought for beryllide-type coatings in which Sn, Cu, Si, and Ag were investigated. The use of silver as a slurry base was found to be most promising, but was not extensively evaluated.

This technical documentary report has been reviewed and is approved.



I. PERLMUTTER

Chief, Physical Metallurgy Branch
Metals & Ceramics Laboratory
Directorate of Materials & Processes

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. TIN-ALUMINUM COATINGS	3
2.1 Background	3
2.2 Slurry Process Development	4
2.3 Effect of Coating and Base Metal Composition	5
2.4 Development of Thicker Coatings	13
2.4.1 Refractory Additives to Increase Coating Viscosity	13
2.4.2 The Use of Surface Treatments to Obtain Thicker Coatings	25
2.5 Coating-Substrate Stability	28
2.6 Diffusion Treatments in Various Protective Atmospheres	37
2.7 Pack Coatings	38
2.8 Duplex Coating Techniques and Sn-Al-Y Compositions	39
2.9 Boundary Condition Experiments	43
2.9.1 Sn-Al Alloy Oxidation Behavior	45
2.9.2 Intermetallic Compounds	46
2.9.3 Al_2O_3 -Alloy Reactions	46
3. EXTENDED EVALUATION OF SPRAYED SLURRY COATING PROCESS	53
3.1 Mechanical Property Evaluation	53
3.2 Furnace Oxidation Evaluation	70
3.3 Simulated Re-entry Pressure Oxidation Evaluation	89
4. ANALYSIS OF AIR-COATING-SUBSTRATE INTERACTION DURING OXIDATION	97
4.1 Metallographic Studies	97

TABLE OF CONTENTS (cont'd)

	<u>Page</u>
4.2 Electron Micro-Beam Probe Analyses	101
4.2.1 Pure Tantalum	110
4.2.2 Ta-10W Alloy	110
4.2.3 Ta-30Cb-7.5V Alloy	111
4.3 X-Ray Analyses	112
5. SILICIDE COATINGS	117
5.1 Sn-Si Slurries	117
5.2 Ti-Si Coating	117
6. BERYLLIDE COATINGS	123
7. DISCUSSION	131
8. SUMMARY AND CONCLUSIONS	135
9. RECOMMENDATIONS FOR FUTURE WORK	137
10. REFERENCES	139
APPENDIX I - Coating Materials	141

LIST OF ILLUSTRATIONS

1. Pure Tantalum After Double Coating With Various Alloys.
2. Tantalum Alloys and Columbium After Double Coating With Sn-25Al.
3. Tungsten and Molybdenum After Double Coating With Sn-25Al.
4. Double Coating of (Sn-25Al)-10TaAl₃ on Ta-10W.
5. Weight Gains of Sn-Al Coatings on Ta-10W at 2800°F.
6. Weight Gains of Coated Ta-10W Samples Tested at 2800°F.
7. Pure Tantalum Titanized and Slurry Coated With (Sn-25Al)-10TaAl₃.
8. Temperature Gradient and Coating Penetration in Ta-10W and Ta-30Cb-7.5V Samples Heated to 3000°F for 1/2 Hour.
9. Temperature Gradient and Coating Penetration in Ta-10W Samples Heated to 3000°F for 1/2 Hour.
10. Temperature Gradient and Coating Penetration in Ta-10W Samples Heated to 3000°F and 3200°F for 1/2 Hour.
11. Coating-Interface Penetration After One Hour Tests at Various Temperatures.
12. (Ta-30Cb-7.5V)Al₃ Arc-Melt #1.
13. Ta-10Hf-5W Samples Flame-Sprayed With Al₂O₃.
14. Tensile Properties of Ta-10W Samples.
15. Tensile Properties of Ta-30Cb-7.5V Samples.
16. Tensile Properties of Cb-5Zr Samples.
17. Stress-Rupture Curves for Ta-10W and Ta-30Cb-7.5V.
18. Stress-Rupture Curves for Cb-5Zr.

LIST OF ILLUSTRATIONS (Cont'd)

19. Ta-10W Tensile Samples.
20. Ta-30Cb-7.5V Tensile Samples.
21. Cb-5Zr Tensile Samples.
22. Ta-10W Stress-Rupture Samples.
23. Ta-30Cb-7.5V Stress-Rupture Samples.
24. Cb-5Zr Stress Rupture Samples.
25. Oxidation Life of Ta-10W Coated Samples at 3000°F.
26. Oxidation Life of Ta-10W Coated Samples at 2800°F.
27. Oxidation Life of Ta-10W Coated Samples at 2500°F.
28. Oxidation Life of Ta-30Cb-7.5V Coated Samples at 2500 and 2800°F.
29. Oxidation Life of Cb-5Zr Coated Samples at 1400, 2000, 2200 and 2400°F.
30. Cb-5Zr and Ta-30Cb-7.5V Oxidation Test Samples.
31. Ta-10W Oxidation Test Samples.
32. Weight Changes in Coated Samples at 0.1 Micron Pressure.
33. Coated Ta-10W Samples After Testing at 0.1 Micron Pressure.
34. Weight Changes in Coated Samples at Reduced Air Pressures.
35. Weight Gains of Coated Samples With Time.
36. Coated Ta-10W Sample After 1-1/2 Hours at 2770°F and 6 mm Pressure.
37. Ta-10W Coated With Sn-25Al and Tested at 3000°F for 5 Minutes.
38. Ta-10W Coated With Sn-25Al and Tested at 3000°F for 5 Minutes.

LIST OF ILLUSTRATIONS (Cont'd)

39. Ta-10W Coated With (Sn-25Al)-10TaAl₃ After 15 Hours Test at 2800°F.
40. Microhardness Traverses on Ta-30Cb-7.5V Coated Samples.
41. (Sn-50Al-Si)-10TaAl₃ Coatings on Ta-30Cb-7.5V.
42. (Sn-50Al-Si)-10TaAl₃ Coatings on Ta-30Cb-7.5V After Oxidation.
43. (Sn-50Al-Si)-10TaAl₃ Coatings on Ta-30Cb-7.5V After Oxidation.
44. (Sn-25Al)-10TaAl₃ Coating on Cb-5Zr After Oxidation.
45. Electron Probe Locations on Coated Pure Tantalum Samples.
46. X-ray Analysis of Coated Ta-10W.
47. Ti-Si Coatings on Ta-10W.
48. Slurry Cu-Be Coating on Ta-10W.
49. Hot Dipped Cu-Be Coatings on Ta-10W and Cb.
50. Slurry Ag-Be Coating on Ta-10W.

LIST OF TABLES

1. Furnace Oxidation Tests on Ta-10W Coated with Sn-25Al and Sn-50Al
2. Thermal Cycling Tests on Coated Ta-10W Tested in an Oxyacetylene Torch Flame
3. Resistance Heating Tests at 3000°F on Various Coatings
4. Furnace Oxidation Tests on Ta-10W
5. Furnace Oxidation Test Data for Ta-10W Coated with Various Additions to Sn-25Al Base
6. Oxidation Tests on Ta-10W Samples Double Coated with Sn-25Al Plus Additives
7. Oxyacetylene Torch Tests on Ta-10W and Ta-30Cb-7.5V Samples
8. Results of Furnace Oxidation Tests on Ta-30Cb-7.5V Coated with (Sn-25Al)-10TaAl₃
9. Effect of Coating Composition on Oxidation Resistance of Ta-30Cb-7.5V
10. Thermal Cycling Tests on Ta-10W and Ta-30Cb-7.5V Coated with (Sn-25Al)-10TaAl₃
11. Coating Data for Pure Ta Titanized and Slurry Coated with (Sn-25Al)-10TaAl₃
12. Furnace Oxidation Data for Pure Ta Titanized and Slurry Coated with (Sn-25Al)-10TaAl₃
13. Oxidation Tests on Alloys Coated by γ -Calorizing and Dipping
14. Oxidation Tests on Alloys Coated by γ -Calorizing and Dipping
15. Oxidation Tests on Ta-10W Coated by γ -Calorizing and Spray Diffusing
16. Oxidation Tests on Ta Coated with Sn-Al-Y Slurries
17. Weight Gain of Sn-Y-Al Slurry Coated Samples at Room Temperature

LIST OF TABLES (cont'd)

18. Arc Melted Buttons of (Ta-30Cb-7.5V)Al₃
19. Weight Gain of Arc-Melted Button Oxidized at Various Temperatures
20. Reactions between Tantalum Alloys and Flame Sprayed Al₂O₃
21. Tensile Test Data for Ta-10W Coated with (Sn-25Al)-10TaAl₃
22. Tensile Test Data for Cb-5Zr Coated with (Sn-25Al)-10TaAl₃
23. Stress Rupture Tests on Ta-10W and Cb-5Zr Coated with (Sn-25Al)-10TaAl₃
24. Tensile and Stress Rupture Tests on Ta-30Cb-7.5V
25. Furnace Oxidation Tests on Ta-10W Coated with (Sn-25Al)-10TaAl₃
26. Furnace Oxidation Tests on Ta-10W Coated with (Sn-25Al)-10TaAl₃
27. Low Temperature Furnace Tests on Ta-10W Coated with (Sn-25Al)-10TaAl₃
28. Furnace Oxidation Tests on Ta-10W Coated with (Sn-50Al)-10TaAl₃
29. Furnace Oxidation Tests on Ta Coated with Sn-Al
30. Furnace Oxidation Tests on Ta-30Cb-7.5V Coated with (Sn-50Al-Si)
31. Furnace Oxidation Tests on Cb-5Zr Coated with (Sn-25Al)-10TaAl₃
32. Coating-Substrate Interface Penetration in Furnace Oxidation Tests
33. Electron Micro-Beam Probe Analyses of Alloy Base Metal Composition
34. X-Ray Diffraction Analyses of Ta-10W Coated with Sn-25Al
35. Hot Camera X-ray Analysis of Ta-10W Coated with (Sn-25Al)-10TaAl₃

LIST OF TABLES (cont'd)

- 36. Coating Data for Pretitanized Alloys in Siliciding Packs**
- 37. Furnace Oxidation Data for Ti-Si Coated Alloys**
- 38. Berylliding Data for Samples Painted with Powder Slurries**
- 39. Silver Diluent Coating Treatments on Ta-10W Samples**

1. INTRODUCTION

Increasing interest in the use of tantalum alloys for elevated temperature applications has stimulated work in the development of high strength tantalum alloys¹ and protective coatings for tantalum alloys against high-temperature oxidizing environments. Coating programs sponsored by the Air Force have led to the development of silicide coatings at Battelle² and a promising tin-aluminum coating³ at Sylcor.* The program reported here is a continuation of the work performed at Sylcor.

The major objective of this program was to optimize the composition and method of application of the tin-aluminum coating and to evaluate reliability and performance of the optimum Sn-Al coating composition on tantalum-base alloys. It was also desired to obtain (1) further information on the applicability of this coating to molybdenum and tungsten and (2) a more extensive evaluation on a columbium alloy. A secondary objective was to develop a similar diluent matrix for beryllide coatings on tantalum alloys.

The alloys investigated were (1) commercially available Ta-10W and Cb-5Zr (D-14) obtained from NRC and Dupont, respectively, and (2) Ta-10Hf-5W and Ta-30Cb-7.5V. Both of the latter alloys, developed under Air Force sponsorship, were obtained from Battelle Memorial Institute. Effort was concentrated primarily on the Ta-10W alloy because of its ready availability.

In this report, the results are organized under the major coating systems discussed. The composition and identification of materials used for the coatings are listed in Appendix I.

* The research facility of Sylcor is now incorporated with the GT&E Laboratories. The manufacturing facility is located at Hicksville, L.I., New York.

Manuscript released by the author January 1963 for publication as an ASD Technical Documentary Report.

2. TIN-ALUMINUM COATINGS

2.1 BACKGROUND

It should be emphasized that the tin-aluminum coating is considered a coating system, and therefore it does not follow that one composition or one method of application will be optimum for all alloys, configurations, and service conditions. Excellent results with this coating have been obtained by hot dipping or by slurry coating followed by a diffusion treatment. The latter process has been more successful and more flexible and has therefore received the most attention to date. Most of the work in the past has been done on tantalum and on Ta-10W (percentages are in weight percent) with good protection to 3000°F. However, excellent results were also obtained with these coatings on pure molybdenum and tungsten at temperatures above 3000°F and on columbium alloys at 2500°F. Most of the early work on this program was with Sn-50Al; however, later results in the program showed that Sn-25Al has considerable promise. As deposited, the coating structure is essentially a layer of aluminide adjacent to the substrate and covered by a film of excess Sn-Al. Protection is essentially provided by the formation of an Al_2O_3 layer during exposure to an oxidizing atmosphere at high temperatures and by the repletion of this film by the Sn-Al layer. In order fully to understand and explain coating protection and its limitations, considerable information is needed regarding phase equilibria and oxide interactions. Unfortunately, little data of this type are available for the Ta-Sn and $\text{Ta}_x\text{O}_y\text{-Al}_2\text{O}_3\text{-SnO}_x$ systems. Of the metallic systems, only the Sn-Al diagram is available.⁴ In addition, certain compounds of tantalum and aluminum (TaAl_3 , Ta_2Al , and Ta_3Al)^{3, 4, 5, 10} and tantalum and tin (Ta_3Sn)⁴ have been reported. The existence of SnTa_2O_7 and $3\text{Al}_2\text{O}_3 \cdot 2\text{Ta}_2\text{O}_5$ is also known,^{6, 7} but no double compounds of aluminum oxide and tin oxide have been reported. Little information has been found regarding ternary compounds in either of the metal¹⁰ or oxide systems.

Data on the physical properties of various phases in these systems is even sparser. Melting points are, for the most part, uncertain. Of the metal compounds, only TaAl_3 is oxidation-resistant.^{3, 5} However, in aluminum alloy dipped tantalum samples, we have shown that when TaAl_3 was completely consumed by interdiffusion and replaced by Ta_2Al , the original Al_2O_3 film was protective to the Ta_2Al .³ Tin has fairly poor oxidation resistance in the liquid state, and its behavior has been reported to be dependent on the particular orientation of the crystallites in the oxide film.⁸

Considerable protection is reported to be afforded by as little as 0.01% aluminum additions.⁹ The extremely high boiling points of both tin and aluminum (4500-4800°F) indicate protection can theoretically be extended to fairly high temperatures close to the melting point of Al_2O_3 (3650°F).

2.2 SLURRY PROCESS DEVELOPMENT

In the development of the Sn-Al coatings, the refractory metal alloys were prepared and coated as follows: The sheet material was sheared to size, a hole drilled in one end to accommodate a tantalum suspension wire, and the sample then blasted with a steel grit. Pre-blended tin and aluminum powders were mixed with a lacquer and then applied to the surface by spraying. The proportion of lacquer to metal depends on which application process is to be used. Most of the work was done by cold spraying, in which case the proportion of lacquer to metal was 1:1 by volume. For painting or dipping processes, a 1:2 proportion of lacquer to metal was used. The lacquer should be quite fluid, fast drying, and have a low residue in vacuum firing at elevated temperatures. After air drying the sample was fired in a vacuum furnace at approximately 1900°F for one-half hour. Most of the work was done at a pressure of approximately 1 micron or less. In order to build up the coating thickness and to insure added reliability, a second coat was applied in the same manner. The as-coated samples were smooth and lustrous with a metallic appearance. However, during the diffusion process the aluminum in the tin reacted with the substrate to form an aluminide layer, and some of the Sn-Al phase which was enriched in tin drained off to form a blob or lump at the bottom of the sample. The amount of excess Sn-Al was greater with higher tin composition, but its size also depended upon the size and configuration of the part being coated. Considerable effort has been made on the present program to remove this excess material and also to prevent its occurrence.

Samples were evaluated at temperatures up to 3000°F by furnace testing. Testing at higher temperatures required the use of an oxyacetylene torch or heating the samples by their own resistance. In the past, arc plasma tests to temperatures over 3000°F have also been performed and have indicated an ability of the coating to withstand substantial gas flow at very high temperatures.

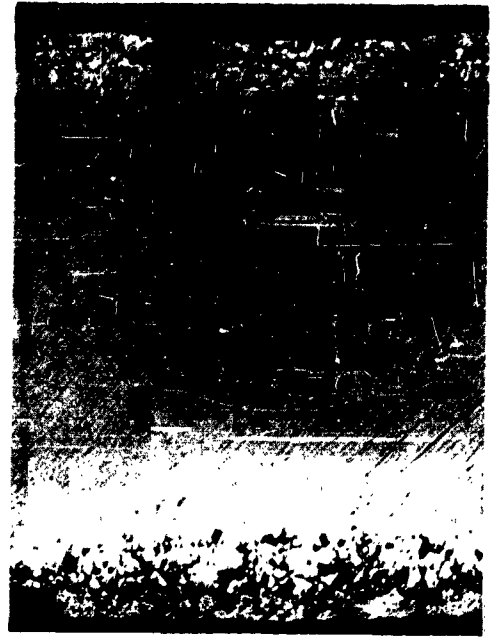
Initial tests were made on samples prepared in triplicate and coated with Sn-15Al, Sn-19Al, Sn-25Al, Sn-30Al and Sn-50Al. Pure tantalum, Ta-10W, Ta-10Hf-5W, and pure columbium, molybdenum and tungsten were examined for comparison. Considerable data were obtained regarding variations in coating behavior by weighing samples at various stages of preparation. The excess lump at the drain-off end of the sample was largest on the tantalum alloys, indicating less reaction with the coating in diffusion. Most of the samples had a bright sheen; however, with increasing aluminum in the coating, the edges of the molybdenum and tungsten samples thickened and the samples lost their glossy appearance. Later metallographic examination showed the edges to be striated or laminated, probably as a result of shearing in sample preparation.

Before testing, the lump of excess SnAl on each sample was removed by heating the end and brush leveling with a wire. A number of samples at the higher aluminum compositions had no appreciable lump, particularly on the molybdenum and tungsten materials, and therefore needed no leveling.

Both the coating and the substrate composition have an effect on the coating thickness, as shown in Figs. 1, 2, and 3. Therefore, it is quite difficult to change the original coating composition and keep other parameters constant, particularly the coating thickness. In all cases, the coating consists of an intermetallic compound layer next to the substrate covered with a film of Sn-Al alloy. The intermetallic compound, which is highly active under polarized light, has been identified as MAl_3 for both the tantalum and columbium alloys. No identification has been made for tungsten and molybdenum. The coatings are characteristically spongy on the pure metals, in contrast to the more well defined interface between the compound and the excess Sn-Al phase on the alloys. The effect of increasing the aluminum content from 15 to 50% Al (see Fig. 1) is to give a thicker coating, mainly by increasing the intermetallic thickness. The aluminum concentration gradient is the main driving force for the diffusion reaction and the reaction is rapid at 1900°F ; consequently, the residual aluminum content in the tin after diffusion is probably the same or approximately the same with all the coatings. This has been calculated to be about 5 to 10% Al. Oxidation tests on Sn-Al alloys appear to verify this range by the superior oxidation resistance of these compositions in the 1 to 50% Al range.



(a) Sn-15Al coating



(b) Sn-25Al coating

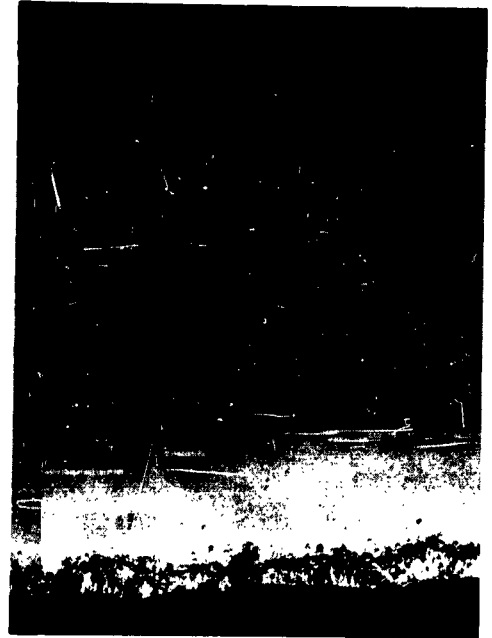


(c) Sn-50Al coating

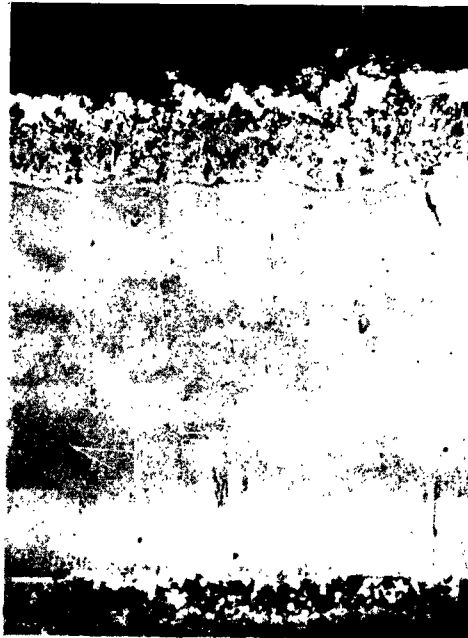
Fig. 1. Photomicrographs of cross sections of pure tantalum after double coating treatment with various alloys. (200X)



(a) Ta-10W alloy

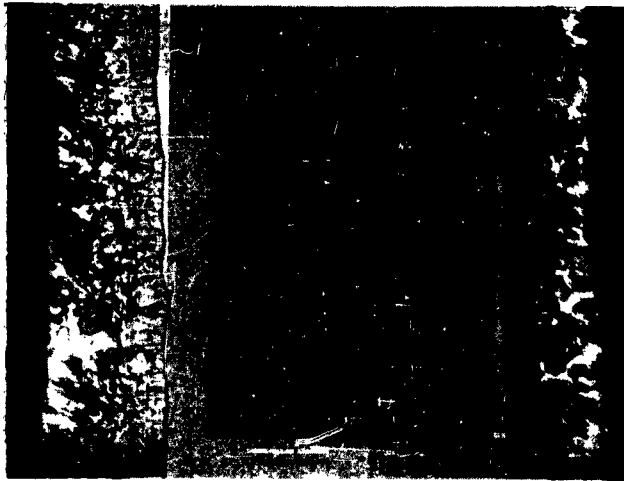


(b) Ta-10Hf-SW alloy

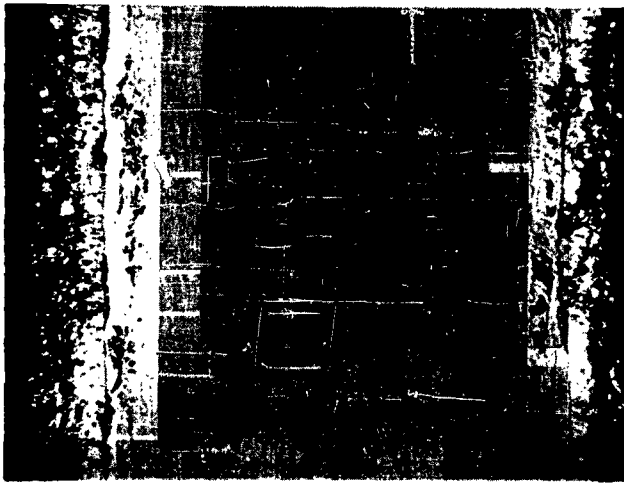


(c) Columbium

Fig. 2. Cross sections of tantalum alloys and pure columbium after double coating with Sn-25Al. (200X)



(a) Tungsten



(b) Molybdenum

Fig. 3. Samples of tungsten and molybdenum after double coating with Sn-25Al. (200X)

In the past³ it was found that oxidation protection was afforded by the Sn-25Al and Sn-50Al coatings on Ta-10W at a temperature of approximately 3300°F for five minutes in an arc plasma torch, and on molybdenum and tungsten at 3350 to 3450°F for almost an hour in oxyacetylene torch tests. In present furnace tests at 2500°F, coatings with 15 to 50% Al protected molybdenum for 8 hours, and 15 to 25% Al coatings protected tungsten for the same time. At 2000°F all of the coatings protected tungsten for 8 hours, however the molybdenum samples had appreciable weight losses with 15 to 25% Al coatings, only the Sn-50Al coating being protective for 8 hours.

Tests of the Sn-Al coatings on tungsten at 2500°F indicated the probability of an intergranularly attacked surface layer. In another program at these Laboratories, it has been found that tungsten wires coated with Sn-Al failed unusually quickly when a stress was applied to the sample at elevated temperature, thus verifying the probability of intergranular attack. This has not been found to be the case with molybdenum or molybdenum alloys.

In similar tests on pure tantalum samples at 2000°F and 2500°F, no failures were noted. The only significant behavior was that the Sn-50Al coating gave the highest weight gains at both test temperatures. This was found to be the general behavior for all substrates.

With the Ta-Hf-W alloy, protection at 2500°F appears to be inversely proportional to the aluminum content in the Sn-Al coating, failing in 1 to 4 hours in furnace tests with 15 to 50% Al coatings. At 2000°F the Sn-50Al coating failed in 4 hours, but the others gave excellent protection for 8 hours; oxidation rates were quite slow. The Ta-10W alloy samples with the Sn-25Al and Sn-50Al coatings failed in less than 8 hours at 2500°F. The other coatings were protective for 8 hours at both 2500 and 2000°F. Similar early failures were obtained with several other coatings on the pure columbium material. These early failures did not appear to be consistent with past performance of this type of coating at these temperatures. Therefore it was felt that the treatment involved in removing the excess Sn-Al from the samples had a detrimental effect. This contrast in behavior was illustrated by duplicate coupon samples which had only one spray diffusion coat of Sn-25Al and Sn-50Al and which did not have the excess Sn-Al removed from the end of the sample. Results of tests at 2000, 2500, and 2800°F on these samples are shown in Table 1. These coatings lasted almost 100 hours at 2500°F and 29 hours at 2800°F with the Sn-25Al coating providing slightly better protection than the Sn-50Al coating at all temperatures.

TABLE 1
Furnace Oxidation Tests on Ta-10W
Coated with Sn-25Al and Sn-50 Al

Run No.	Sample No.	Coating	Test temp. (°F)	Time to failure (hours)	Remarks
U-155-17	5	Sn-25Al	2000	743	O.K. -stopped test
"	6	"	"	743	-
"	7	Sn-50Al	"	232	-
"	8	"	"	407	-
"	1	Sn-25Al	2500	93-109	-
"	2	"	"	93-109	-
"	3	Sn-50Al	"	88- 93	-
"	4	"	"	88- 93	-
U-155-20	9	Sn-25Al	2800	29	O.K. -stopped test
"	10	"	"	29	O.K. -stopped test
"	11	Sn-50Al	"	29	O.K. -stopped test
"	12	"	"	22- 29	-

It was apparent from these results that removal of the excess Sn-Al reservoir at one end was detrimental, and also that considerable protection was afforded by a single coating treatment. Because of the reservoir effect, the thickness of the substrate becomes critical with higher aluminum compositions. To study this effect, samples 0.01 in. and 0.04 in. thick were coated with Sn-25 and Sn-50Al and were thermally cycled using an oxyacetylene torch. In these tests, the flame was directed at a point about one-quarter of the length from the free end of the sample which had the excess lump of Sn-Al. Therefore, a temperature gradient radiates outward in all directions from the directly heated area, about 1/2 in. in diameter. At the beginning of the test and after each 100 cycles, the samples were given a 30-minute isothermal exposure at 2500°F. Some of the samples were preoxidized in a furnace before testing. The results of these tests are shown in Table 2.

The Sn-25Al coating gave excellent protection for 400 cycles. However, the first two Sn-50Al samples did not fail by oxidation but rather distorted and cracked at the hot zone. Preoxidizing the Sn-50Al coating gave significantly improved behavior, although not as good as the Sn-25Al coating. On thicker samples little difference was noted in the effect of aluminum composition. Samples with Sn-19Al were used for further comparison of composition effects. In most cases, the Sn-25Al coating appeared to be slightly superior.

The poorer behavior of the Sn-25Al coating on the thicker Ta-10W substrates indicated that removal of the excess lump of Sn-Al was detrimental. With the thicker samples, however, the flame side must be heated slightly hotter to give a 2500°F reading on the air side, and where a large temperature gradient exists on the sample, the cooler portions act as an aluminum reservoir for the rest of the sample. Wherever the temperature is about 1200°F and the coating contains a liquid phase, aluminum diffuses rapidly through the liquid phase to all areas of the sample and serves to heal any breaks in the protective Al_2O_3 film. This behavior is considered a primary advantage of this type of coating. However, if the substrate is thin enough and the reservoir heavy enough, the residual free aluminum may react with the substrate sufficiently to form a complete thickness of aluminide. It was quite evident, therefore, that any excess Sn-Al lump on the ends of samples would have to be removed or prevented from forming before any further critical evaluation of this type of coating could be performed on a laboratory scale.

TABLE 2

Thermal Cycling Tests on Coated Ta-10W Samples Tested in an Oxyacetylene Torch Flame.

(Cycle is one minute at 2500°F and 1/2 minute at black heat.)

Run No.	Sample	Substrate thickness	Coating	2500°F test time, (hours)	No. of cycles	Remarks
U-155-23	1	0.010	Sn-25Al	10.5	400	O.K.
"	2	"	Sn-50Al	0.8	18	Cracked - hot zone
"	3	"	"	0.7	12	Bulged - hot zone
U-155-24	4*	0.010	Sn-50Al	4.8	167	Failed - hot zone
U-155-35	1	0.040	Sn-25Al	5.7	253	Melting - flame side
"	2	"	Sn-50Al	5.7	253	Melting - flame side
U-173-36	1	0.040	Sn-50Al	2.5	123	Failed - air side
-36	2	"	Sn-25Al	3.3	166	Failed - both sides
-37	3	"	Sn-19Al	3.1	155	Failed - flame side
-37	4*	"	Sn-50Al	3.2	100	Failed - flame side
-37	5*	"	Sn-25Al	3.2	100	O.K.
-37	6*	"	Sn-19Al	3.2	100	Failed - flame side

Note: All samples except first four had excess Sn-Al removed from test end before testing.

* Preoxidized entire sample in furnace at 2500°F for 1 hour before testing.

2.4 DEVELOPMENT OF THICKER COATINGS

2.4.1 Refractory Additives to Increase Coating Viscosity

In coating samples larger than coupons the excess Sn-Al run-off not only caused the formation of a lump at the end of the sample, but also limited the thickness of the Sn-Al overlay. Therefore, attempts were made to increase the viscosity, and thereby the thickness of the coating by adding to it refractory components such as Cr, Ti, Ta, Mo, W, and Al_2O_3 . Additives that tended to form intermetallic aluminide particles in the excess Sn-Al phase were most successful in preventing run-off. The best results were obtained initially with additions of tantalum and excess aluminum to form TaAl_3 particles. The structure is illustrated in Fig. 4. Later, it was found that the addition of molybdenum and excess aluminum to form " MoAl_3 " particles was more effective in preventing run-off, so that thicker coatings could be obtained with this additive. About 10% of an additive to Sn-25Al appeared to give optimum results; weight gains appeared equivalent as shown in Fig. 5. In order to provide a nondestructive basis for comparison, the unit coating weight has been adopted as an average indication of the thickness.

The efficacy of the (Sn-25Al)-10 TaAl_3 coating on larger samples is indicated in Table 3. These samples were oxidized at 3000°F by resistance heating, i.e., passing an electrical current through the sample. For this type of test most of the sample could be heated to 3000°F with a small, sharp thermal gradient zone near the water-cooled grips. The sample with the 10 MoAl_3 additive to the coating gave the longest life, 35 minutes and 7 thermal cycles. However, the coating was somewhat thicker than that on the sample with the 10 TaAl_3 additive.

It should be noted that in this type of heating, the surfaces of the sample may be appreciably cooler than the interior. Therefore, diffusion reactions may proceed a little more rapidly than with other heating methods. Also, owing to the heavy grips, there are stresses set up which are absent in other forms of heating. However, these conditions do not nullify the conclusions derived from the test results.

The optimum amount of additive was derived from furnace test data obtained at 2000, 2800, and 3000°F with hourly thermal cycles as listed in Table 4. There appeared to be very little difference in protectiveness during the 8-hour time period for the 10% or 20% TaAl_3 additives to the coating. In fact, all three compositions tested survived 10 hours at 3000°F. However, as shown in Fig. 6, the rate of weight gain with the

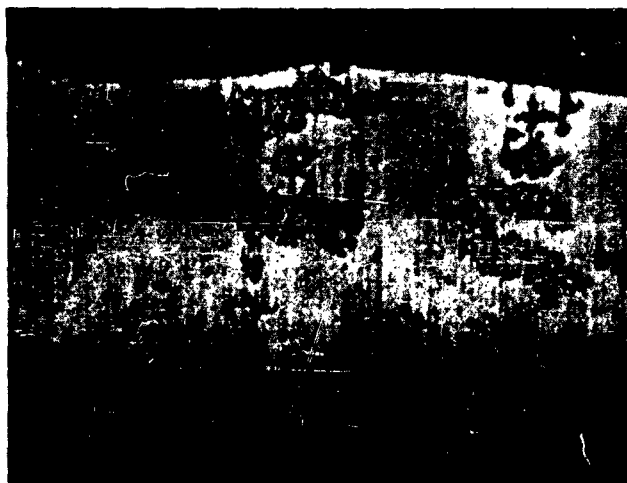


Fig. 4. Double coating of (Sn-25Al)-10TaAl₃ on Ta-10W. (750X)

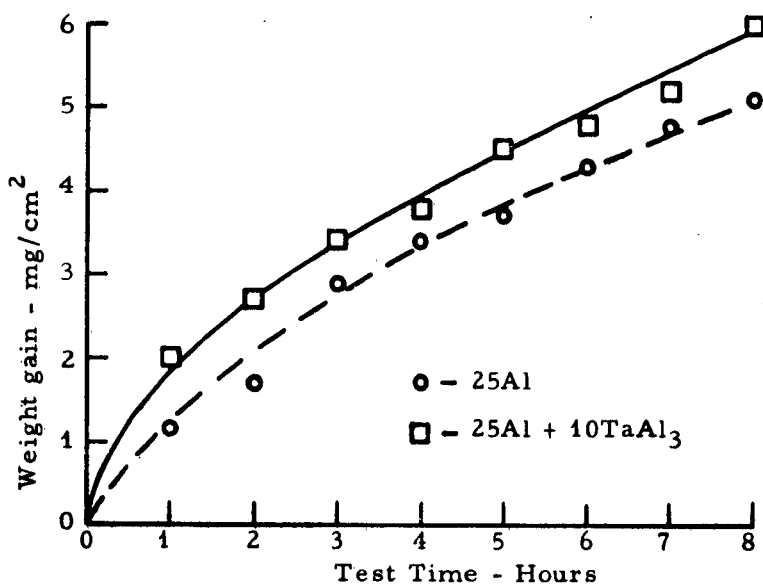


Fig. 5. Oxidation weight gains of Sn-Al coatings on Ta-10W in furnace tests at 2800°F. Samples were 0.010" x 1/2" x 3/4" and end lump was not removed.

TABLE 3

Resistance-Heating Tests at 3000° F on Various Coatings

Run No.	Alloy	Sample	Size (inches)	Coating	Test time (min.)	No. of cycles	Failure location
171-34	Ta-10W	1	0.04 x 3/4 x 1-3/4	Sn-25Al	5*	1	Edge & center
"	"	4	"	Sn-25Al	5	1	Center
"	"	2	"	Sn-25(Al- 5Cr-5Ti)	11	2	Center
"	"	3	"	"	15	3	None
173-53	Ta	1	0.04 x 1 x 2	Sn-25Al	7	1	Center
"	"	2	"	Sn-25(Al- 5Cr-5Ti)	7	1	Center
173-54	Ta-10W	3	"	Sn-25Al	5*	1	Center
"	"	4	"	Sn-25(Al- 5Cr-5Ti)	11	2	Center
173-59	Ta-10W	1	0.04 x 1/2	Sn-25Al (3 coats)	9	1	Center
173-60	"	5	"	(Sn-25Al)- 10TaAl ₃	27	5	Center
173-63	"	7	"	(Sn-25Al)- 10TaAl ₃	24	4	Center
173-63	"	8	0.04 x 1 x 2	Sn-50Al	1	-	Center
174-6	"	1	0.04 x 0.5 x 4	(Sn-25Al) 10MoAl ₃	35	7	Center

* Failed on reheating.

TABLE 4

Furnace Oxidation Tests on Ta-10W

Run No. U-473-	Coating comp.	Coating weight (mg/cm ²)	Test temp., (°F)	Test time, (hrs.)	Weight gain (mg/cm ²)	Remarks
94-1	(Sn-25 Al) 10 TaAl ₃	72	2000	8	8.8	O. K.
94-3	(Sn-25 Al) 20 TaAl ₃	89	2000	8	2.0	O. K.
94-4	(Sn-15 Al) 10 TaAl ₃	80	2000	8	0.6	O. K.
65-1	(Sn-25 Al) 10 TaAl ₃	60	2800	8	6.6	O. K.
65-2	(Sn-25 Al) 20 TaAl ₃	89	2800	8	12.6	O. K.
65-3	(Sn-15 Al) 10 TaAl ₃	70	2800	8	4.7	O. K.
84-2	Sn-25 (Al-5 Cr-5 Ti)	-	2800	7	8.6	Failed
84-3	(Sn-25 Al)*-Al ₂ O ₃	-	2800	5	5.3	Failed
84-4	(Sn-25 Al)*-Al ₂ O ₃	-	2800	8	7.0	O. K.
87-1	(Sn-25 Al) 10 TaAl ₃	70	3000	10	7.3	O. K.
87-2	(Sn-25 Al) 20 TaAl ₃	88	3000	10	12.0	O. K.
87-3	(Sn-15 Al) 10 TaAl ₃	75	3000	10	8.1	O. K.

* Excess Sn-Al removed from one end.

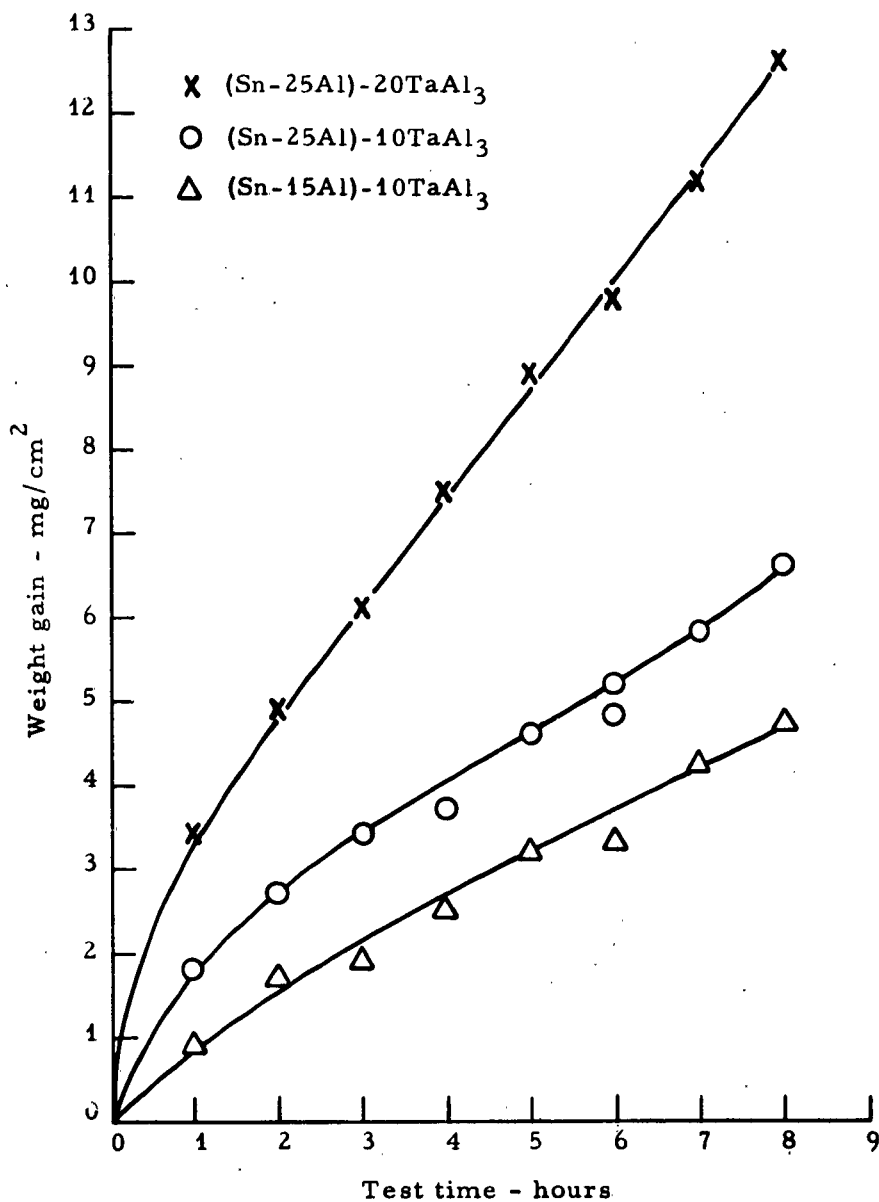


Fig. 6. Weight gain curves of coated Ta-10W samples tested at 2800°F.

20% TaAl₃ sample was higher than the two others. Although the (Sn-15Al)-10TaAl₃ coating weight gain rate was the lowest, there were some indications during the coating process that wetting of the substrate was marginal. Therefore, the (Sn-25Al)-10TaAl₃ composition was selected as optimum.

Although the addition of chromium and titanium to the Sn-25Al spray served to increase the coating thickness somewhat, it did not reduce run-off to any appreciable degree. The additions of 5 and 10% Al₂O₃ to the Sn-25Al spray did prevent run-off and gave comparatively thick coatings. However, the Al₂O₃ tended to separate out at the surface and form a powdery, flaky layer. Therefore this approach was abandoned.

The effect of Ta, Mo, W, and Cr additives on furnace test oxidation behavior at lower thermal cycling rates are shown in Table 5. These data indicate that the tantalum and molybdenum additives are superior. Several runs were made at 2800°F in which neither additive demonstrated a clear-cut superiority. However, it was later demonstrated that much heavier coatings could be applied with the molybdenum additive without encountering run-off.

Further comparison was made at 1100, 1400, and 2000°F and the data are shown in Table 6. The molybdenum additive appeared to be superior to the tantalum additive under these test conditions.

As a result of promising results obtained later with Ta-30Cb-7.5V, a few experiments were made to determine the effect of silicon additions to the coating. The results of oxidation tests at 2500 and 2800°F with (Sn-50Al-Si)-10TaAl₃ coatings on the Ta-Hf-W alloy were not particularly promising; failure occurred in 1 to 2 hours. No significant improvement was obtained on the Ta-10W alloy; a (Sn-25Al-Si)-10TaAl₃ coating was protective for 8 hours at 2800°F, but the (Sn-50Al-Si)-10TaAl₃ coating failed in 5 hours.

In order to determine maximum temperature capabilities and some measure of erosion resistance, coated samples were tested in an oxy-acetylene torch flame. The flame was concentrated about 1/2 in. from one end of the sample, and control was attained by moving a torch toward or away from the sample and monitoring the temperature continually by means of an optical pyrometer. No correction was made for emissivity. The results obtained on both Ta-10W and Ta-30Cb-7.5V samples are tabulated in Table 7. It was felt that a flame or plasma sprayed overlay of Al₂O₃ would improve the erosion behavior of the Sn-25Al coating;

TABLE 5

Furnace Oxidation Test Data for Ta-10W Coupons,
0.01" x 1/2" x 3/4" Coated with Various Additions
to the Sn-25 Al Base.

Sample	Addition Comp. Coating	Coating Weight (mg/cm ²)	Test Temp. (°F)	Test Time (hrs.)	Cycles	Failure Location
U 160-48-24	10TaAl ₃	58.9	2800	33	3	Edge
U 160-76-1	10MoAl ₃	58.9	2800	98-104	4	Destroyed
U-160-76-6	10Mo ₃ Al	58.8	2800	9-25	2	Destroyed
U-160-77-3	10WAl ₃	57.2	2800	9-25	2	Destroyed
U-160-77-7	10W ₃ Al	60.7	2800	27	3	Destroyed
U-160-48-26	10TaAl ₃	61.8	3000	7-8	8	Edge
U-160-76-2	10MoAl ₃	61.8	3000	10-11	10	Destroyed
U-160-48-29	10TaAl ₃	63.6	2800	70	5	Edge
U-160-76-3	10MoAl ₃	62.9	2800	73	6	Destroyed
U-160-77-5	10MoAl ₃	65.2	2800	22-25	4	Destroyed
U-160-77-4	10WAl ₃	62.3	2800	22-25	4	Destroyed
U-160-77-6	10W ₃ Al	66.6	2800	25-26	4	Hole
U-160-83-1	CrAl	58.1	2800	18-21	3	Destroyed

TABLE 6

Oxidation Tests on Ta-10 W Samples Double Coated
With Sn-25Al Plus Additive

Sample No. U160-	Additive in Coating	Coating Wt. (mg/cm ²)	Test Temp. (°F)	Life		Failure Location
				(hours)	(cycles)	
48-28	10 TaAl ₃	58	1100	43	21	Hole
87-4	10 MoAl ₃	50	1100	120	41	Good
87-3	10 MoAl ₃	54	1100	92	34	Bottom corner
48-30	10 TaAl ₃	53	1400	132-148	46	Top corner
87-1	10 MoAl ₃	45	1400	150	48	Good
87-2	10 MoAl ₃	49	1400	150	48	Good
48-27	10 TaAl ₃	58	2000	71	22	Spalled face
87-6	10 MoAl ₃	44	2000	100	34	Good
87-6	10 MoAl ₃	50	2000	100	34	Good

TABLE 7

Oxyacetylene Torch Tests on 0.04 in. x 1/2 in. x 2 in. Ta-10W and 0.020 in. x 1/2 in. x 2 in. Ta-30Cb-7.5V Samples

Run no.	Alloy	Coating comp.	Coating weight (mg/cm ²)	Temp., (°F)	Time, (min.)	No. of cycles	Remarks
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-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	114	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-160-93-11	Ta-W	(Sn-25 Al) 10 MoAl ₃	51	3200	80	-	Failed
U-160-93-12	Ta-W	(Sn-25 Al) 10 MoAl ₃	57	3200	120	-	O. K.
U-160-93-13	Ta-W	(Sn-25 Al) 10 MoAl ₃	54	3300	45	-	Failed
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	6	-	O. K.
				3300 max.	-	-	Failed
U-160-2-2	Ta-Cb-V	(Sn-25 Al) 10 TaAl ₃	Thick	2400-3150	6	-	O. K.
				3270 max.	-	-	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

however, the thin Al_2O_3 sprays gave a nonuniform emissivity to the overall coating and made it quite difficult to select a good 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 under these test conditions. It was significant that the plasma sprayed sample had the excess tin-aluminum at one end removed before the Al_2O_3 overlay was made, and appeared to fail at a lower temperature than did the others. This indicated that under these conditions the subcoating was more important.

Most of the coatings on the Ta-10W are quite heavy. The best results were obtained with the two Sn-25Al coated samples that did not have the excess Sn-Al at one end removed. One sample was tested for two hours at 3375°F (optical) with eight 15-minute thermal cycles without failure.

The other results on Ta-10W indicate that the maximum optical temperature attainable is approximately 3450°F . This probably corresponds to the temperature at which the Al_2O_3 film melts. There is some protection at temperatures up to approximately 3400°F for at least several minutes. At temperatures up to 3350°F , protection for one hour appeared attainable. Although these tests show that the Sn-25Al coating gave the most protection, the refractory metal additives minimized the formation of the excess lump and provided a thicker coating over the entire sample, thus reflecting a more practical means of protecting larger and longer samples.

The (Sn-25Al)-10TaAl₃ coating was not quite as protective to the Ta-30Cb-7.5V alloy as on Ta-10W. Results of furnace tests at 2500 to 3000°F are shown in Table 8. 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 in. thicker overall. The Sn-25Al coatings were much heavier because of the excess Sn-Al at one end and gave better protection.

At 2500°F the failure sites were dark in color and grew progressively to form a solid oxide. At 2800°F failure 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.

As indicated in Table 7 the TaAl₃ modified Sn-25Al coating on the Ta-Cb-V alloy 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 capability is closer to 3000°F .

TABLE 8

Results of Furnace Oxidation Tests on Ta-30Cb-7.5V Coated with (Sn-25Al)-10TaAl₃ and Sn-25Al

Run No.	Sample	Coating composition	Coating weight (mg/cm ²)	Test temp., (°F)	Test time, (hrs)	Remarks
U-173-91	1	Sn-25Al	95	2000	8	O.K.
U-173-97	A	(Sn-25Al)-10TaAl ₃	Thick*	2500	8	O.K.
U-173-97	1	(Sn-25Al)-10TaAl ₃	27.6	2500	2	Hole failure
U-173-97	2	(Sn-25Al)-10TaAl ₃	27.6	2500	8	O.K.
U-173-84	1	Sn-25Al	85	2800	8	O.K.
U-160-3	5	(Sn-25Al)-10TaAl ₃	24.2	2800	2	O.K.
U-160-3	6	(Sn-25Al)-10TaAl ₃	23.9	2800	3-8	Failed
U-160-3	7	(Sn-25Al)-10TaAl ₃	23.9	2800	3-8	Failed
U-160-3	9	(Sn-25Al)-10TaAl ₃	23.2	2800	3	Failed
U-160-3	10	(Sn-25Al)-10TaAl ₃	Thin*	2800	4	Failed
U-160-3	11	(Sn-25Al)-10TaAl ₃	21.5	2800	6-8	Failed
U-160-7	1	(Sn-25Al)-10TaAl ₃	48.6	2800	7-8	Failed
U-160-7	2	(Sn-25Al)-10TaAl ₃	57.9	2800	8	Failed
U-173-87	4	Sn-25Al	84	3000	4	Failed
U-160-3	3	(Sn-25Al)-10TaAl ₃	28.1	3000	2	O.K.
U-160-3	4	(Sn-25Al)-10TaAl ₃	23.8	3000	2	O.K.

* Exact weight not determined.

In furnace tests at 1100 and 1400°F, duplicate samples of this alloy were in excellent condition after 260 hours, thus indicating the absence of any low-temperature anomaly with this coating-alloy combination within any reasonable time interval.

Since the (Sn-25Al)-10TaAl₃ coating appeared to give only borderline 8-hour protection to Ta-30Cb-7.5V at the thick end of the coating range, the effect of coating composition was investigated further. The results of furnace oxidation tests are tabulated in Table 9. Aluminum additions higher or lower than 25% were not particularly advantageous. However, the use of a prealloyed Al-11% silicon powder appeared promising. 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 indicated there was no low-temperature anomaly.

Thermal cycling tests were performed with the (Sn-25Al)-10TaAl₃ coating on a Ta-Cb-V alloy specimen and on a Ta-10W sample for comparison. The cycling regimen is similar to that reported in Table 2. The test results are listed in Table 10. The samples have excellent thermal cycling resistance and survived 400 cycles at 2500°F without failure. The Ta-10W sample was subsequently heated to 2700°F in a furnace for one hour without failure. Similar tests were not run on Sn-(50Al-Si)-10TaAl₃ coated samples. A more extensive furnace testing program was performed instead.

2.4.2 The Use of Surface Treatments to Obtain Thicker Coatings

Two techniques were used to treat the surfaces of pure tantalum coupons in order to deposit heavier protective coatings. The first was to deposit a porous layer of pure tantalum over the solid substrate to act as a sponge in soaking up the Sn-Al phase. This was done by spraying a slurry of tantalum powder in lacquer onto pure tantalum sheet coupons and then vacuum sintering at 3800°F for one hour. The resultant tantalum coatings averaged 1.7 to 2.9 mils thick, but thinned out at the edges; porosity was estimated from weight, thickness, and metallographic evidence to be approximately 30%. Metallographic examination of samples with Sn-25Al slurry overlays showed incomplete wetting and poor oxidation resistance. Therefore, coating was completed by hot dipping in Sn-10Al at 1800°F for 10 minutes. Oxidation resistance was good, but not better than Sn-Al slurry coated samples without porous tantalum bases. Thicker tantalum coatings were applied, but showed no advantage. It is felt that

TABLE 9

Effect of Coating Composition on Furnace Oxidation Resistance of Coated Ta-30Cb-7.5 Coupons.
All Coatings Modified by Addition of 10% TaAl₃. (Al-Si) is Al-11% Si Alloy Powder.

Run No	Coating comp. w/o (bal. Sn)	Coating weight, (mg/cm ²)	Test Temp., (°F)	Test Time, (hrs)	Weight gain (mg/cm ²)	Remarks
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.

TABLE 10

Oxyacetylene Torch Thermal Cycling Tests on Ta-10W and Ta-30Cb-7.5V Samples Coated with
a Thick Layer of (Sn-25Al)-10TaAl₃.
(Samples thermally cycled once every minute.)

Run No.	Sample	Test temp., (°F)	Time (hrs)	Cycles	Remarks
U-173-95	Ta-W	2500	6.6	400	O.K.
		2700 (furnace test)	1		O.K.
U-173-100	Ta-Cb-V	2500	6.6	400	O.K.

this technique is feasible for obtaining thicker coatings, but considerably more work would have to be done in refining the technique to obtain better edge coverage and more uniform coatings. In special cases, for small parts, it may prove advantageous.

During the course of a separate coating project performed at these Laboratories, it was found that precoating a pure tantalum part with titanium considerably reduced run-off of the excess Sn-Al slurry. Therefore, a number of pure tantalum test coupons were titanized by heating them in vacuum for 16 hours while packed in titanium sponge. The coupons were then given a (Sn-25Al)-10TaAl₃ slurry overlay. The coating data are listed in Table 11. The equivalent titanium thickness applied is quite thin at 1900°F, but served to soak up the Sn-Al slurry and prevent run-off. A photomicrograph of the structure obtained is shown in Fig. 7. Results of the oxidation tests on these samples are listed in Table 12.

Although the titanium serves to absorb the Sn-Al coating and prevent run-off, it also decreases the oxidation resistance of the coating at very high temperatures in comparison with previous tests on non-titanized material. Data at temperatures lower than 2500°F were not obtained. However, it is believed that titanium should enhance lower temperature behavior.

2.5 COATING-SUBSTRATE STABILITY

Coating-substrate interface movement was studied as a function of temperature first on locally heated samples and later on oven-heated samples. The torch-heated samples, approximately 0.01 in. x 1/2 in. x 1 1/2 in., had reference notches at 1/8 in. intervals along one edge. Temperature was measured optically below each notch during heating. The temperature profile of the sample could then be plotted as a function of distance from one end. First, samples of Ta-10W and Ta-30Cb-7.5V were coated with (Sn-25Al)-10TaAl₃ and tested in an oxyacetylene torch for 1/2 hour at 3000°F. Metallographic samples were used to obtain the penetration data shown in Fig. 8, penetration being the term used to represent the coating substrate interface movement. It is interesting to note that on the Ta-10W sample, penetration is not a maximum at the 3000°F maximum temperature location but at a point corresponding approximately to a temperature of 2300°F. In contrast, the Ta-Cb-V alloy behaves more normally, that is, maximum penetration occurs at the point of maximum temperature and there is no anomalous behavior at 2300°F.

TABLE 11

Coating Data for Pure Tantalum Coupons Titanized for
16 Hours in Vacuum While Packed in Sponge Titanium,
and then Slurry-Coated with (Sn-25Al)-10TaAl₃

U 160-72 Sample	Ti coating			
	Temp. (°F)	Weight (mg/cm ²)	Equiv. thickness (inches)	Sn-Al coating wt. (mg/cm ²)
1	1900	1.0	0.0001	55.1
2	1900	1.0	0.0001	52.9
3	1900	1.0	0.0001	59.4
4	2200	13.9	0.0012	57.9
5	2200	13.9	0.0012	54.6
6	2200	13.9	0.0012	58.0

TABLE 12

Furnace Oxidation Test Data for Pure Tantalum
Coupons Titanized and Slurry-Coated With
(Sn-25Al)-10TaAl₃

U 160-72 Sample	Ti-coating	Test temp. (°F)	Test time to failure (hrs)	Remarks
2	Thin	3000	3-4	General
4	Thick	2800	1-2	General
1	Thin	2800	7-8	Edges
5	Thick	2500	3-4	Edges
3	Thin	2500	18-19	Edges



Fig. 7. Pure tantalum titanized and slurry-coated with $(\text{Sn-25Al})\text{-10TaAl}_3$. Coating 58 mg/cm^2 . (250X)

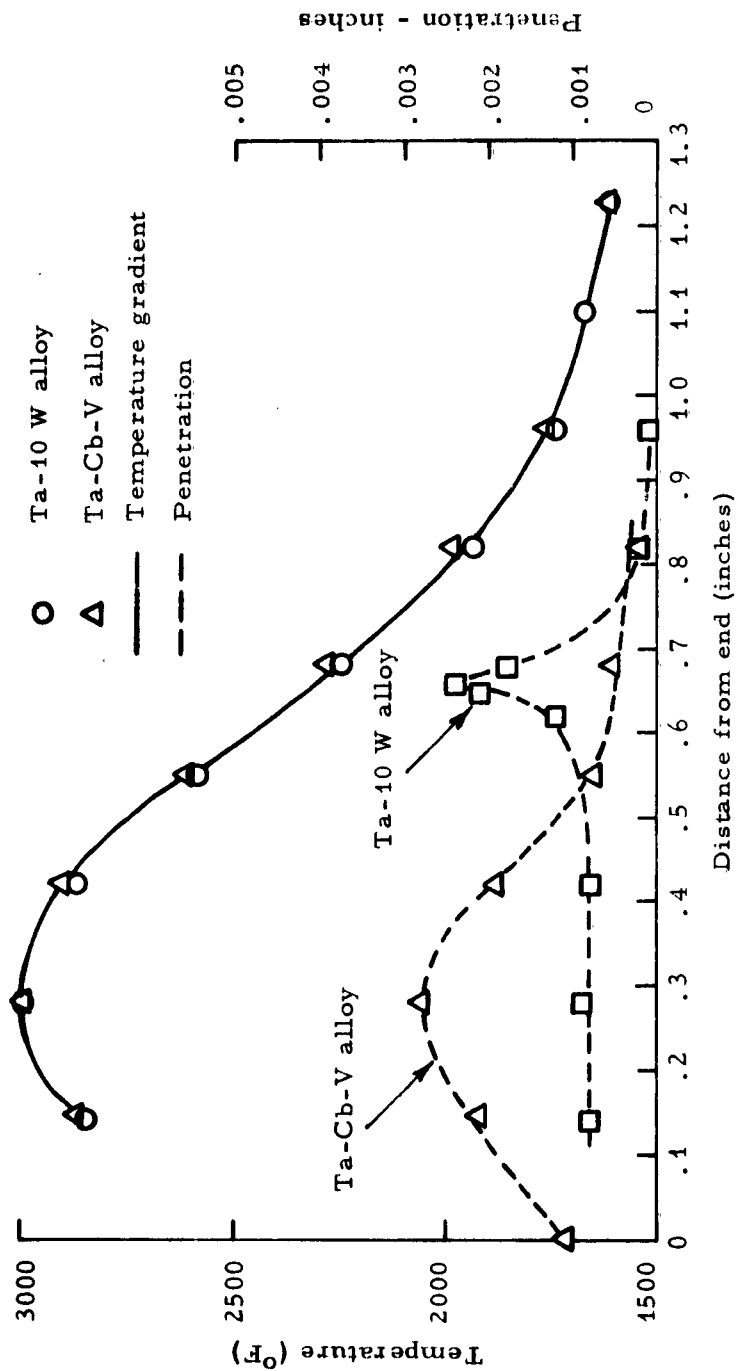


Fig. 8. Temperature gradient and coating penetration in samples of Ta-10 W and Ta-Cb-V alloys coated with (Sn-25 Al) 10 TaAl₃ and heated in an oxyacetylene torch at 3000°F for 1/2 hour.

In order to get a relatively larger excess of Sn-Al at one end of the sample, a second Ta-10W specimen was coated with Sn-25Al. In addition the sample was heated to 3000°F at a more central location along its length. As shown in Fig. 9, maximum penetration increased significantly and again occurred at a location equivalent to approximately 2300°F. However, this phenomenon occurred at a point between the excess Sn-Al lump and the maximum temperature point, but not at an equivalent location on the other side of the 3000°F location from the excess Sn-Al. From these tests it was apparent that the amount of interaction between coating and substrate is mainly dependent on the Sn-Al excess phase reservoir and that this interaction is a maximum at around 2300°F.

Two additional samples of Ta-10W were coated so that during coating treatment any tendency toward an excess Sn-Al run-off would occur at the end not to be heated in test. One sample was then heated for a half-hour at 3000°F and the other at 3200°F. Results are shown plotted in Fig. 10. Penetration has actually been defined as interface migration, since diffusion zones have not been too well delineated, even in carefully prepared samples. In the present case, the 3000°F test sample revealed a more well-defined diffusion zone, with a maximum interaction corresponding to the 3000°F location. However, a deeper interface penetration was noted at a location approximating 2200°F. On the 3200°F sample no diffusion zone was delineated; the maximum penetration occurred at 2340°F but was somewhat less than in the 3000°F sample. Both samples showed less penetration than previous ones coated in the position which allowed even a small excess of Sn-Al towards the end heated later in test. From the lower penetration data on the 3200°F sample, it can be inferred that at the higher temperature the oxidation process consumes more aluminum than at lower temperatures and therefore reduces interaction with the substrate. This comparison can be made because both samples had practically the same coating weight.

Furnace tests were used to check isothermal behavior over a broad temperature range. Penetration data are illustrated in Fig. 11. The actual penetration data are given in the lower group of curves. In the upper group of curves the data are weighted so that variation in coating thickness are taken into account. The Ta-10W samples coated with (Sn-25Al)-10TaAl₃ show that a slightly faster diffusion rate occurs at 2300°F. Penetration then drops off with temperatures above 2300°F until a temperature of approximately 3000°F is reached. In contrast, the Ta-Cb-V alloy with a similar coating shows gradually increasing penetration with temperature from 2000 to 2800°F. With the coating

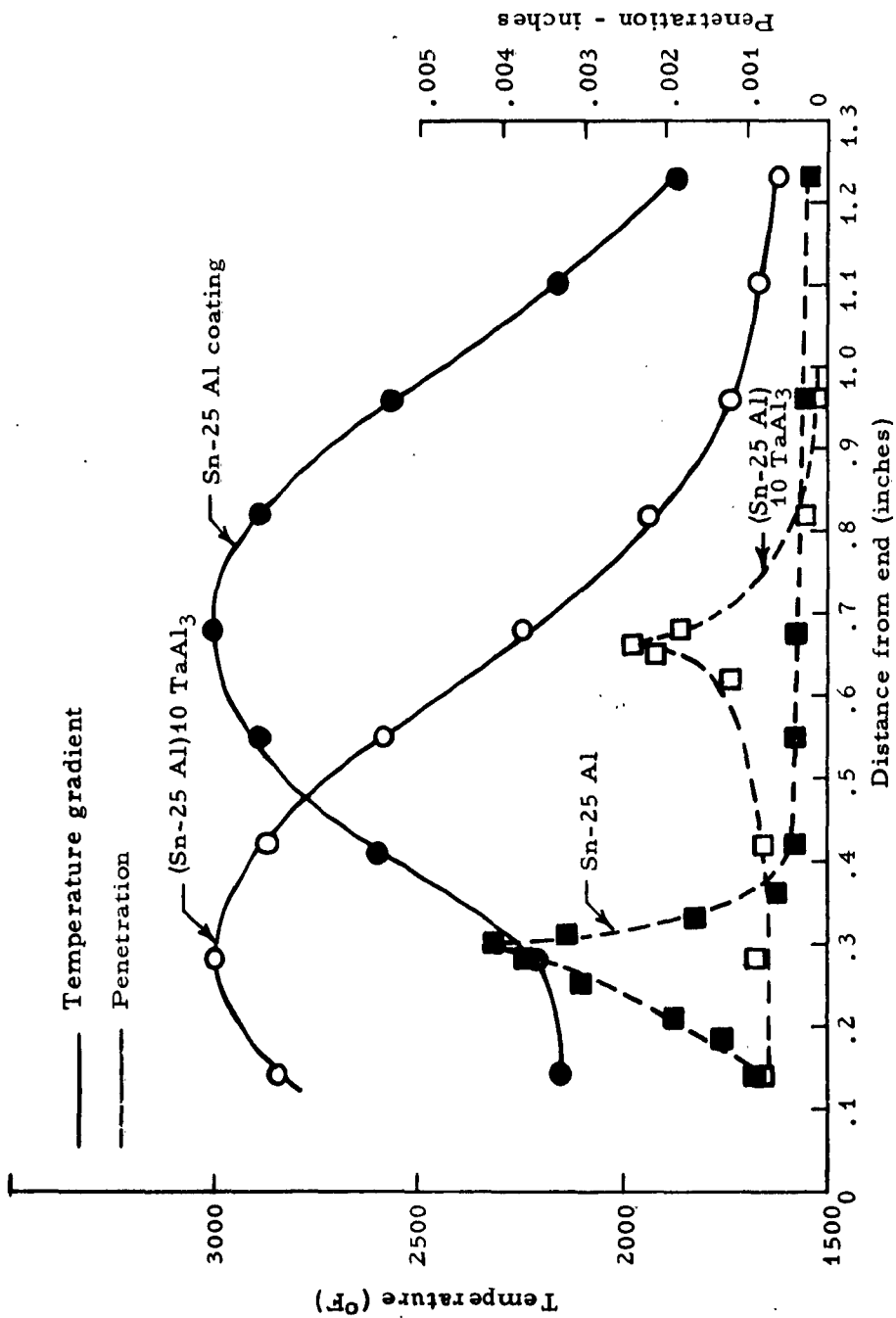


Fig. 9. Temperature gradient and coating penetration in samples of Ta-10 W alloys heated in an oxyacetylene torch at 3000°F for 1/2 hour.

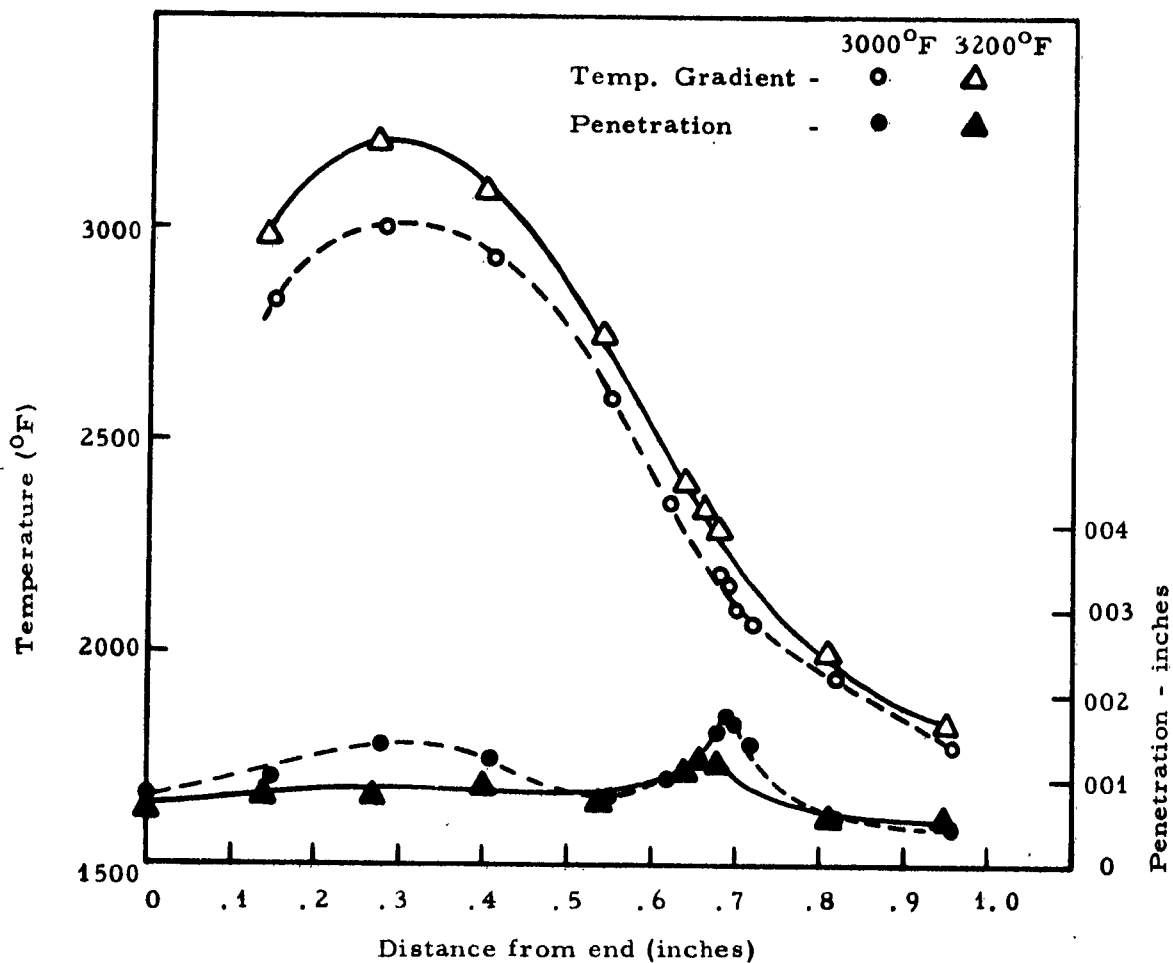


Fig. 10. Temperature gradient and coating penetration in Ta-10W samples coated with (Sn-25Al)-10TaAl₃ and heated in an oxyacetylene torch for 1/2 hour.

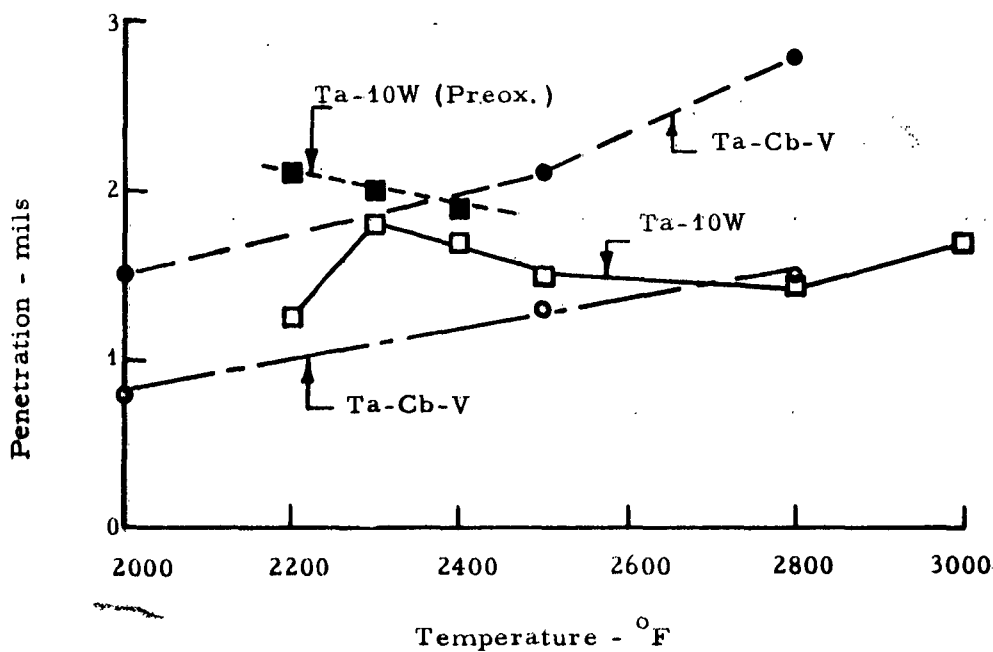
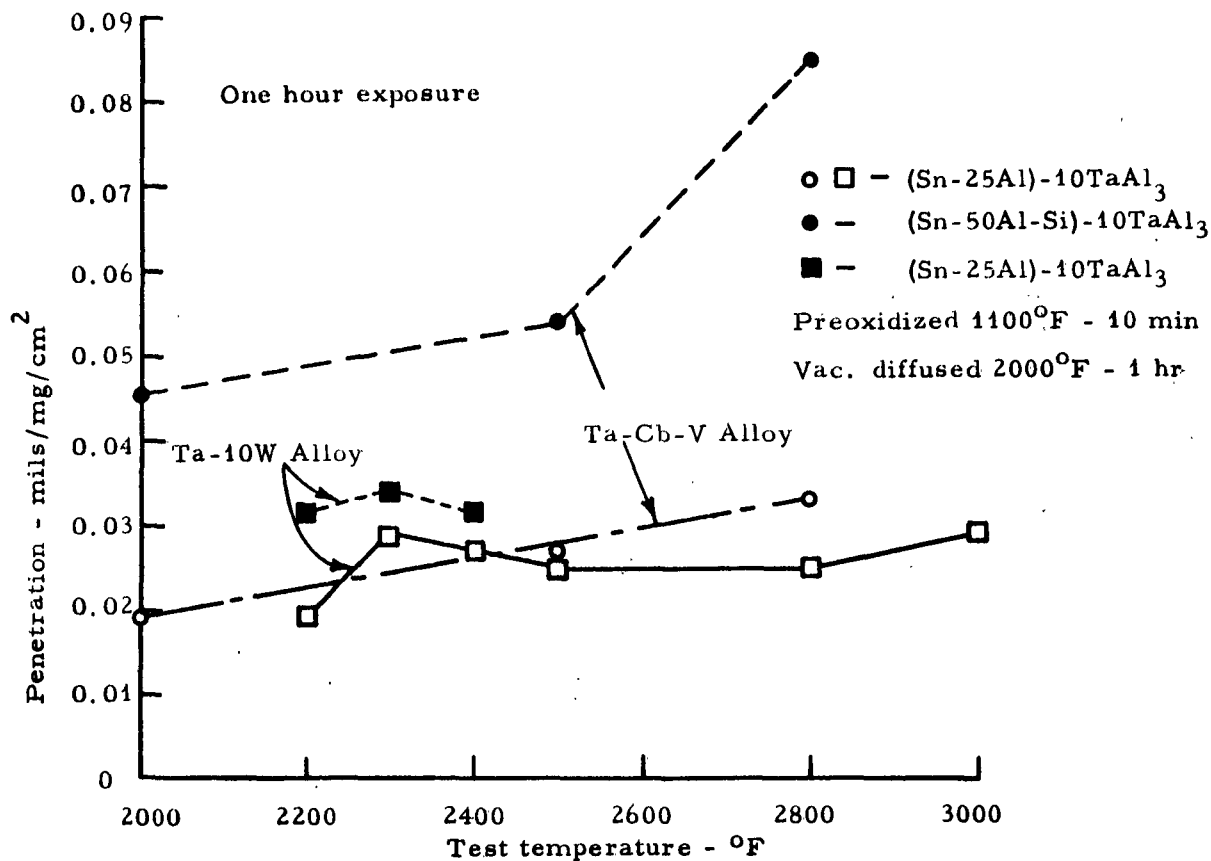


Fig. 11. Coating-interface penetration after one hour oxidation tests at various temperatures.

thickness taken into account, penetration appears to be more rapid in the Ta-Cb-V alloy. The (Sn-50Al-Si)-10TaAl₃ coating has much higher penetration rates over the same temperature range than the lower aluminum coating.

Metallographic examination showed the optically active MA1₃ intermetallic compound to persist to 2500°F with the (Sn-25Al)-10TaAl₃ coating on the Ta-Cb-V alloy, whereas no evidence of this phase is found on the Ta-10W alloy above 2200°F. With the 50Al-Si coating on Ta-Cb-V, this phase was detected even on the 2800°F sample. These findings corroborate to a degree the coating penetration effects noted, since the high aluminum surface concentration provides the driving force for diffusion.

Attempts were made to provide a diffusion barrier by preoxidizing samples before coating. In order to get a visible oxide film and barely measurable weight gain, it was necessary to heat Ta-10W samples in air to 1000°F for 15 minutes. The film was then diffused inward in vacuum at 1900°F for 1/2 hour. However, subsequent attempts to slurry coat with Sn-Al resulted in areas that were not wetted. Additional coupons were oxidized in air at 1100°F for 10 minutes, forming a tenacious, blue oxide film. The samples were then vacuum-diffusion treated for 1 hour at 2000°F prior to coating with slurry coatings of (Sn-25Al)-10TaAl₃. Complete coverage was obtained.

In subsequent penetration treatments in air at 2200°, 2300°, and 2400°F for 1 hour, all samples had incipient failures, mainly at the suspension holes, which indicated these were small unwetted areas. Penetration data for these samples are also listed in Fig. 11. The coating weighted plot in the upper graph indicates that, if anything, penetration was greater than in samples not preoxidized. Maximum interaction was again obtained at 2300°F. It is significant that an as-coated sample showed no evidence of an intermetallic compound layer, indicating erosion or delayed interaction during the coating treatment; however, particles of oxide were evident in the coating. A nonactive intermetallic layer was noted on the samples, with the 2300°F sample having the thickest layer.

2.6 DIFFUSION TREATMENTS IN VARIOUS PROTECTIVE ATMOSPHERES

The usual diffusion treatment involves heating the spray-coated samples to 1900°F for 1/2 hour under a vacuum pressure of 1 micron or less. For practical purposes, some attention was given to the feasibility

of using cruder atmospheres for the diffusion treatments. Sample coupons were spray coated with (Sn-25Al)-10TaAl₃. A good coating appearance was obtained with Ta-10W coupons treated in a vacuum system at 30 microns pressure, using only a mechanical backup vacuum pump. The resultant coatings were protective for eight hours at 2500°F and 2800°F.

Additional Ta-10W samples were diffusion treated in hydrogen. Although the samples were intact after removal from the hot zone, they completely disintegrated on cooling, probably as a result of internal hydriding.

On tungsten and molybdenum samples, the coatings wet satisfactorily in hydrogen on the first diffusion treatment, but were quite spotty after the second coat. Similar nonwetting spots were obtained on Ta-10W 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 behavior was confirmed by coating Ta-10W samples by resistance heating in a small bottle container which could be thoroughly purged of residual air. The resultant second coatings were excellent in appearance and completely wetted.

In connection with the latter treatments in argon, an anomalous 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 TaAl₃ but a lower aluminide, as is usually the case after such a temperature exposure, (2) there was an excess Sn-Al 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 Al₂O₃ film approximately 0.3 mils thick. No explanation has been formulated which explains all aspects of this anomalous behavior.

2.7 PACK COATINGS

Attempts were made to form both pure Al and Sn-Al coatings by pack cementation. Coatings approximately 4 mils thick were applied, using a pack with 40% Al-4%NH₄Cl-balance Al₂O₃. Pure Ta and Ta-10W samples were coated for one hour at 2300°F in argon; Ta-30Cb-7.5V

samples were coated at 1900°F for 4 hours in argon. In tests at 2800°F the Ta samples failed within 2 hours and samples of both alloys failed within 4 hours. Ta-30Cb 7.5V samples were also tested at 2500°F. The coatings were protective for 28-33 hours.

It was possible to get Sn-Al type coatings by pack cementation on pure Ta, Ta-10W, and Ta-30Cb-7.5V samples. The typical bright, lustrous, tin-covered surface was obtained most readily with the Ta-10W alloy. The effects of carrier, carrier concentration, temperature, and time were studied together with several different pack compositions. To get tin-rich surfaces, it was necessary to have low aluminum concentrations in the pack relative to tin. NH_4Cl appeared to be the best carrier for this purpose; however, it was not possible to obtain very thick coatings. The coatings ranged up to slightly more than 1 mil thick, the relative proportion of tin-rich phase being quite small. Oxidation tests at 2500°F indicated that relatively poor protection was provided by these thin coatings. For example, a Ta-10W sample coated at 1900°F for 16 hours in a Al_2O_3 -30 (Sn-10Al)-1% NH_4Cl pack failed within 2 hours at 2500°F. Failure occurred at an edge. A double treatment served to increase the coating thickness somewhat, but the sample failed within 3 hours at 2500°F. It should be emphasized that these coatings were still quite thin. In general, investigations at these Laboratories have shown that pack cementation-type coatings with aluminum can be made fairly heavy in the absence of tin and have fairly good isothermal oxidation resistance, but poor cyclic behavior. However, where short-time isothermal protection is required, in some cases it may be advantageous to provide a pack coating.

2.8 DUPLEX COATING TECHNIQUES AND Sn-Al-Y COMPOSITIONS

Other work at these Laboratories on columbium has indicated certain advantages in building up the Sn-Al coating by first producing an aluminide layer by pack diffusion, followed by an Sn-Al overlay by hot dip coating. The advantages appear to lie in a separate control over the thickness, uniformity, and composition of the aluminide and Sn-Al layers. Therefore, similar coating techniques were used on tantalum alloys.

Tables 13, 14 and 15 tabulate the results of high-temperature oxidation tests on calorized-dipped and calorized-spray diffused coatings. Calorizing was done by packing the samples in a preblended powder mix of Al_2O_3 , aluminum, and a chloride carrier, and firing the pack in argon. The calorized-hot-dipped coatings gave good protection at 2000°F on Ta-10W for 8 hours regardless of the aluminum composition of the cal-mix, and

TABLE 13

Oxidation Tests on Alloys Coated by Calorizing and Dipping

Run No.	Alloy	Coating treatment*	Coating thickness (mils)		Test time (hrs)	Weight gain (mg/cm ²)	Remarks
			Cal.	Dip			
<u>2000°F tests</u>							
U171-25	Ta-10 W-3	1	3.0	0.8	8	2.1	O.K.
U171-25	Ta-10 W-4	2	1.8	0.7	8	0.8	O.K.
U173-68	Ta-10 W-1	1a	3.0	0.5	8	0.9	O.K.
U173-68	Ta-10 W-2	2a	1.8	0.5	8	0.6	O.K.
U171-25	Ta-10 Hf-5 W-3	1	3.2	0.9	5	-	Failed
U171-25	Ta-10 Hf-5 W-4	2	2.5	1.3	8	10.0	O.K.
U173-68	Ta-10 Hf-5 W-1	1a	3.2	0.7	8	7.2	O.K.
U173-68	Ta-10 Hf-5 W-2	2a	2.5	0.7	8	8.3	O.K.
<u>2500°F tests</u>							
U171-25	Ta-10 W-1	1	3.0	0.8	2	-	Failed
U171-25	Ta-10 W-2	2	1.8	0.7	2	-	Failed
U173-65	Ta-10 W-1	1a	3.0	0.5	2	-	Failed
U173-65	Ta-10 W-2	2a	1.8	0.5	8	6.7	O.K.
U171-25	Ta-10 Hf-5 W-1	1	3.2	0.9	1	-	Failed
U171-25	Ta-10 Hf-5 W-2	2	2.5	1.3	2	-	Failed
U173-65	Ta-10 Hf-5 W-1	1a	3.2	0.7	1	-	Failed
U173-65	Ta-10 Hf-5 W-2	2a	2.5	0.7	1	-	Failed

* 1. Calorized in $\text{Al}_2\text{O}_3 + 20\text{Al} + 1\text{NH}_4\text{Cl}$ at 1900°F for 17 hrs; dipped in Sn-10 Al at 1700°F for 27 min.2. Calorized in $\text{Al}_2\text{O}_3 + 5\text{Al} + 1\text{NH}_4\text{Cl}$ at 1900°F for 17 hrs; dipped in Sn-10 Al at 1700°F for 2 min.1a. Calorized in $\text{Al}_2\text{O}_3 + 20\text{Al} + 1\text{NH}_4\text{Cl}$ at 1900°F for 17 hrs; dipped in Sn-10 Al-5 Zn at 1700°F for 10 min.2a. Calorized in $\text{Al}_2\text{O}_3 + 5\text{Al} + 1\text{NH}_4\text{Cl}$ at 1900°F for 17 hrs; dipped in Sn-10 Al-5 Zn at 1700°F for 10 min.

TABLE 14

Oxidation Tests on Samples Coated by Calorizing and Dipping. (Samples were calorized in $\text{Al}_2\text{O}_3 + 80\text{Al} + 10 \text{NH}_4\text{Cl}$ for 4 hours at 1900°F in argon followed by dipping in Sn-10Al-5Zn for 10 minutes at 1700°F .)

Run No.	Alloy	Coating thickness	Test temp. ($^\circ\text{F}$)	Test time (hrs)	Weight gain (mg/cm^2)	Remarks
U160-53	Ta-1	4.2	2500	8.0	3.4	O.K.
U160-53	Ta-10W-2	4.0	2500	6.0	6.4	Failed - 7 hrs
U160-53	Ta-30Cb-7.5V-3	4.0	2500	8.0	1.9	O.K.
U160-55	Ta-1	4.2	2800	6.0	7.6	Failed - 7 hrs
U160-55	Ta-10W-2	4.0	2800	7.0	7.6	Failed - 8 hrs
U160-55	Ta-30Cb-7.5V-3	4.0	2800	1.0	-	Failed

TABLE 15

Oxidation Tests on Ta-10 W Samples Coated by Calorizing and Spray Diffusing. (Samples were calorized in $\text{Al}_2\text{O}_3 + 40 \text{ Al} + 2 \text{ NH}_4\text{Cl}$ at 1900°F for 4 hours in argon followed by spray diffusing with (Sn-25 Al) 10 TaAl_3 .)

Run No.	Sample No.	Coating thickness (mils)	Test temp. ($^\circ\text{F}$)	Test time (hrs)	Weight gain (mg/cm^2)	Remarks
U160-33	1	4.5	2800	7	7.6	Failed - 8 hrs
U160-33	4	4.5	2800	8	6.1	O.K.
U160-43	3	4.5	1400	264	1.1	O.K.
U160-43	2	4.5	1100	264	0.2	O.K.

with slightly lower weight gains afforded by a zinc addition to the Sn-10Al hot dip. In contrast, protection was poorer and weight gains were much higher on the Ta-10Hf-5W alloy samples; the zinc additive again appeared slightly beneficial. However, at 2500°F the coatings were not nearly as protective. Only one Ta-10W sample survived 8 hours.

Better results were obtained on samples calorized in a mix containing a higher percentage of aluminum, resulting in a somewhat thicker coating. However, the protection given is not equivalent to, or superior to, spray diffused coatings developed in the past. In general, the hot dipped coatings do not appear to wet the calorized surfaces perfectly, and the resultant coatings were also not as smooth and striking in appearance as previous coatings.

A slightly thicker Sn-Al overlay was obtained by a single spray-diffusion treatment. These coated samples were well protected at 2800°F but again do not compare with the best previous spray diffused coatings. Low-temperature behavior at 1100 and 1400°F appeared to be excellent.

Several Sn-Al-Y compositions were used to slurry coat another series of tantalum samples. Yttrium was substituted for aluminum in varying degrees because, theoretically, it would not diffuse into the tantalum but would stay at the surface to help replenish formation of the protective oxide when the tin became depleted eventually in aluminum. The coating compositions used and the test results are listed in Table 16.

It was found that yttrium additions of 2 to 10% gave reasonably good protection at 2500°F, and marginal protection at 2800°F as long as the aluminum content was 25%. Lowering the aluminum content gave poorer coatings, which had a dull appearance and were thinner than with the other coating mixes. A close check was kept on as-coated samples to determine whether the coatings were stable in air. As shown in Table 17, all of the coatings had some weight gain after 66 hours at room temperature in air, with the higher yttrium samples having higher weight gain. Therefore, work was discontinued on this phase of the investigation.

2.9 BOUNDARY CONDITION EXPERIMENTS

Several limited investigations were carried out to indicate whether certain surface reactions might be responsible for limitations in maximum temperature capabilities of the coatings on the tantalum-base alloys.

TABLE 16

**Oxidation Tests on Tantalum Coupons Coated with
Sn-Al-Y Slurries**

Sample	Coating		Test temp. (°F)	Test time (hrs)	Weight gain (mg/cm ²)	Comments
	Mix. No. *	Wt.(mg/cm ²)				
U159-25-1	1	56.0	2500	30-32	6.6	-
-2	1	69.1	2800	7-8	5.4	Top edge
-4	2	35.4	2500	18-20	4.3	-
-6	2	51.9	2800	5-6	5.7	Hole failure
U159-28-10	3	32.5	2500	1	-	-
-11	3	32.9	2200	1	-	-
-12	3	34.7	2500	1	-	-
-16	4	36.1	2500	14-16	5.1	-

Mix No.

w/o	1	2	3	4
Sn	73	71	80	65
Al	25	25	10	25
Y	2	4	10	10

TABLE 17

Weight Gain of Sn-Al-Y Slurry Coated Samples at
Room Temperature in Air and in Argon After
66 Hours Exposure

Coating mix	Weight gain - mg	
	In air	In argon
1	0.02	Nil
2	0.02	Nil
3	1.4	0.03
4	3.5	0.02

2.9.1 Sn-Al Alloy Oxidation Behavior

To obtain a better idea of the oxidation protection of various tin-aluminum compositions as coatings, their behavior as bulk material was studied for comparison. Compositions up to 50% aluminum were prepared in the form of coupons approximately 1/8 to 1/4 in. thick x 1/2 in. wide x 3/4 in. long cut from cast ingots. In oxidation tests only rough approximations of weight gains were obtained, since the oxidation temperatures were far above the melting points of the alloys, with the result that the coupons changed shape slightly. However, where protection occurred, the oxide film held the sample together sufficiently to reveal certain trends in behavior. At 2500°F, after one hour exposure, voluminous nonprotective oxides were obtained on pure tin, Sn-1Al, and Sn-2Al. Alloys with 5, 10, 25 and 50% aluminum appeared protected for 8 hours with weight gains increasing with aluminum content. There was a considerable jump in weight gain in going from 10% aluminum to 25% aluminum. A similar relationship was noted at 2800°F.

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

2.9.2 Intermetallic Compounds

It is reasonable to assume that the large percentages of columbium and vanadium in the Ta-30Cb-7.5V alloy would lower considerably the melting point of the trialuminide formed on such an alloy compared with $TaAl_3$. Therefore 12 gram arc-melted buttons were prepared of (Ta-30Cb-7.5V) Al_3 for investigation. Since $TaAl_3$, $CbAl_3$, and VA_3 are isomorphous, no difficulty was expected in obtaining a solid solution.

The melts are listed in Table 18. 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. 12. 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°F 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.

Tests were performed at lower temperatures on samples taken from Melts No. 2 and 2-A. Oxidation behavior was excellent at 2200 and 2500°F for 8 hours; but an 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. Unmodified aluminide coatings might be expected to behave similarly on the Ta-Cb-V alloy in equivalent times. The Sn-Al base coatings, however, did not evidence this 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 19.

2.9.3 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 the part of the

TABLE 18

Arc-Melted Buttons of (Ta-30Cb-7.5V) 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



(a) as arc-melted (100X)



(b) after 8 hours oxidation at 2800°F
(100X)



(c) after 2 hours oxidation at 3000°F
200X

Fig. 12. (Ta-30Cb-7.5V) Al₃ Melt #1.

TABLE 19

Weight Gain of (Ta-30Cb-7.5V) 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

coating in contact with the Al_2O_3 protective film. To check these possibilities, samples of Ta-10W, Ta-10Hf-5W, and Ta-30Cb-7.5V 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. The results are tabulated in Table 20. The Ta-Hf-W was most reactive, the entire cross section becoming completely contaminated with but little residual surface oxide left at 3100°F and 3300°F. Representative photomicrographs are shown in Fig. 13. The Ta-10W 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.

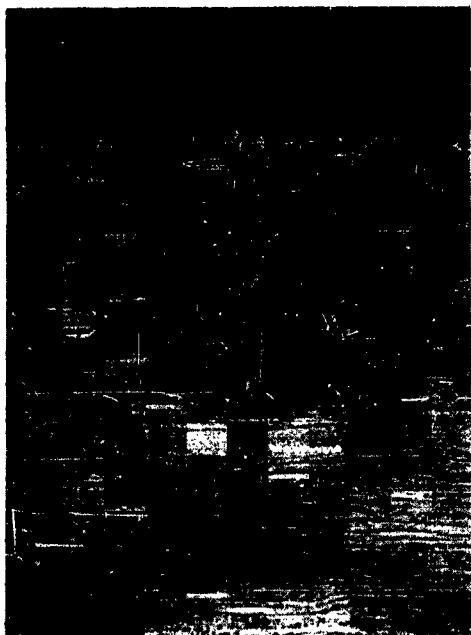
It should be noted that the as-flame-sprayed samples, particularly the Ta-10W alloy, showed some slight evidence of oxidation beneath the Al_2O_3 coating. This may have been the result of heating during the flame spraying process. It is possible that the later reactions with the Ta-10W alloy began as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

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

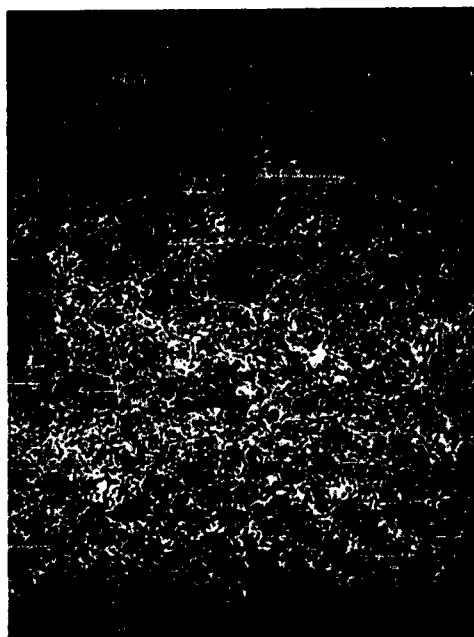
TABLE 20

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

Alloy	Condition	Heat treat., temp., (°F)	Reaction
Ta-10W	As-sprayed	-	Thin Oxide Beneath Al ₂ O ₃
		3100 3300	None Reaction Plus Grain Boundary Attack
Ta-10Hf-5W	As-sprayed	-	None
		3100 3300	Complete Reaction Complete Reaction
TA-30Cb-7.5V	As-sprayed	-	Possibly Thin Oxide Beneath Al ₂ O ₃
		3100 3300	None None



(a) as coated



(b) coated after 1/2 hr in vacuum at 3300°F



(c) non-coated sample after 1/2 hour in vacuum at 3300°F

Fig. 13. Ta-10Hf-5W samples flame-sprayed with Al_2O_3 . (500X)

3. EXTENDED EVALUATION OF SPRAYED SLURRY COATING PROCESS

In the later stages of the program, considerable effort was devoted toward obtaining data which would define in more detail protectiveness of the coating on alloys of interest to the Air Force. The work comprised three major areas of investigation. These included: (1) the determination of mechanical properties of coated alloys, (2) performing oxidation tests at various temperatures on batches of coated samples, and (3) determining the effects of low-pressure static reentry conditions on coating behavior. The alloys of interest included Ta-10W, Ta-30Cb-7.5V, and Cb-5Zr. Some work was also done with pure tantalum for comparison.

3.1 MECHANICAL PROPERTY EVALUATION

Tensile-type samples were machined from 0.040-in.-thick Ta-10W, 0.020-in.-thick Cb-5Zr (D-14), and 0.022-in.-thick Ta-30Cb-7.5V. Except for some room-temperature tests, the samples were 4 in. long x 1/2 in. wide with a 1/4 in. wide reduced section 2 in. long. The Ta-10W and the Cb-5Zr alloys were double spray slurry coated with (Sn-25Al)-10TaAl₃ and the Ta-30Cb-7.5V alloys coated with (Sn-50Al-Si)-10TaAl₃. For the elevated temperature tensile tests, the Ta-10W was thick enough to heat a 1 in. gage length to 3000°F by induction without using a susceptor. All of the other tensile and stress rupture test samples were heated by means of a susceptor sleeve in the form of 0.01-in.-thick material 1 in. in diameter x 2 in. long, roll formed and seam welded. Pure tantalum, molybdenum and Ta-10W were used as a susceptor material; the best results were obtained with Ta-10W coated with (Sn-25Al)-10MoAl₃. For the elevated temperature tests, samples were held at temperature for 15 minutes before starting the test. Stresses for the stress-rupture tests were selected from tensile data so as to obtain rupture lives up to a maximum of several hours or so.

The data are tabulated in Tables 21 through 24. Tensile strength data are shown plotted in Figs. 14, 15 and 16. In all cases the strengths were calculated on the basis of the original cross sectional area prior to coating. The strengths shown plotted for Ta-10W in Fig. 14 agree fairly well with data taken from the literature. Ductility of the coated samples was quite good at elevated temperatures; no visual evidence of oxidation at the fractures was noted in spite of the 8 to 30% deformation that occurred.

TABLE 24

Tensile Test Data for Ta-10W Samples Coated with
(Sn-25Al)-10TaAl₃. Strain rate was 0.02 in./in. min.

Sample	Coating weight (mg/cm ²)	Heat treatment	Test temp. (°F)	Y. S. (psi) 0.2% offset	U.S. (psi)	% Elong.	Gage length
B-405-8	None	None	RT	149,000	156,000	2.4	1.0
B-405-16	None	None	RT	122,000	169,000	4.0	1.5
B-405-17	42	As-Coated	RT	123,000	148,000	13.0	1.5
B-405-6	53	As-Coated	2000	62,100	64,800	8.0	1.0
B-405-9	48	As-Coated	2500	22,800	25,600*	14.0	1.0
B-405-5	52	As-Coated	2800	14,900	18,900	30.0	1.0
B-405-7	45	As-Coated	3000	12,600	14,800	32.0	1.25
B-405-11	44	2500-1 hr.	RT	67,000UYP 61,500LYP	71,000	20.0	1.00
B-405-10	42	3000-1 hr.	RT	66,200UYP 61,800LYP	72,100	23.0	1.0
Literature**			RT	172,000	180,000	4.0	
"			1500	97,800	103,000	4.0	
"			2500	19,900	22,200	30.0	
"			3000	11,800	12,100	94.0	

* Serrated curve

** Vacuum tests

TABLE 22

Tensile Test Data for D-14 (Cb-5Zr) Samples Coated with (Sn-25Al)-10TaAl₃. Strain rate was 0.02 in./in./min.

Sample	Coating weight (mg/cm ²)	Heat treatment	Test temp. (°F)	Y.S. (psi) 0.2% offset	U.S. (psi)	% Elong.	Gage length
B-405-18		As-coated	RT	53,300	68,500	23	2.0
B-405-21	41	As-coated	2000	31,300	39,000*	21	1.0
B-405-19	41	As-coated	2200	20,100	27,700*	31	1.0
B-405-22	42	As-coated	2400	14,900	18,500*	47	1.0
B-405-24	34	2000-1 hr.	RT	44,300	60,300	19	1.0
B-405-23	40	2400-1 hr.	RT	27,200	49,700	24	1.0

* Serrated curves

TABLE 23

Stress Rupture Tests on Ta-10W and
Cb-5Zr Samples Coated With (Sn-25Al)-10TaAl₃

Sample No. B 405	Alloy No.	Coating Wt. (mg/cm ²)	Test Temp. (°F)	Stress (psi)	Life (hours)	% Elong.
26-9	D-14	55	2200	17,000	0.67	34
25-8	D-14	49	2200	16,000	0.93	37
27-10	D-14	55	2200	14,500	1.63	38
28-11	D-14	45	2400	12,850	0.25	42
29-12	D-14	46	2400	10,000	0.83	44
30-13	D-14	46	2400	8,000	1.92	49
33-13	Ta-10 W	55	3000	11,500	1.02	37
34-14	Ta-10 W	54	3000	10,000	2.22	36
35-15	Ta-10 W	55	3000	13,000	0.38	40
36-16	Ta-10 W	58	2800	18,000	0.08	35
53-1	Ta-10 W	53	2800	16,000	0.42	33
54.2	Ta-10 W	61	2800	14,000	1.50	38
37.1	Ta-10 W	50	2800	12,000	5.67	41

TABLE 24

Tensile and Stress-Rupture Tests on Ta-30Cb-7.5V Samples Coated with (Sn-50Al-Si)-10TaAl₃ (Strain rate in tensile tests was 0.02 in./in./min.)

TENSILE TESTS

Sample No. B-405-	Coating weight (mg/cm ²)	Heat treatment	Test temp. (°F)	Y.S. (psi) 0.2% Offset	U.S. (psi)	% Elong.
52-11	Uncoated	As received	R. T.	106,800 UYP 106,000 LYP	120,000	23.0
42-1	32	As coated	R. T.	97,300	121,400	14.5
45-4	35	As coated	2500	19,300	23,800	44.0
44-3	30	As coated	2700	17,000	17,500	39.0
47-6	39	1 hr. 2000°F	R. T.	77,000	100,300	29.0
46-5	36	1 hr. 2500°F	R. T.	78,900	89,500	22.0
43-2	29	1 hr. 2700°F	R. T.	66,300	80,600	21.0

STRESS RUPTURE TESTS AT 2700°F

Sample No. B-405-	Coating weight (mg/cm ²)	Stress (psi)	Life (hours)	% Elong.
48-7	42	17,000	0.033	31
49-8	37	14,000	0.083	32
50-9	32	10,000	0.291	36
51-10	31	6,000	1.80	40

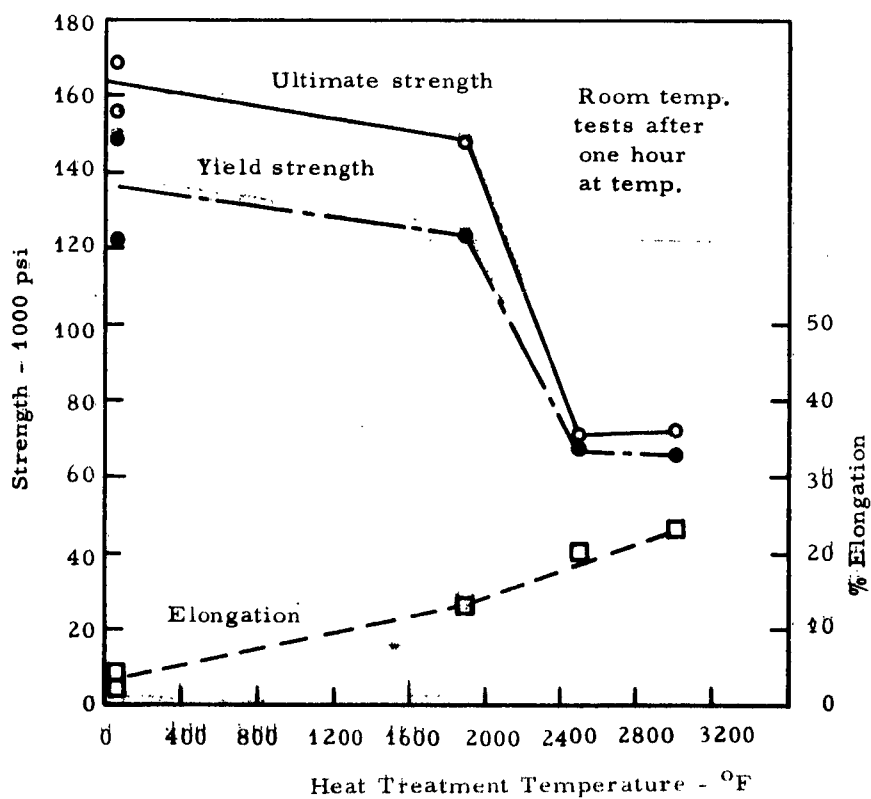
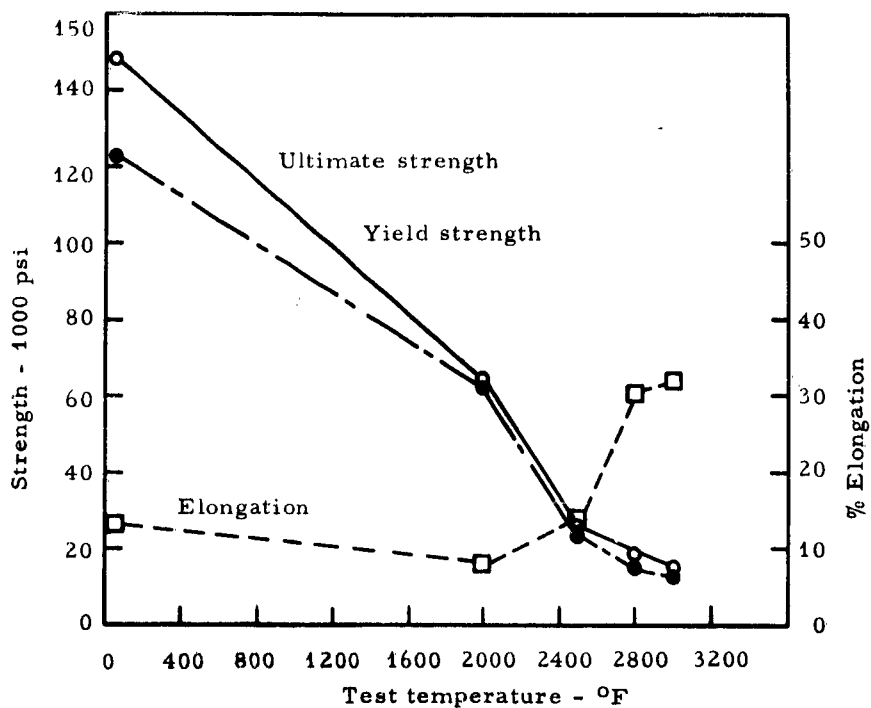


Fig. 14. Tensile properties of Ta-10W samples coated with (Sn-25Al)-10TaAl₃ and tested in air.

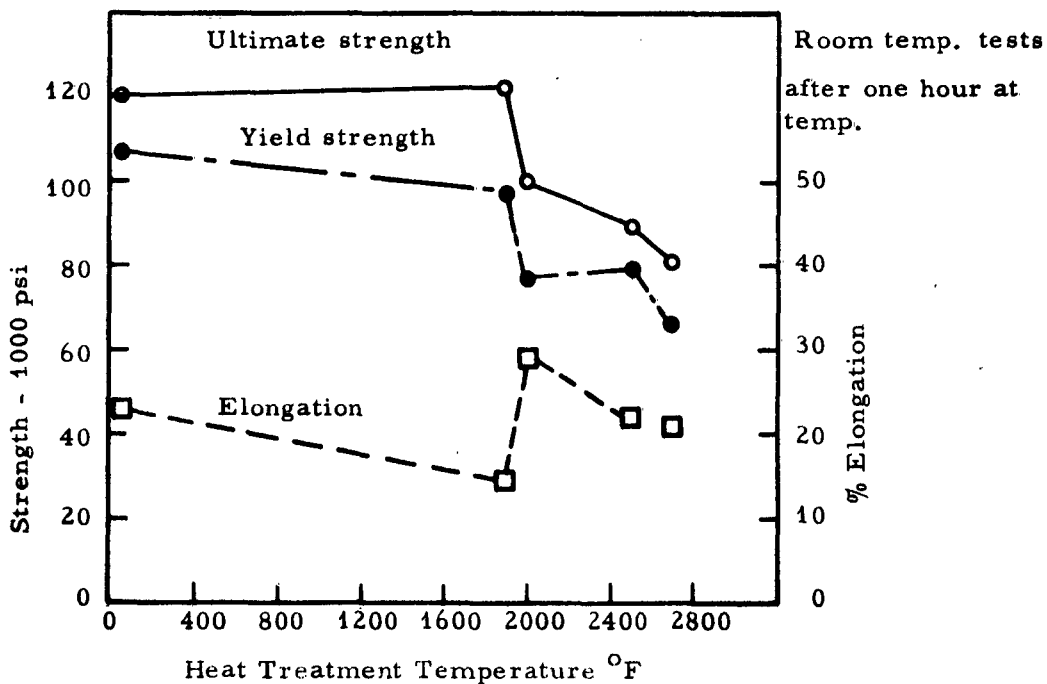
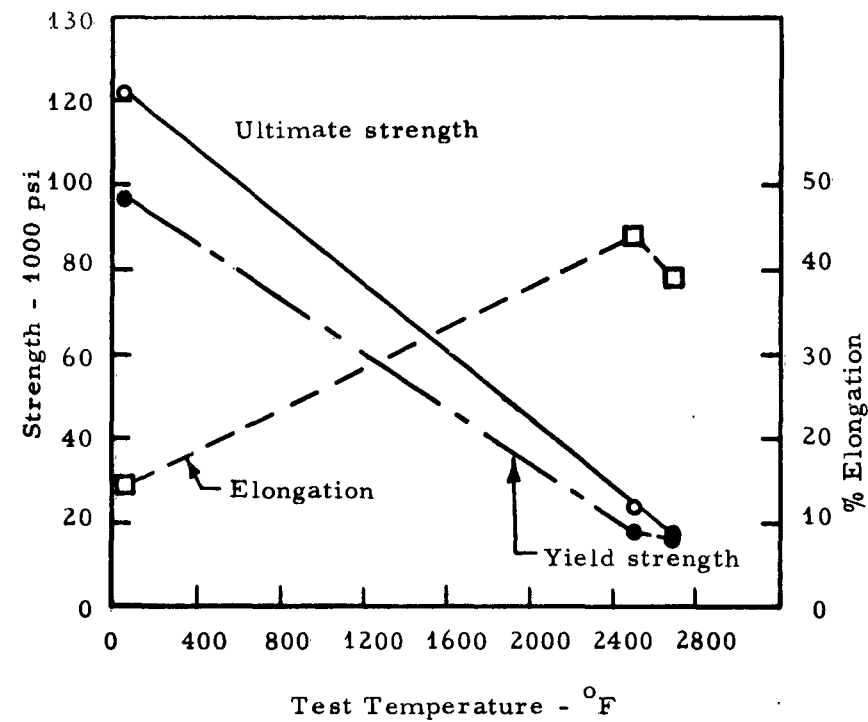


Fig. 15. Tensile properties of Ta-30Cb-7.5V samples coated with (Sn-50Al-Si)-10TaAl₃ and tested in air.

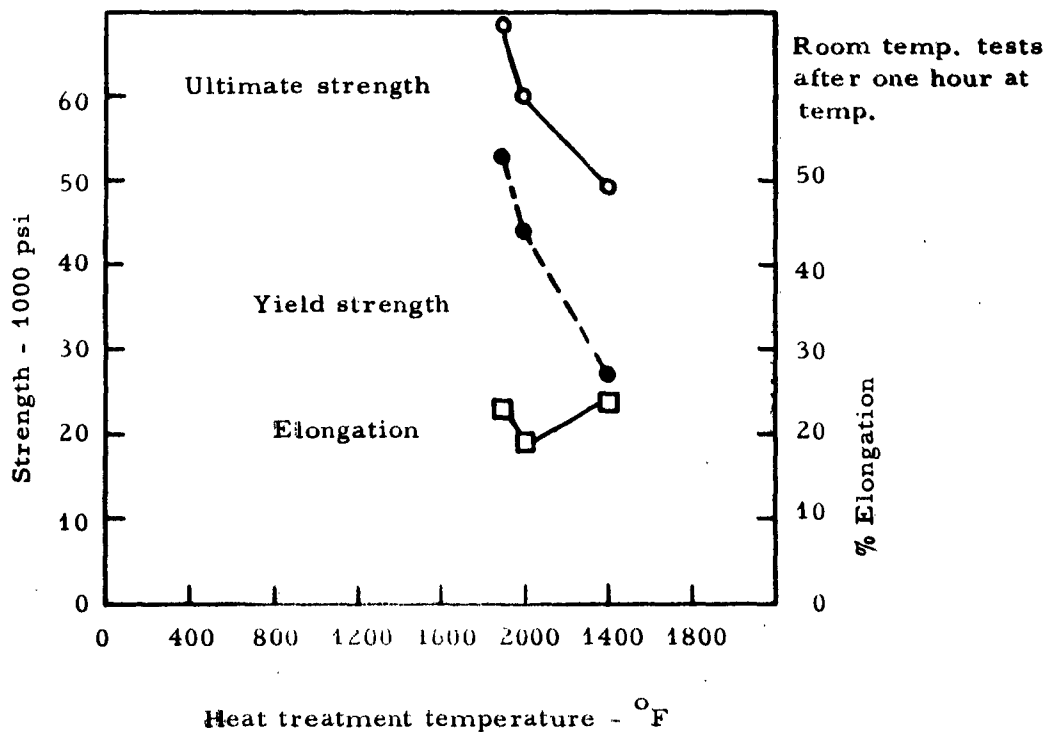
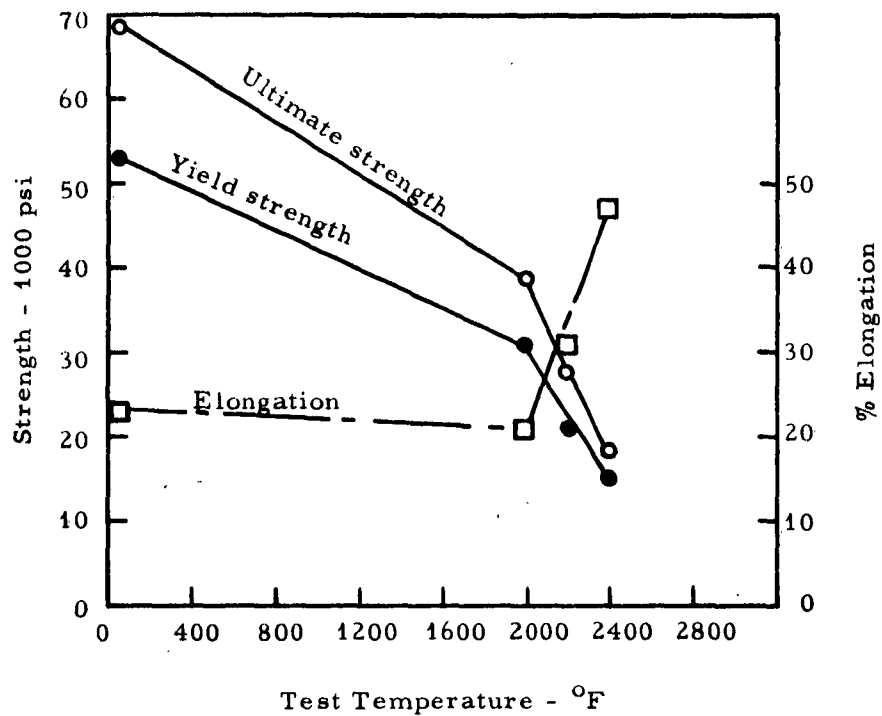


Fig. 16. Tensile properties of Cb-5Zr samples.

Samples, as-coated or coated and oxidized for 1 hour at 2500°F and 3000°F, had good ductility in subsequent room temperature tests. There were serrations in the load-extension curves recorded for the sample tested at 2500°F. Also, samples that were pretreated prior to testing at room temperature developed the yield point phenomenon. Comparison with samples tested or treated equivalently under vacuum conditions would have to be made to determine whether this is an intrinsic property of the Ta-10W material or whether these phenomena were brought about due to coating substrate interaction or limitations in contamination protection.

The Ta-Cb-V alloy had considerable ductility at elevated temperatures. Strength also dropped off with increasing test temperature with the ultimate and yield strengths coming very close together. The load-extension curves bent over quite sharply at the proportional limit, particularly at 2700°F. In general, strength data appeared to agree fairly well with that found in the literature.¹¹ The room temperature tests appear to indicate that the coating has some effect on substrate properties in this thickness material when the heat treatments are carried out at 2500 and 2700°F. In increasing the heat treatment temperature from 2000 to 2700°F, ductility falls from approximately 30% to approximately 21%. The yield strength seems to increase slightly from 2000 to 2500°F and then drops off in a normal fashion at 2700°F.

The strength data for the Cb-5Zr alloy plotted in Fig. 16 appeared to drop off normally with increasing test temperature. Ductility also appears to change normally by increasing with increasing test temperature. Heat treatment of the coated samples resulted in sharply decreased room-temperature strength with increasing heat treatment temperature. Load-extension curves obtained at elevated temperature had rather large serrations in the moderate to extensive deformation portion of the curves. None were noted in the curves for the samples oxidized at 2000°F and 2400°F for 1 hour and then tested at room temperature.

The short-time stress rupture data are shown in the log-log plots of Figs. 17 and 18. Data taken from the literature¹² for Ta-10W tested in vacuum at the same temperatures are plotted for comparison. The data obtained here on coated samples at 3000°F appear to fall in between two sets of data obtained by other investigators in vacuum tests at 3000°F. The 2800°F data obtained here fall quite close to that plotted from the literature.

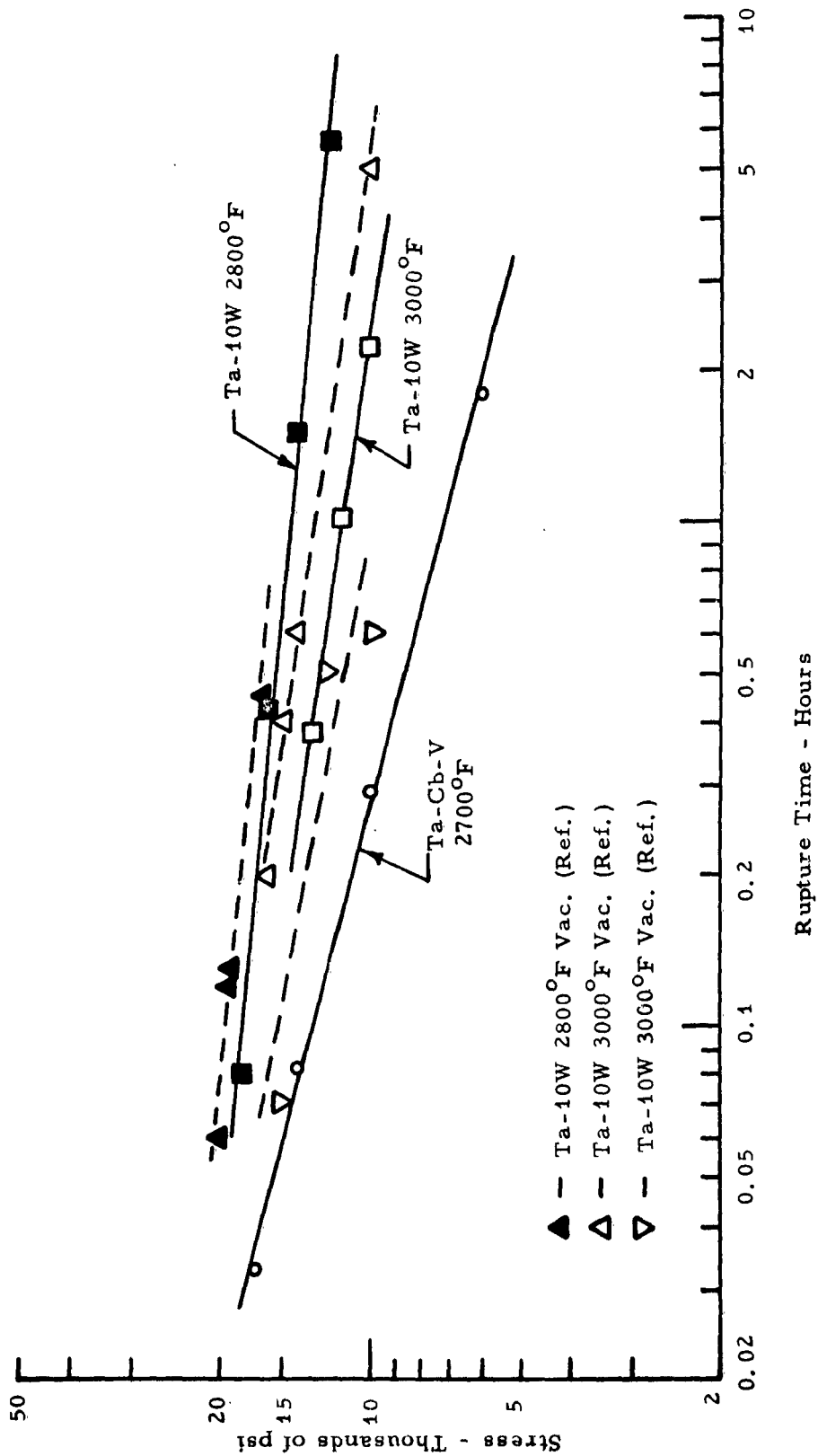


Fig. 17. Stress-rupture curves for Ta-10W and Ta-30Cb-7.5V coated samples tested in air.

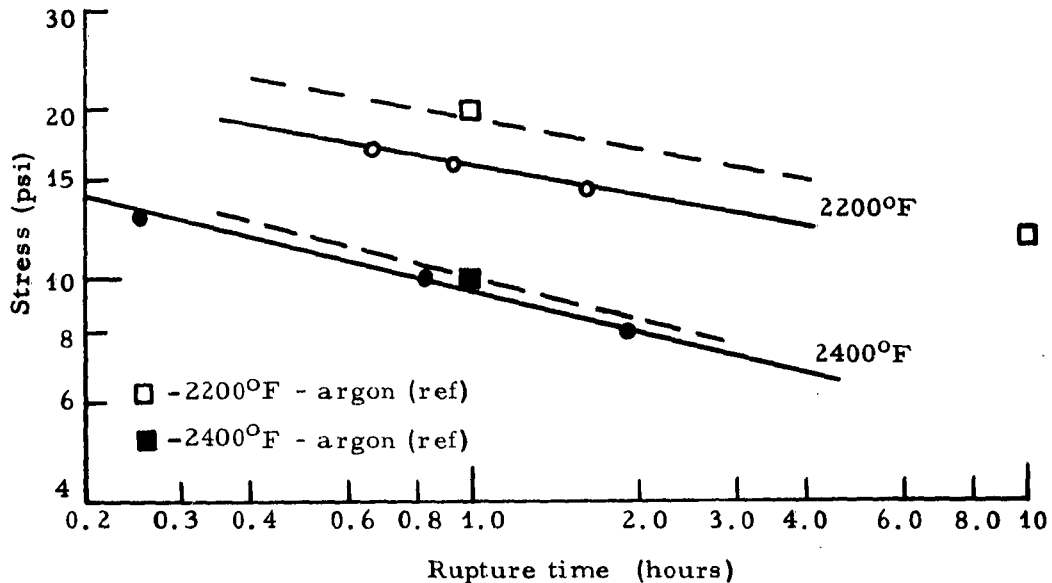


Fig. 18. Stress-rupture curves for Cb-5Zr coated samples tested in air.

It can be seen that the stress rupture strength of the Ta-Cb-V alloy is much lower than the Ta-10W, even though the ternary alloy data were obtained at a lower temperature. In fact, the slope of the curve is quite steep for the Ta-Cb-V alloy at 2700°F, and if extrapolated to a 100-hour rupture life, the stress would be about 2000 psi. No stress rupture data on uncoated material tested under equivalent conditions are available for comparison.

The stress rupture data for the Cb-5Zr alloy shown in Fig. 18 are compared with data approximated from the literature,¹³ given by the manufacturer of the alloy. Since the reference strength data were obtained in argon, it is not surprising that they are somewhat higher than the coated alloys listed here.

The appearance of all the tensile and stress rupture samples after testing is shown in Figs. 19 through 24. Owing to the very high amounts of deformation occurring, some of the coating tended to chip off or flake off, particularly in the last stages of rupture. This behavior is particularly noticeable in the Ta-Cb-V alloy samples tested at room temperature after oxidation exposure at 2500 and 2700°F. The only visual evidence of oxidation occurring at or in the vicinity of fracture in the elevated temperature tests was in the Ta-Cb-V alloy stress rupture tested at 2700°F at 6000 psi.

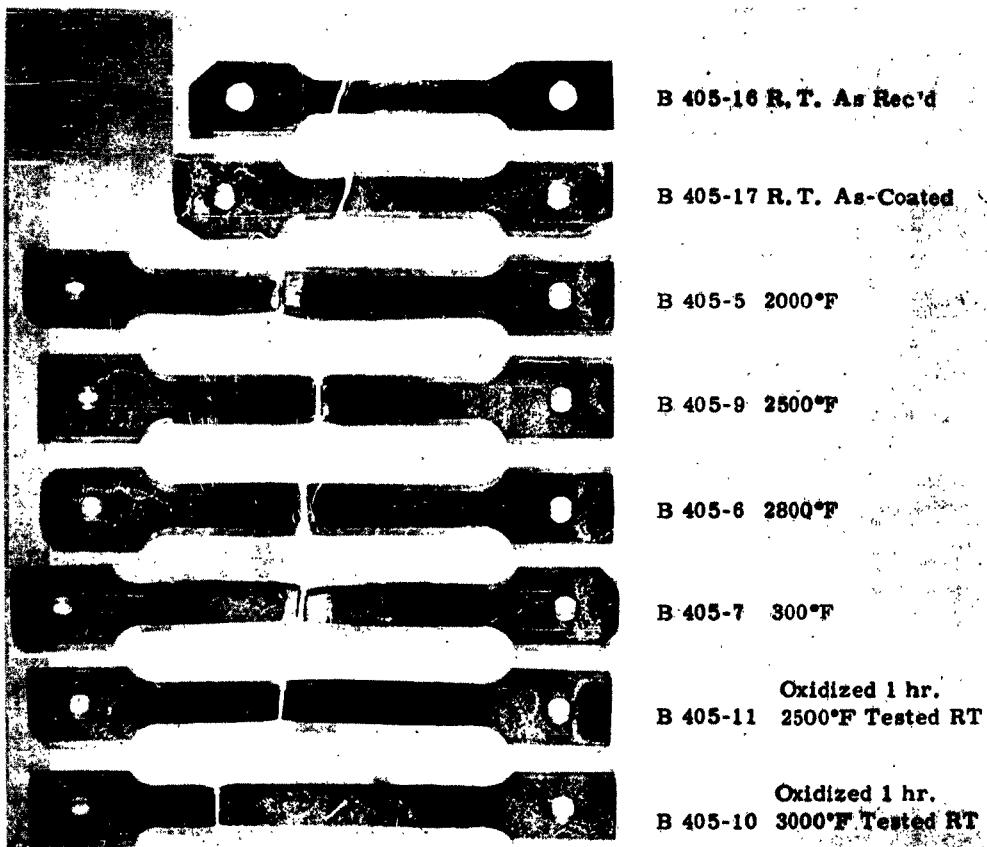


Fig. 19. Ta-10W Tensile Samples.

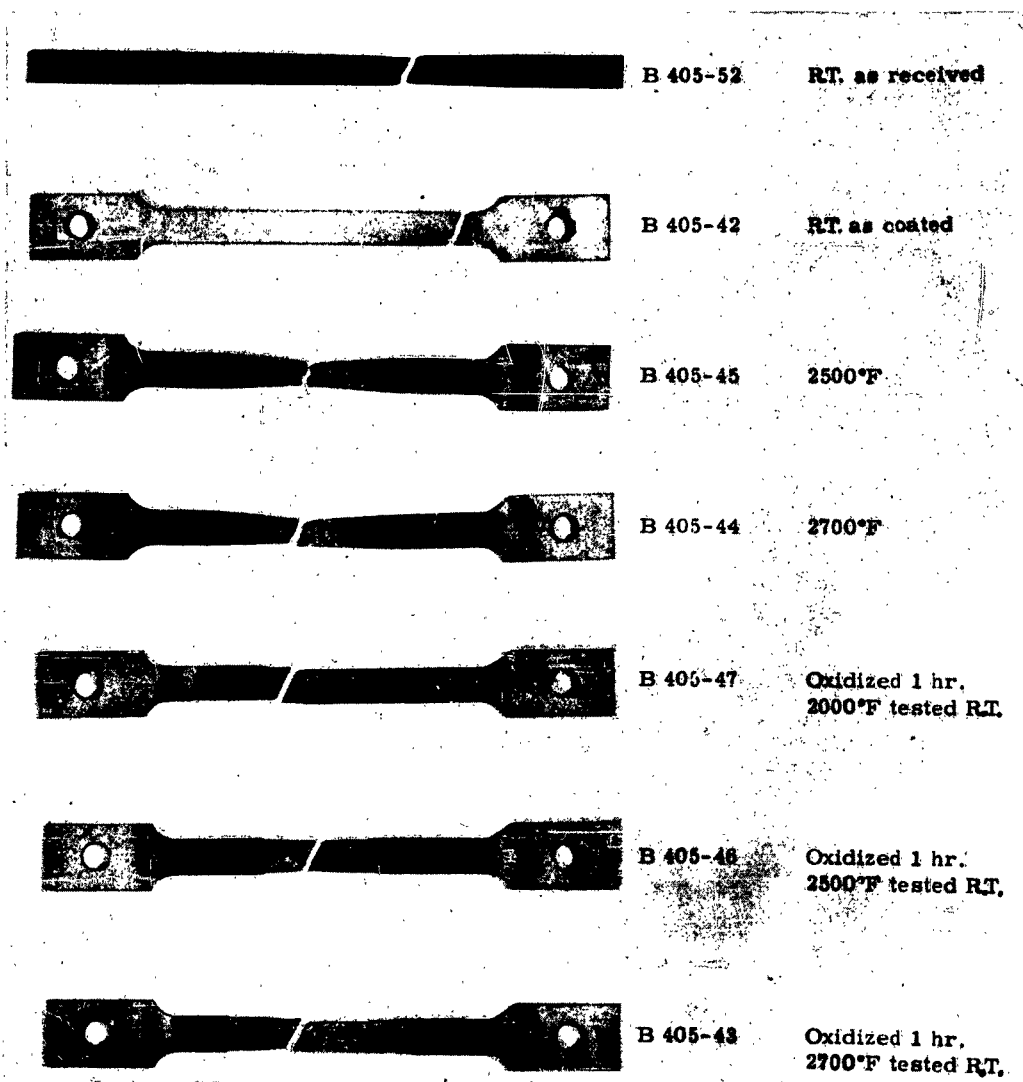


Fig. 20. Ta-30Cb-7.5V Tensile Samples.

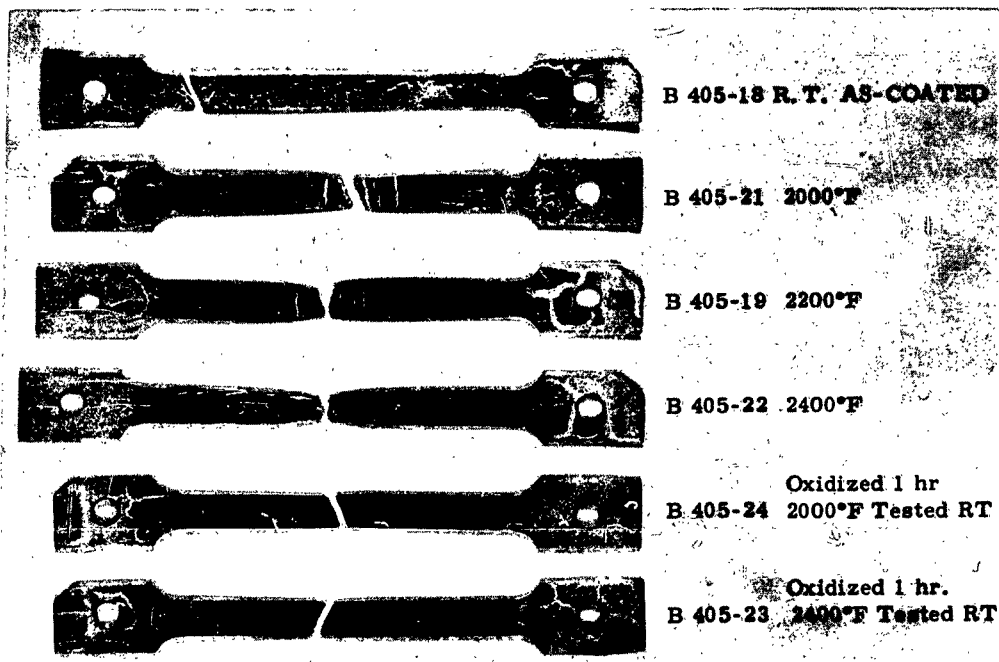


Fig. 21. Cb-5Zr Tensile Samples.

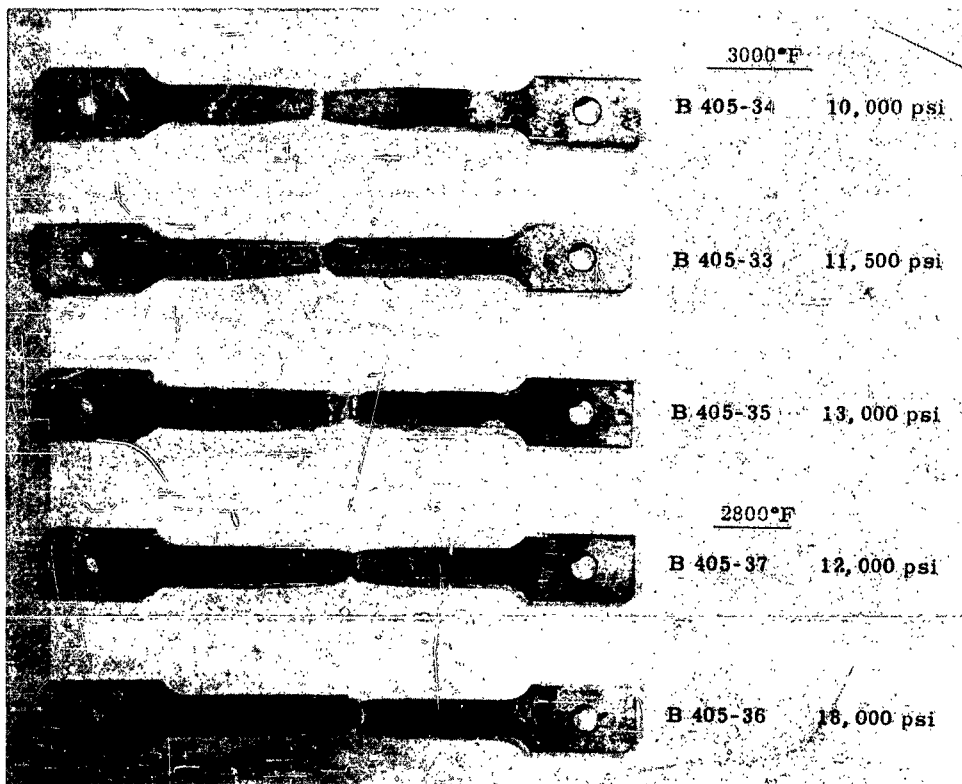


Fig. 22. Ta-10W Stress-Rupture Samples.



Fig. 23. Ta-30Cb-7.5V Stress-Rupture Samples.

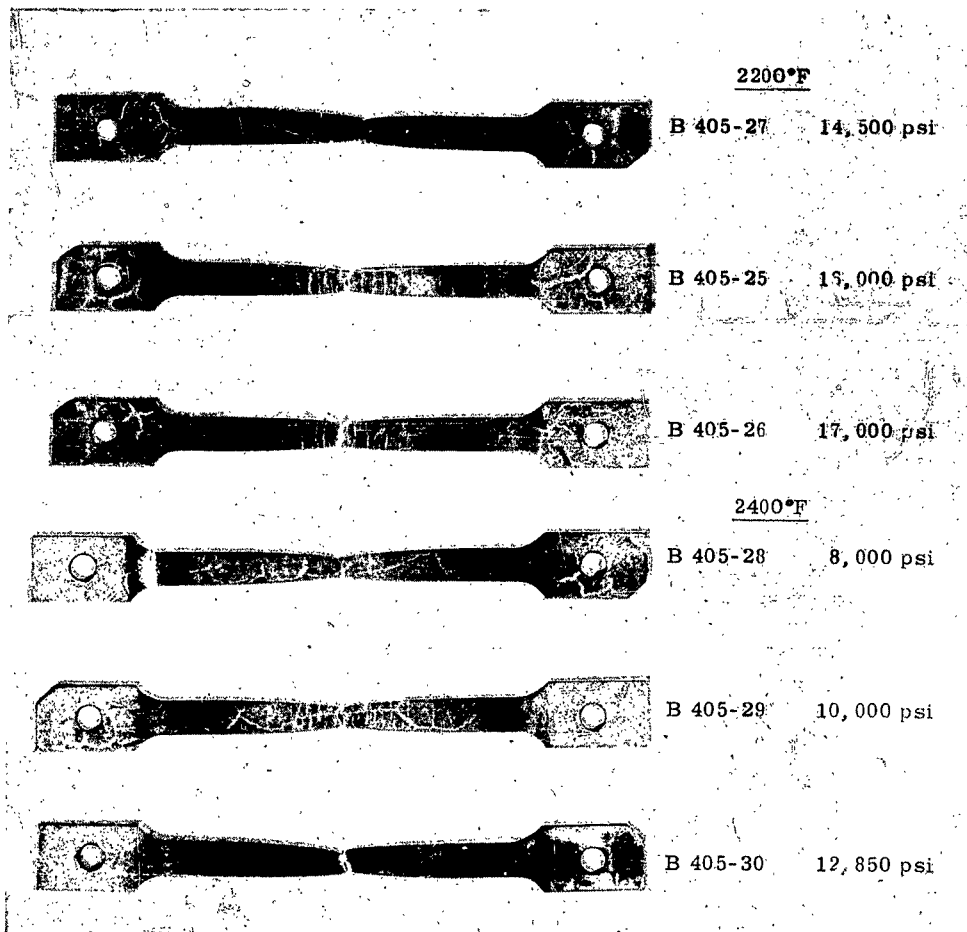


Fig. 24. Cb-5Zr Stress Rupture Samples

3.2 FURNACE OXIDATION EVALUATION

Since the Ta-10W alloy was in maximum supply, it was used to determine the effects of: (1) edge rounding, (2) sample thickness, (3) sample length, (4) number of coats, (5) coating thickness, and (6) test temperature on the oxidation resistance of samples coated with (Sn-25Al)-10TaAl₃. In the later stages of this work, (Sn-25Al)-10MoAl₃ and (Sn-50Al)-10TaAl₃ coatings were also studied.

The surfaces were prepared by sandblasting with G-120 angular steel grit at 40 psi air pressure. Corners were rounded on the first batch of samples by belt sanding, whereas a later batch was finish tumbled in a mixture of silicon carbide and porcelain balls for 16 hours. Edge rounding was followed by sandblasting in these cases. The samples were then cold-slurry spray coated and diffusion treated in vacuum. Since larger batches of samples were to be investigated than in the past, an induction heated bell-jar type diffusion furnace with a steel susceptor was used for diffusion treating. Because of the somewhat slower cooling rate of this furnace, the samples were held at the diffusion temperature for only 20 minutes. After a large number of samples had been coated and tested in this furnace, it was found that the optical temperature measurements were in error because of a film which was deposited on the Vycor jar, presumably as a result of volatilization from the coated samples. The furnace was carefully rechecked and a thermocouple measuring system introduced, so that more precise temperature measurements could be obtained. It was found that the temperature which had actually been used approximated 1750°F. Therefore, in later diffusion runs the temperature was raised to approximately 1860°F. Above this temperature sufficient volatilization of metallic components from the coating occurred so that the deposits on the Vycor jar were sufficient to provide reflective insulation and thereby raise the temperature of the furnace still further. Therefore, the maximum diffusion temperature used was kept at 1860°F. It was later found that the diffusion treatment temperature was critical in its effects on low-temperature oxidation resistance of coated Ta-10W samples.

Oxidation tests were performed by placing the sample on recrystallized alumina boats so that they leaned on the shoulder of the boat and rested on the bottom. At least five samples were tested in any one run. Initially, samples were thermally cycled once every hour during the day and then left in the furnace overnight. However, the overnight procedure was later restricted to tests at 2500°F and lower, since many failures occurred at the higher temperatures overnight.

Samples were selected so that each batch represented the entire range of coating thicknesses obtained. Trends due to coating thicknesses could then be revealed concurrently with other property comparisons. A deliberate effort was made to produce coatings with thicknesses ranging from 2 to 5 mils (25 to 90 mg/cm² with (Sn-25Al)-10TaAl₃). It was not possible to reproduce the exact range for each of the test runs; however, where comparisons were intended, the coating ranges usually overlapped. Results of the tests on the Ta-10W samples are tabulated for reference in Tables 25 through 28. The more pertinent data for 2500° to 3000°F tests are shown plotted in Figs. 25, 26, and 27.

It was found, in general, that substrate thickness, size, or edge rounding had little effect on oxidation resistance. The most significant effects were due to coating thickness and to the cycling rate. Failures occurred predominantly at edges at all temperatures. At 3000°F, as shown in Fig. 25, oxidation life increases slightly with increased coating thickness. Little effect of sample size is indicated between 3/4 in. and 1-1/2 in. long samples. Samples given only one coating had fairly respectable lives of 3 to 6 hours. It was felt that the higher diffusion temperature or preoxidizing the samples at 2300°F might have a beneficial effect on 3000°F oxidation behavior by reducing the aluminum concentration at the coating surface somewhat. However, as can be seen from Table 26, the average life remained at about 6 hours for the various groups of samples tested.

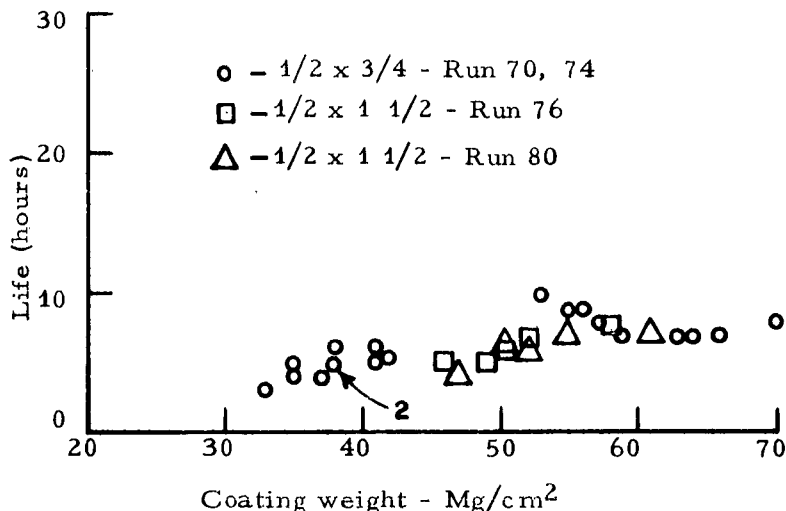


Fig. 25. Oxidation life in furnace tests of Ta-10W samples coated with (Sn-25Al)-10TaAl₃ and tested at 3000°F.

TABLE 25

Furnace oxidation test data on Ta-10W samples
coated with (Sn-25Al)-10TaAl₃

Run U159-	Sample Thick- ness	Edge* Prep.	No. of Coats	Coating Weight Mg/cm ²	No. Samples	Test Temp. °F	Life (Range)		Avg. Hrs.
							Hours	Cycles	
-42	0.040	R	2	57-71	5	2500	46-66	16-21	57
"	"	N	"	66-87	5	"	64-69	19-24	67
-44	"	"	"	72-90	5	"	67-74	22-29	70
"	.010	"	"	65-80	5	"	72-77	27-32	75
-46	.040	R	"	58-71	5	"	48-50	17-19	49
"	.010	N	"	71-84	5	"	50-58	19-27	54
-58	.040	N	1	28-40	10	"	23-27	5-9	24
-48	.040	R	2	60-75	5	2750	23-29	7-13	26
"	.010	N	"	77-97	5	"	23-29	7-13	26
-50	.040	"	"	72-92	5	"	23-32	4-17	24
"	.010	"	"	70-82	5	"	25-33	10-18	28
-52	.040	R	"	61-77	5	2800	12-15	12-15	13
"	.010	N	"	71-84	5	"	9-15	9-15	12
-56	.040	"	1	28-40	10	"	3-7	2-6	5
-70	.040	"	2	53-70	10	3000	7-10	6-9	8
-74	.040	"	1	33-42	8	"	3-5	2-4	4
-66	.040 [†]	"	2	41-55	5	2500	16-25	14-23	20
"	"	"	2	45-58	5	2800	7-10	5-8	8
-72	.040	TR	2	50-57	10	2800	8-12	7-11	10

* R - Rounded

N - None

TR - Rounded & Tumbled

[†] 1-1/2" long

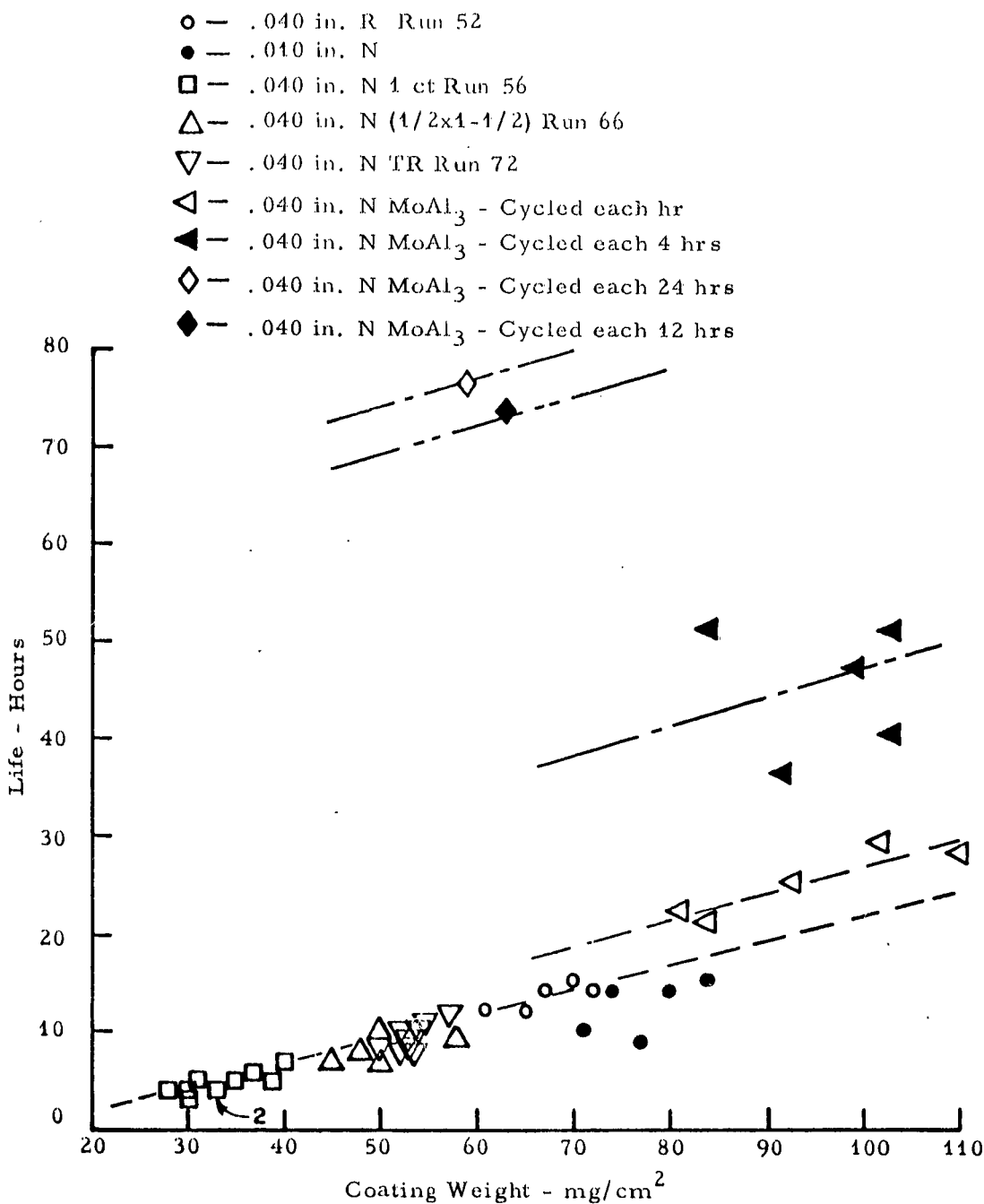


Fig. 26. Oxidation life in furnace tests of Ta-10W samples coated with (Sn-25Al)-10TaAl₃ and (Sn-25Al)-10MoAl₃ and tested at 2800°F.

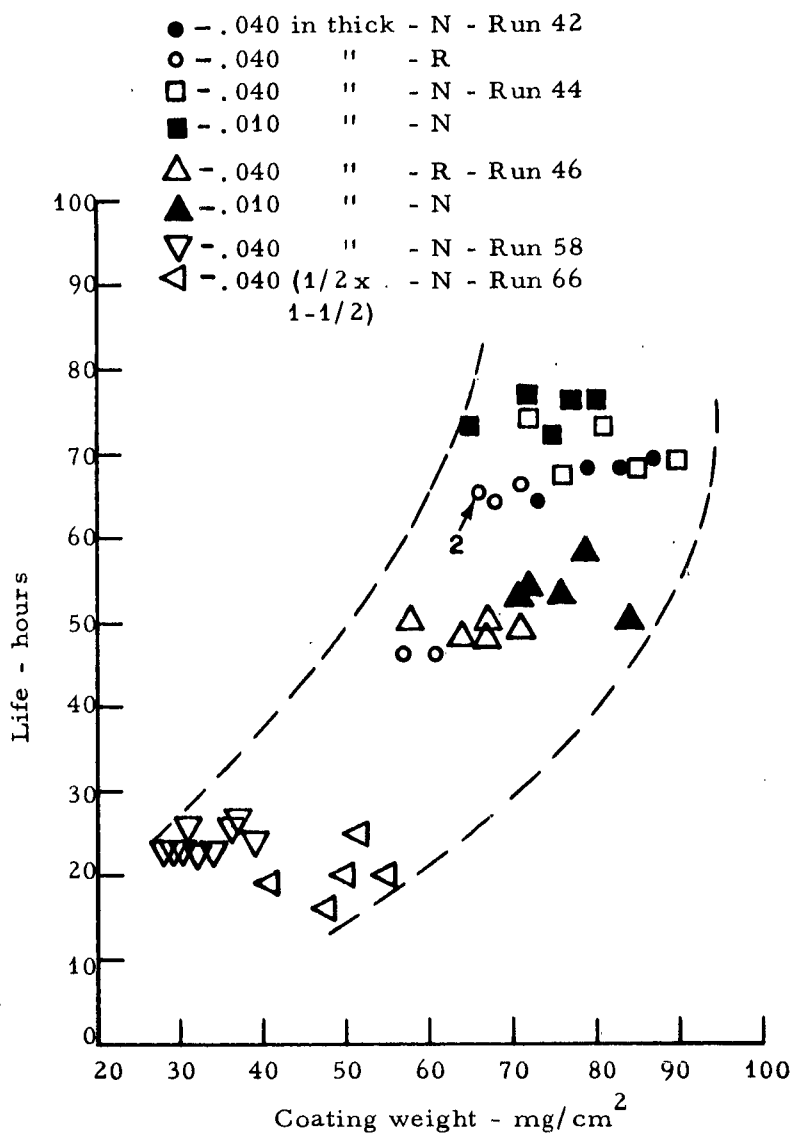


Fig. 27. Oxidation life of Ta-10W coated samples at 2500°F.

At 2800°F, as shown in Fig. 26, there is practically a linear relationship between the coating thickness and oxidation life. In fact, the major effect of the MoAl_3 additive is clearly to increase the coating thickness and the data fall in line with the thinner coatings. It can also be seen that the cycling rate has a profound effect on the life of samples at 2800°F. In reducing the cycling rate to once a day, lives over 75 hours can be obtained.

Results of tests at 2500°F, shown in Fig. 27, are quite scattered, relating more to the particular batch being tested than to any other parameter. However, there does appear to be an exponential relationship between coating thickness and life. This should be the case where diffusion becomes the limiting mechanism in governing oxidation behavior. It is difficult to rationalize why samples that were 1 1/2 in. long had relatively shorter lives than all of the other coupons which were 3/4 in.

Self-healing effects were studied on double coated samples, and the results are summarized in Table 26. Prior to oxidation testing, one batch of samples was bent cold 15° and a second batch 19° in a hand brake. This treatment was quite drastic in that it was done so that considerable permanent set occurred in each of the samples. In tests at 2000, 2500, and 3000°F with 1-hour cycles, the 19° bend samples were more erratic in behavior at all temperatures. At 3000°F lives with both bends were equivalent to unbent samples tested previously. One sample in each group had failed noticeably at the bend; the others were too badly oxidized in the final hour to identify the failure location.

Lives of the bent samples at 2500°F appeared to be somewhat less than unbent samples tested later. However, most of the failures that finally did occur were not located at the bend sites. At 2000°F lives of the 15° bends were fairly good, with 90 to 98 hours of protection and 43 to 50 thermal cycles, 2 samples failing at bend edges. Lives of samples with the 19° bends were 8 to 93 hours. In general, the results indicate that self-healing occurs to varying degrees at 2000°F and becomes more effective at 2500°F or at higher temperatures.

Oxidation lives of samples tested in the 1100 to 2000°F range are shown in Table 27. Double-coated samples in general had lives over 100 hours at 1400 and 2000°F. Since one sample failed at 92 hours at 1400°F, the others were tested for longer time periods to determine the spread in life. At 1100°F behavior was quite erratic, with lives ranging from 21 to 162 hours. Single-coated samples behaved fairly well at 2000°F, 7 out of 10 samples having lives over 100 hours and the other three having at least 93-hour lives. However, behavior was quite erratic at 1400°F, lives ranging from 23 to over 100 hours.

TABLE 26

Furnace Oxidation Test Data on Ta-10W Samples Coated with
2 Coats of (Sn-25Al)-10TaAl₃ (No edge preparation was used.)

Run No.	Sample size	Diffusion temp. (°F)	Coating wt. (mg/cm ²)	No. Samples	Test temp. (°F)	Life		Avg. hours
						(hours)	(cycles)	
U 159-66	0.040 x 1-1/2	1750	41-55	5	2500	16-25	14-23	20
U 159-66	0.040 x 1-1/2	1750	45-58	5	2800	7-10	5-8	8
U 159-82	0.040 x 1-1/2	1750	47-55	5	2800	8-9	7-8	9
U 159-76	0.040 x 1-1/2	1750	46-52	5	3000	5-8	4-7	6
U 159-80	0.040 x 1-1/2	1750	47-61	5	3000	4-7	3-6	6
U 175-16	0.010 x 3/4	1860*	53-68	5	2800	3-11	2-10	8
U 175-2	0.040 x 3/4	1860**	57-74	5	3000	5-7	4-6	6
U 175-14	0.040 x 1-1/2	1750	81-110†	5	2800	21-29	20-28	25
U 175-32	0.040 x 1-1/2	1750	84-103†	5	2800	36-51	9-13	45
<u>Bend Samples (150°)</u>								
U 159-86	0.010 x 3/4	1750	54-69	5	2000	91-98	43-50	95
U 159-84	0.010 x 3/4	1750	56-70	5	2500	23-28	21-27	25
U 159-88	0.010 x 3/4	1750	57-73	5	3000	5-7	4-6	6
<u>Bend Samples (190°)</u>								
U 159-86	0.010 x 3/4	1750	53-65	5	2000	8-93	6-45	33
U 159-84	0.010 x 3/4	1750	55-66	5	2500	21-26	19-25	24
U 159-88	0.010 x 3/4	1750	55-67	5	3000	2-8	1-7	5

* Preoxidized at 2300°F for 1/2 hour before test

** Preoxidized at 2300°F for 1 hour before test

† MoAl₃ additive in coating

TABLE 27

Low-Temperature Furnace Tests on Ta-10W Samples
Coated with (Sn-25Al) 10TaAl₃
(Comparison is made of number of coats, of diffusion
temperature effect, and of preoxidation effects.)

Run No.	Sample size	Diffusion temp. (°F)	Number of coats	Coating wt. (mg/cm ²)	Test temp. (°F)	Life	
						(hours)	(cycles)
U 159-68	0.040 x 3/4	1750	2	57, 64, 64 66, 66	1100	162, 21, 34, 87, 34	45, 5, 10, 25, 10
U 159-68	0.040 x 3/4	1750	2	60, 61, 62 63, 67	1400	123, 157, 157 157, 92	37, 47, 47 47, 30
U 159-78	0.040 x 3/4	1750	2	56 - 71	2000	100 (10 samples)	39
U 159-62	0.040 x 3/4	1750	1	25 - 39	1400	23, 77(4), 78, 80, 90, 100(2)	6, 28, 29, 30, 38, 43
U 159-60	0.040 x 3/4	1750	1	26 - 39	2000	93, 98, 99 100(7)	40, 44, 46, 47(7)
U 175-18	0.010 x 3/4	1860	2	46 - 61	1100	100 (5 samples)	37
U 175-2	0.040 x 3/4	1860*	2	57 - 65	1100	101	40

* preoxidized 1 hour at 2300°F.

It was found that a higher diffusion temperature during the coating treatment was beneficial for 1100°F test samples, all five samples having lives in excess of 100 hours. Preoxidizing samples for 1 hour at 2300°F was not detrimental to 1100°F protection, since all five samples thus treated had lives in excess of 100 hours.

Data obtained on samples coated with (Sn-50Al)-10TaAl₃ and tested at 1100, 2000 and 2800°F are tabulated in Table 28. The results obtained were somewhat inferior to those with coatings having a lower aluminum concentration, particularly at the lower temperature. They also do not measure up to earlier results obtained with Sn-50Al coatings. However, the thermal cycling rate used here is considerably higher than that previously used, and the coating thicknesses are not equivalent to those obtained with excess lumps of Sn-Al at one end of the samples in the past.

Some data were also obtained with pure tantalum coupons coated with (Sn-50Al)-10TaAl₃ and (Sn-25Al)-10TaAl₃. The results are given in Table 29. Somewhat better results were obtained with the lower aluminum coating composition. At 2000 and 2800°F lives were equivalent to or slightly longer than those obtained on the Ta-10W. At 1100°F the protective life was somewhat inferior to that on Ta-10W. This lower temperature behavior is probably related to the oxidation resistance of the substrates, that of the Ta-10W being considerably better at this temperature.

The (Sn-50Al-Si)-10TaAl₃ coating was selected for extensive evaluation on the Ta-30Cb-7.5V alloy. Most of these samples were 22 mils thick x 1/2 in. wide by 3/4 in. long and were prepared with the edges carefully rounded off on a belt sander. Only double-coated samples were investigated.

Results of the tests are tabulated in Table 30 and data obtained at 2500 and 2800°F are plotted in Fig. 28. No failures were noted in samples tested at 1100, 1400, and 2000°F in 100 hours with 38 or 39 cycles. At 2500°F there was a very sharp increase in life with coating thickness. The first batch of samples had lives varying from 40 to over 85 hours. With somewhat thicker coatings provided by the addition of 10MoAl₃ to the coating, none of the five samples tested failed in 100 hours at 2500°F. At 2800°F most of the samples failed in 7 to 11 hours, with several lasting up to 30 hours. Coating thickness did not appear to have any particular effect in the range studied. However, the batch of samples with the 10MoAl₃ additive had considerably thicker coatings and had longer lives of 24 to 39 hours. In general, the coatings are much thicker than those with equivalent coating weights in the (Sn-25Al)-10TaAl₃ composition.

TABLE 28

Furnace Oxidation Test Results on Ta-10W Coupons 0.01 in x 1/2 in.
 x 3/4 in. Double Coated with (Sn-50Al)-10TaAl₃ and Diffusion Treated
 at 1860°F for 1/2 Hour

Run No.	Coating weight (mg/cm ²)	Test temp. (°F)	Life (hours)	Cycles
<u>U 175-2</u>	43	1100	48	17
	44	1100	63	25
	46	1100	47	16
	48	1100	45	14
	52	1100	44	13
<u>U 175-4</u>	43	2000	71	25
	45	2000	96	35
	46	2000	94	33
	51	2000	71	25
	56	2000	96	35
<u>U 175-6</u>	42	2800	6	5
	44	2800	7	6
	46	2800	7	6
	48	2800	7	6
	51	2800	7	6

TABLE 29

Furnace Oxidation Tests on Pure Tantalum Coupons 0.010 in. x 1/2 in. x 3/4 in. Spray Coated Twice with Sn-Al. (No edge preparation. All samples vacuum diffusion treated at 4860°F for 30 minutes.)

Run No.	Coating	Coating weight (mg/cm ²)	No. samples	Test temp. (°F)	Life		Avg. hours
					(hours)	(cycles)	
U 175-12	(Sn-50Al)-10TaAl ₃	40-44	5	1100	24-41	8	32
U 175-8	(Sn-50Al)-10TaAl ₃	39-44	5	2000	101	37	101
U 175-10	(Sn-50Al)-10TaAl ₃	40-45	5	2800	8-16	7-13	11
U 175-12	(Sn-25Al)-10TaAl ₃	68-84	5	1100	32-100	8-37	86
U 175-8	(Sn-25Al)-10TaAl ₃	60-77	5	2000	101	37	101
U 175-10	(Sn-25Al)-10TaAl ₃	71-89	5	2800	6-16	5-15	13

TABLE 30

Furnace Oxidation Tests on 0.022 in. Thick Ta-30Cb-7.5V Coupons Spray Coated Twice with (Sn-50Al-Si). (All samples had rounded corners and edges except last 3 runs)

Run No.	Size (in.)	Coating additive	Coating wt. (mg/cm ²)	No. Samples	Test temp. (°F)	Life		Avg. hours
						(hours)	(cycles)	
U 159-90	1/2 x 3/4	10TaAl ₃	39-49	5	1100	100	38	100
U 159-90	1/2 x 3/4	10TaAl ₃	41-51	5	1400	100	38	100
U 159-92	1/2 x 3/4	10TaAl ₃	40-51	10	2000	100	39	100
U 159-96	1/2 x 3/4	10TaAl ₃	40-53	10	2500	43-87	42-68	79
U 159-94	1/2 x 3/4	10TaAl ₃	40-53	10	2800	7-31	6-30	12
U 175-20	1/2 x 1-1/2	10MoAl ₃	56-74	5	2500	100	56	100
U 175-20	1/2 x 1-1/2	10 MoAl ₃	69-85	5	2800	24-40	23-39	28
U 175-26	1/2 x 3/4*	10TaAl ₃	35-50	5	2000	3	2	3
U 175-26	1/2 x 3/4†	10TaAl ₃	33-50	5	2000	3	2	3
U 175-28	1/2 x 3/4*	10TaAl ₃	38-53	5	2500	1-100	0-46	-
U 175-28	1/2 x 3/4†	10TaAl ₃	35-51	5	2500	1	0	1
U 175-36	1/2 x 3/4††	10TaAl ₃	34-43	5	2800	6-16	5-15	9
U 175-38	1/2 x 3/4††	10TaAl ₃	34-40	5	2500	1-60	0-1	-
U 175-38	1/2 x 3/4††	10TaAl ₃	32-39	5	2000	2-6	1-5	4

(All samples diffusion treated twice in vacuum at 1750°F for 20 minutes, except last 3 runs which were treated at 1860°F for 1/2 hour.)

* Bent cold 15° before testing

† Bent cold 20° before testing

†† Bent cold 10° before testing

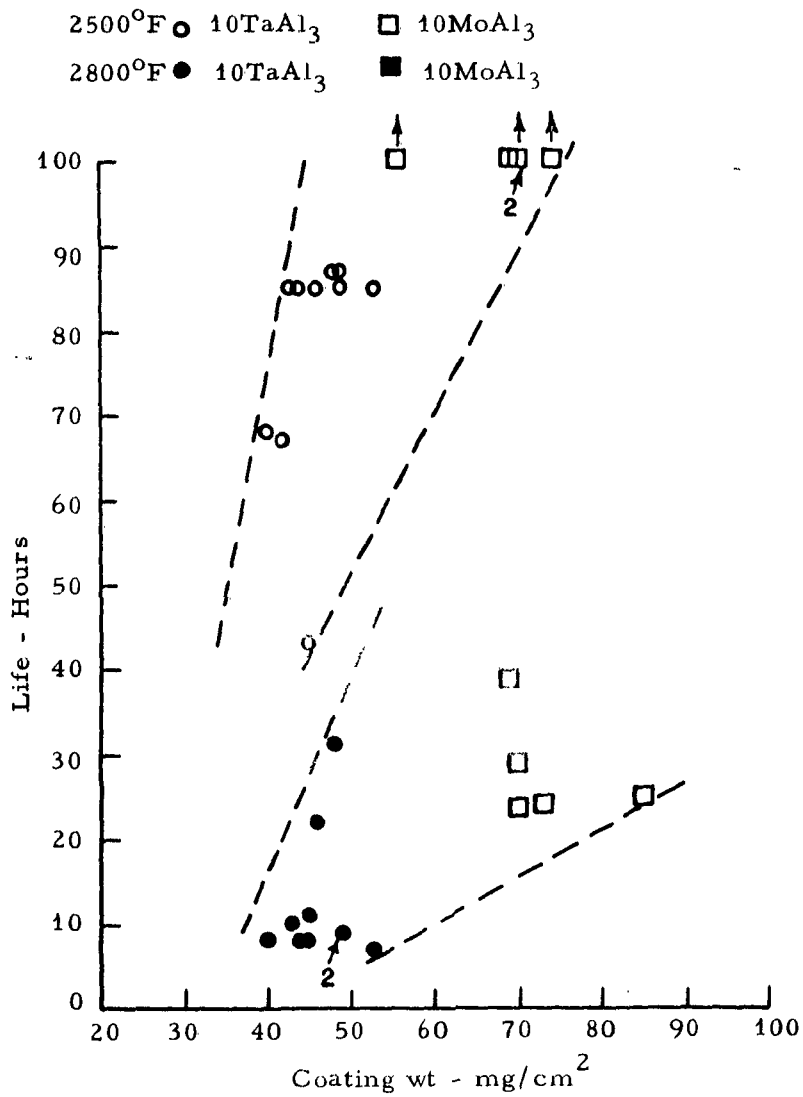


Fig. 28. Oxidation life of Ta-30Cb-7.5V coated samples at 2500 and 2800°F.

The excellent and consistent behavior of the Ta-Cb-V alloy samples at the lower test temperatures prompted a qualitative check on uncoated alloy oxidation resistance at 1100°F. In one hour at 1100°F the Ta-Cb-V alloy had a light blue tarnish film, the Ta-10W alloy had streaks of white oxide on the surface, and pure tantalum was completely covered with a heavy white oxide. After 4 hours the Ta-10W was heavily oxidized and the Ta-Cb-V tarnish film had become considerably darker but otherwise was in excellent condition. This is consistent with all past experience at our Laboratories, which has shown that alloys with better uncoated oxidation resistance possess superior low-temperature coating behavior.

It was found, however, that self-healing effects in this coating substrate system were quite inferior to those in the lower aluminum coating on the Ta-10W alloy. Samples after coating were bent cold 10°, 15° and 20° in a brake before testing. At 2000°F they had lives of 2 to 6 hours. At 2500°F none of the 20° samples lasted more than an hour, whereas the lower bend samples had quite erratic behavior with protection varying from 1 hour to 100 hours. At 2800°F the 10° bend samples had good self-healing properties, since lives averaged about 9 hours.

Single and double coatings of (Sn-25Al)-10TaAl₃ were evaluated on the Cb-5Zr alloy at 1400, 2200 and 2400°F and double coats evaluated at 2000°F. The data are tabulated in Table 31 and the results plotted in Fig. 29. At 1400°F coating life is increased considerably by using the double coating technique. At 2000°F, 4 of the 5 samples had lives in excess of 100 hours. White oxide specks which formed at the surface at this temperature were probably tin oxide since they could be brushed off at room temperature without any subsequent ill effect at 2000°F. These spots also formed at 2200°F. Within the scatter of the results, it appeared that oxidation life was proportional to coating thickness at both 2200 and 2400°F.

Some of the samples are shown after oxidation testing in Figs. 30 and 31. The purpose of the photographs is to impart some idea of the surface conditions of samples tested with various coatings at different temperatures and for different lengths of time. The photographs are not meant to be representative of all the tests performed.

Several comments can be made regarding the visual surface changes occurring in the coatings during oxidation testing. The samples are coated by hanging them on tantalum wires during the diffusion treatment. These wires usually stick to the samples and have to be removed by heating near the hole in the sample or by heating the wire lightly with a

TABLE 31

Furnace Oxidation Tests on D-14 Samples 0.020 in. x 1/2 in. x 3/4 in. Spray Coated with (Sn-25Al)-10TaAl₃. (No edge preparation. All samples diffusion treated in vacuum at 1750°F twice for 20 minutes, followed by 20 minutes at 1860°F.)

Run No.	No. Coats	Coating weight (mg/cm ²)	No. Samples	Test temp. (°F)	Life (range)		Avg. hours
					hours	cycles	
U 175-24	1	16-28	5	1400	5-17	4-16	9
U 175-24	2	44-54	5	1400	40-100	21-35	88
U 175-24	2	42-50	5	2000	75-100	34-45	95
U 175-22	1	19-36	10	2200	9-19	8-18	14
U 175-30	2	43-55	10	2200	18-54	2-23	45
U 175-34	1	18-32	10	2400	1-6	0-5	4
U 175-34	2	43-55	10	2400	14-27	5-10	21

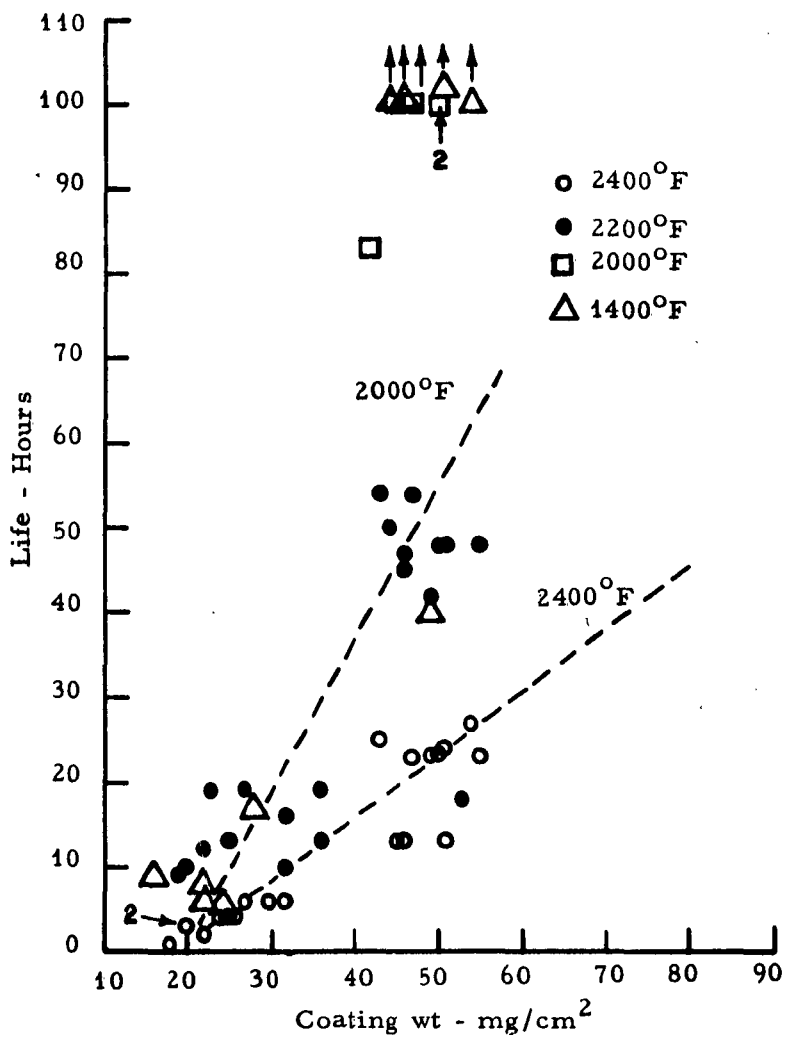


Fig. 29. Oxidation life of Cb-5Zr coated samples at 1400, 2000, 2200, and 2400°F.

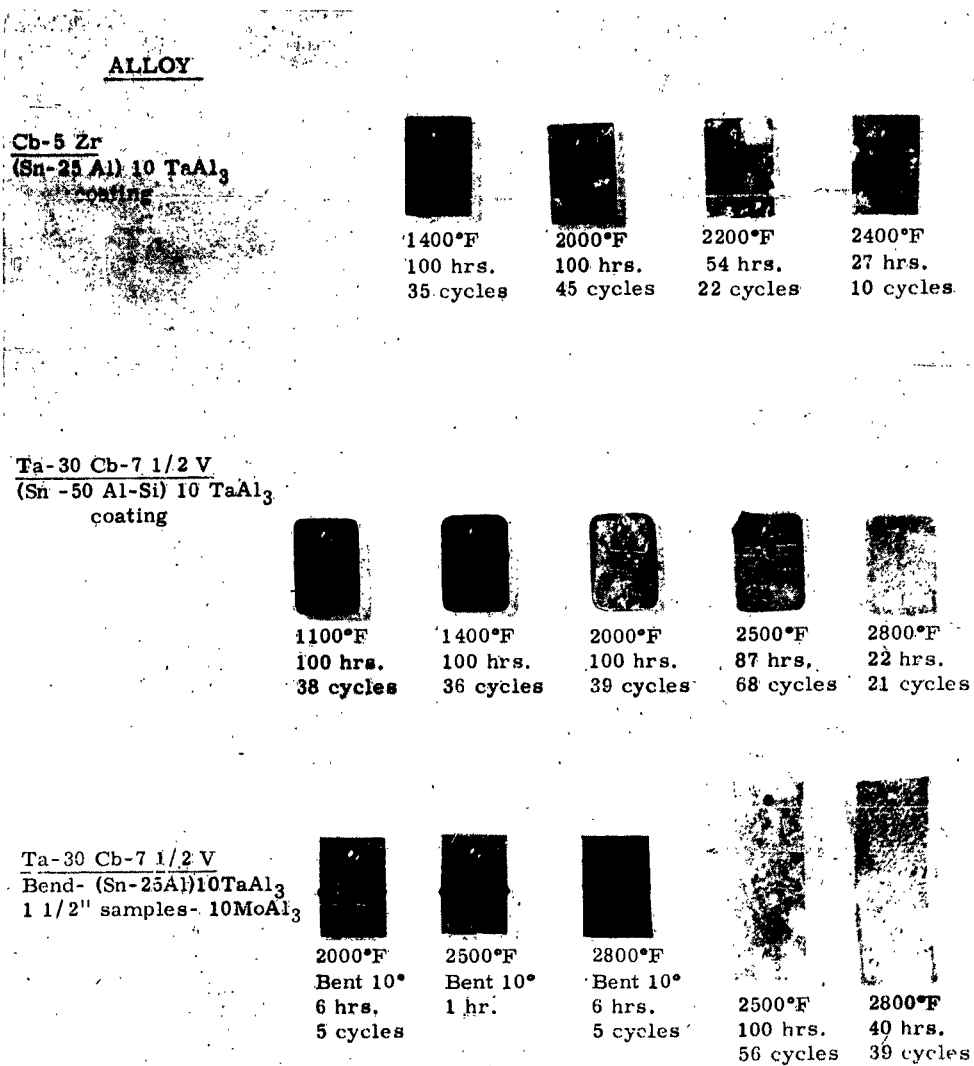


Fig. 30. Cb-5Zr and Ta-30Cb-7.5V Oxidation Test Samples.

IDENTIFICATION						
<u>Normal Coupons</u>						
						
Temperature °F	1100	1400	2000	2500		
Time - hours	100	157	100	68		
No. of cycles	37	47	39	23		
Coating additive	10TaAl ₃	10TaAl ₃	10TaAl ₃	10TaAl ₃		
No. of Coats	2	2	2	2		
<u>Normal Coupons</u>						
						
Test Temp. °F	2800	2800	2800	2800	3000	3000
Time - hours	5	14	28	51	5	10
No. of cycles	4	13	27	13	4	9
Coating additive	10TaAl ₃	10TaAl ₃	10MoAl ₃	10MoAl ₃	10TaAl ₃	10TaAl ₃
No. of coats	1	2	2	2	1	2
<u>Bend Tests</u>						
10 TaAl ₃ Additive						
						
Bend Angle °	15	19	15	19		
Temp. °F	2000	2000	2500	2500		
Time - hours	96	93	26	21		
No. of cycles	48	45	25	19		

Fig. 31. Ta-10W Oxidation Test Samples.

gas torch and pulling the wire away when a molten phase is formed. A visible line associated with incipient melting of the coating is formed on the sample surface near the wire and moves rapidly towards the opposite end as more heat is applied. When the samples are oxidized at 1100°F, this heat-affected area darkens more rapidly than the original, unaffected areas. There is a noticeable shading difference at all times during test. A few liquid metal beads may also form at random locations on the surface. No tendency for failure has been noted at the beads or in darker or lighter areas. However, it appears from metallographic examination of samples tested at 1100°F that the formation of this liquid film and the thermal cycling applied for dozens of removal and entry into the furnace causes the liquid phase of the coating to pull itself away from the intermetallic compound phase in some places beneath it.

Some "beading" was also observed on Ta-10W samples at 1400 and 2000°F, but hardly any at higher temperatures. At 2000°F more beads were noted on the (Sn-50Al)-10TaAl₃ coating than on (Sn-25Al)-10TaAl₃ coatings; the oxide formed was also lighter on the former. At higher temperatures the lower aluminum coating surface becomes more irregular or "wrinkled." Apparently, at the higher temperatures this wrinkling, together with spalling and cracking of the oxide, is a limiting factor in oxidation life.

Failures in furnace tests at 2800°F or lower usually result in light or colored oxide nodules, and with some yellow-orange staining with Ta-10W alloys. Pure tantalum does not have the yellow-orange staining. At 3000°F, when failure is initiated it propagates quite rapidly, usually resulting in a complex molten oxide mass. Therefore, samples may appear to be intact on examination, but in the next ensuing hour will be completely destroyed. It has been possible, with resistance heated samples, to observe the initiation of failure at 3000°F. This is evidenced by the appearance of smoke and of a small dark stain which seems to spread just below the surface of the sample. Therefore, it is quite possible that a complex low-melting oxide, probably involving tin oxide, is formed during or after failure at 3000°F.

With the (Sn-50Al-Si)-10TaAl₃ coating on the Ta-Cb-V alloy, there appears to be considerable "beading" at the lower test temperatures. However, this seems to have very little effect on the protective nature of the coating, since there appears to be no tendency toward failure in 100 hours at these temperatures. The "beads" are quite small and can be easily brushed from the surface during examination at room temperature. The remaining coating appears completely intact. At 2500°F and

at lower temperatures, the surface appearance is smooth; however, at 2800°F considerable roughening or wrinkling of the surface occurs. Failure at 2500°F is accompanied by the growth of an oxide nodule up through the coating. At 2800°F failure is accompanied by the formation of a molten oxide.

Failures on the Cb-5Zr alloy do not appear to be due to the growth of oxide nodules up through the coating, but rather to a general deterioration in multiple areas of the surface. This is one of the columbium alloy compositions which does not receive the best protection from the Sn-Al type coatings.

3.3 SIMULATED RE-ENTRY PRESSURE OXIDATION EVALUATION

This work was done to obtain some preliminary information regarding the relative stability of the Sn-Al type of coating in reduced pressure atmospheres. In the first phase, pressures in the 0.1 to 100 micron range were studied. However, the range of practical interest is somewhat higher; therefore later tests were done at 1.5-12 mm. For the studies in the micron range, a tantalum resistance-heater vacuum furnace was employed. Ordinary sheet coupons 1/2 in. x 3/4 in. were used with a coating of (Sn-25Al)-10TaAl₃. Practically all of the work was done with Ta-10W; however a few tests were made with Ta-30Cb-7.5V in the micron pressure range.

The results of up to 1 hour exposure in the range 2000 to 2800°F are plotted for Ta-10W and for Ta-30Cb-7.5V in Fig. 32. Weight losses in 10 minutes for Ta-10W were not high until a temperature of approximately 2500°F was reached. Above 2500°F the coating was considerably depleted within 10 minutes. Preoxidizing the samples at 2000°F for 1 hour had little effect on coating losses. However, preoxidation treatments at 2500 and 2800°F caused a decrease in coating weight loss in subsequent exposure to vacuum at 2200°F. Neither treatment had any effect on losses at 2500°F. No decrease in weight loss was effected by increasing the pressure of the system from 0.1 micron to 100 microns in testing at 2500 and 2800°F.

Typical coating structure changes due to instability at 0.1 micron are illustrated in Fig. 33. At 1900°F the coating appears normal, containing the TaAl₃ compound and the excess Sn-Al phase. At 2000°F the weight loss is primarily of the Sn-Al phase. After 1 hour at 2500°F, the structure consists of a lower aluminum compound layer adjacent to the substrate;

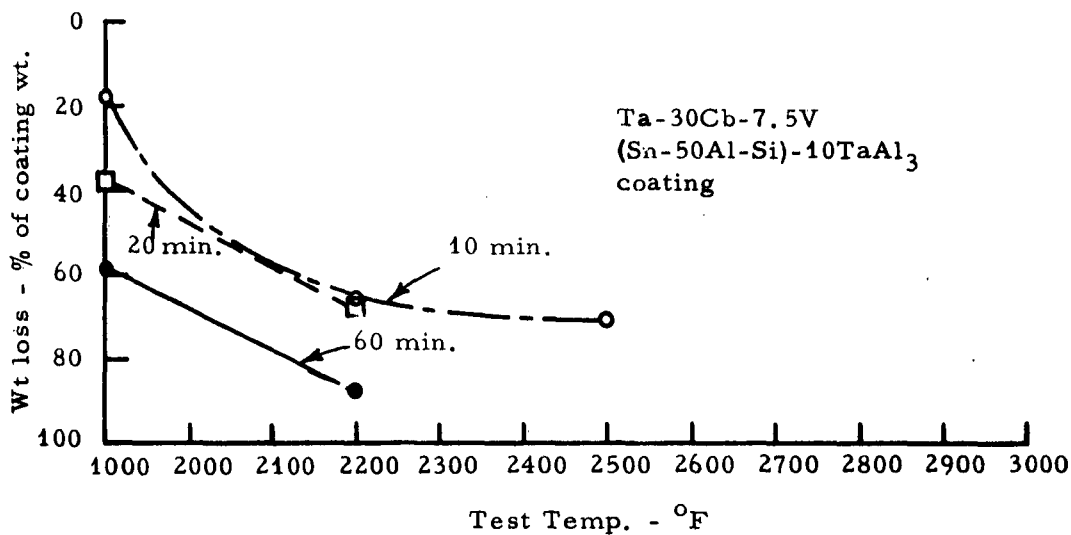
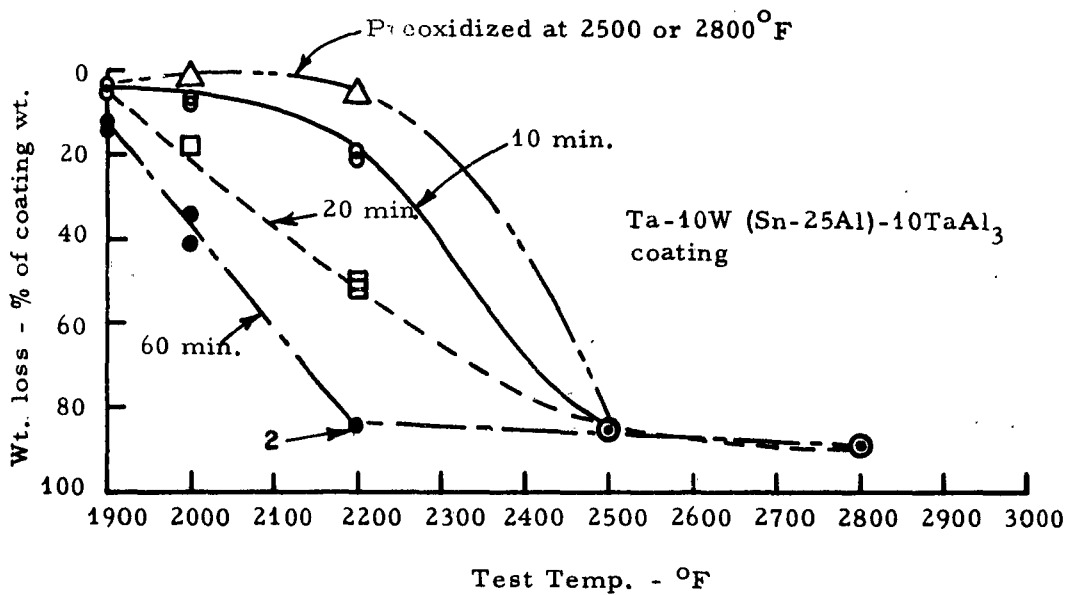
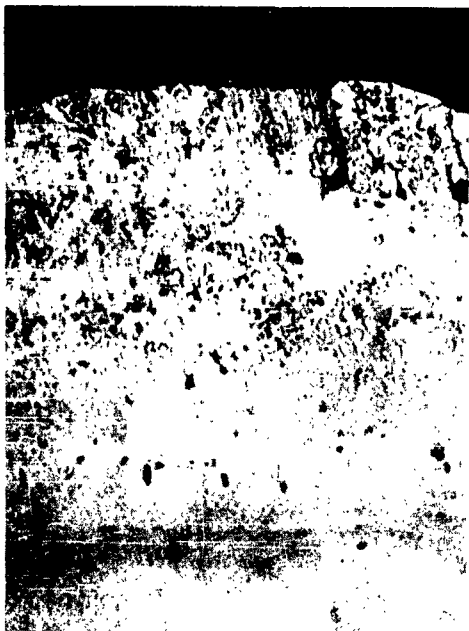


Fig. 32. Weight changes in coated samples at 0.1 micron pressure.



(a) 1900°F



(b) 2000°F



(c) 2500°F

Fig. 33. Ta-10W samples coated with (Sn-25Al)-10TaAl₃ and heated for one hour in 0.1 micron pressure. (500X)

the original TaAl_3 compound has decomposed, leaving behind a skeleton of a lower aluminum intermetallic. None of the Sn-Al phase is left. The weight losses of samples of Ta-30Cb-7.5V coated with (Sn-50Al-Si) are in general somewhat higher than with the lower aluminum coating on Ta-10W.

To study coating changes in the range of 1 to 15 mm of air pressure, a modified Sieverts apparatus was set up together with a resistance heating chamber. A cartesian manostat was used to regulate air pressure in the range of interest. Various attempts were made to minimize the temperature gradient resulting from clamping the specimen in water-cooled electrical grips. Initially this was done by contouring the sample so that the grip ends were narrowest and the sample widened gradually to a maximum of 1/4 in. at the center. Samples of Ta-10W, from 0.01 in. to 0.04 in. thick by approximately 2 in. long were coated with (Sn-25Al)-10TaAl₃. Tests showed, however, that the coating thickness variations within the sample test section were sufficient to cause a temperature gradient in the sample. Therefore, subsequent samples were coated with the 10MoAl₃ additive to obtain much more uniform coatings. Additional difficulties were encountered because of the relatively small grip ends which led to hot spots and poor contact. This difficulty was alleviated by using completely rectangular samples, 0.010 in. thick x 1/4 in. wide, but the restraint imposed by the vacuum seals around the grips caused these samples to buckle at the center. In some cases this resulted in shorting out against the wall of the chamber.

Samples were usually exposed for 1/2 hour at temperature, taken out, examined, weighed, reassembled into the apparatus, and retested for another 1/2 hour. Many of the samples developed hot spots in some localized area, which resulted in a burnout. Therefore it was not possible to specify the type of failure that occurred. Accordingly, the results plotted in Fig. 34 are those for which a uniform weight loss or weight gain was obtained. None of these samples had failed in the sense of an oxidation failure. In fact most of them suffered little change in structure or appearance. It is apparent, however, that at 1.5 mm pressure considerable coating loss occurs in the vicinity of 2570°F in 1/2 hour. Similar losses are obtained at a lower temperature, 2450°F, in one hour. In general, the surface condition of the sample is quite dark and probably resembles the structure shown in Fig. 33 tested at 2500°F at a lower pressure. It can be seen from Fig. 34 that the coating is quite stable at approximately 2600°F at 3 mm pressure, at 2780°F at 6 mm pressure, and at 2850°F at 12 mm pressure. The effect of time at

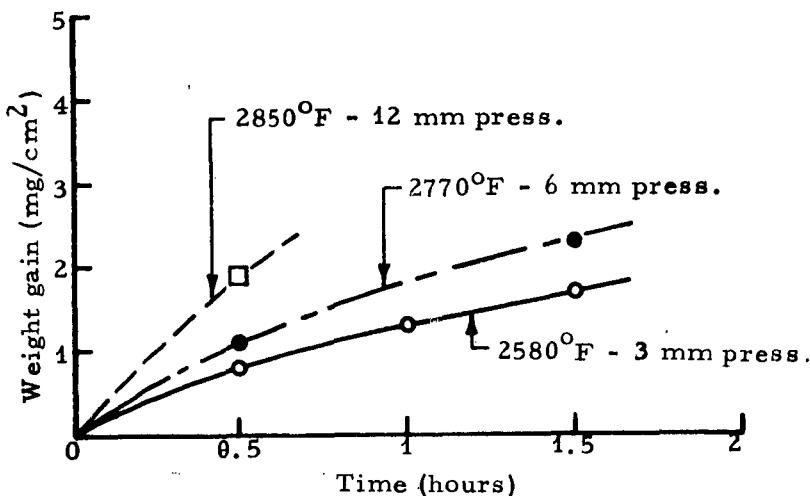


Fig. 35. Weight gains of samples of Ta-10W coated with (Sn-25Al)-10MoAl₃ and heated by their own resistance.

temperature is shown in Fig. 35. Where weight gains occur they appear to be continuous. Figure 36 is representative of the microstructure of the sample tested at 2770°F for 1 1/2 hours. It is apparent that local areas can be depleted of the coating within this test time; these depleted areas are probably related to the hot spots within the sample caused by nonuniformities. In order to establish the range of pressures and temperatures at which the coating is stable, it would be preferable to use an outside heating source to attain necessary temperatures.

The above results show that the coatings are much more stable in the millimeter range than in the micron range. These studies also indicate that where a protective oxide film forms, stability is increased and can probably be increased to temperatures in the vicinity of 3000°F. However, considerably more work would have to be done in order to establish the precise temperature-pressure boundary conditions for stability.



Fig. 36. Ta-10W sample coated with (Sn-25Al)-10MoAl₃ and tested for 1-1/2 hours at 2770°F at 6mm pressure. (250X)

4. ANALYSIS OF AIR-COATING-SUBSTRATE INTERACTION DURING OXIDATION

4.1 METALLOGRAPHIC STUDIES

Structural changes occurring in Ta-10W samples can be seen in the photomicrographs of Figs. 37 and 38. The sample shown was tested by resistance heating to 3000°F for 5 minutes and had the Sn-25Al coating with no additive. At the cold end of the sample in the vicinity of the grip, the structure is practically in the as-coated condition, with the TaAl₃ layer covered by the excess Sn-Al. In the unfailed area of the hot zone, an appreciable thickness of protective Al₂O₃ has formed, Ta₂Al has grown by interdiffusion, and blocks of Ta₂Al appear to be dissolving in the Sn-Al. These blocks probably represent the original TaAl₃ layer. In the vicinity of failure, as seen in Fig. 38, the first stage of failure appears to be the rapid oxidation of the Sn-Al phase and the appearance of loose Ta₂Al particles. Oxidation attack appears to accelerate rapidly at the base of the Ta₂Al layer. The oxide film formed in 5 minutes at 3000°F is approximately 0.4 mils thick and would require six to seven times the amount of aluminum available in the Sn-Al phase for its formation. There must therefore be a second source of aluminum supply, from the intermetallic compound, which diffuses through the Sn-rich layer to the oxide. Consequently, it appears that failure occurs when the aluminum concentration falls off to some very low critical level in the Sn-rich phase so that repletion of, or continued growth of, the oxide film is locally impaired.

Increasing the coating thickness, principally the amount of Sn-Al phase, should and does increase the oxidation life. This is illustrated structurally by the sample in Fig. 39, in which the (Sn-25Al)-10TaAl₃ coating has been exposed at 2800°F for 15 hours. There is a considerably larger Sn-Al phase and a much thicker oxide film has been able to grow. At this temperature the intermetallic compound is broken up considerably and intermixed with the Sn-rich phase.

In general Ta-30Cb-7.5V samples coated with (Sn-25Al)-10TaAl₃ undergo similar metallographic changes to Ta-10W with the same coating. The ductility of the substrate was checked after testing for 8 hours at 2800°F and 2 hours at 3000°F. It was found that samples so tested could be bent over a 2T radius to a 90° angle. Metallographic examination of these samples showed that the 2800°F sample had tensile cracks in the intermetallic compound layer which did not extend into the base metal substrate. In the 3000°F sample the cracks penetrated to a considerable depth into



(a) cold end near grip

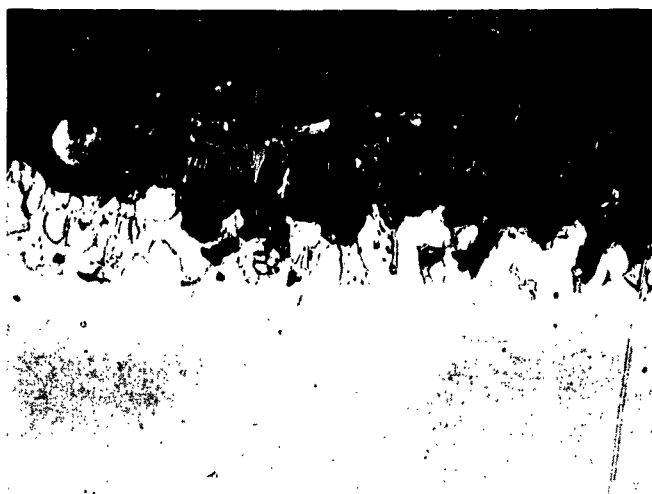


(b) hotter area



(c) hot zone unfailed

Fig. 37. Ta-10W coated with Sn-25Al and oxidized 5 minutes at 3000°F by resistance heating. (500X)



(a) Adjacent to failed area



(b) Failed area

Fig. 38. Ta-10W coated with Sn-25Al and oxidized 5 minutes at 3000°F by resistance heating. (500X)

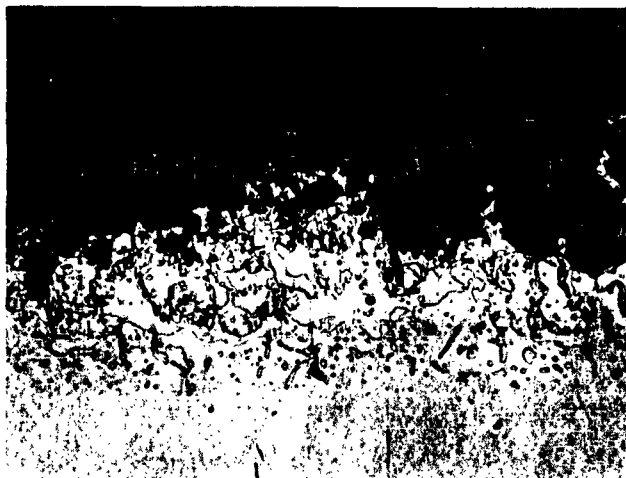


Fig. 39. Ta-10W coated with (Sn-25Al)-10TaAl₃ and furnace tested for 15 hours at 2800°F. (250X)

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 2-hour oxidation tests are shown plotted in Fig. 40.

Structural features of Ta-30Cb-7.5V samples coated with (Sn-50Al-Si)-10TaAl₃ are shown in Figs. 41, 42 and 43. In the relatively short-time tests and the as-coated samples shown in Figs. 41 and 42, 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. These structural features have not been noted on Ta-10W samples after testing. In the longer time tests, as shown by Fig. 43, it is interesting to note that there are islands of tin-rich phase around which the aluminide has sintered. Under polarized light, after 100 hours at 2500°F, there is a zone of optically active MA₁₃ bounded on either side by a lower aluminum aluminide. During exposure at 2800°F for 24 hours, the tin-rich islands have coalesced into larger patches completely surrounded by presumably a M₂Al phase. There is no evidence after this time and temperature exposure of any optically active phase. Considerable coating-substrate interface migration has occurred in both of these heavily coated samples. It should be emphasized, however, that this penetration is closely related to the thickness of the original coating, as can be seen in Table 32, where the weighted penetration values are quite close in spite of the large differences in time at different temperatures for three of the alloys tested.

The Cb-5Zr structure is shown in Fig. 44. After 23 hours at 2400°F it can be seen that failure is approaching over a fairly broad area and commences at the tin-rich phase region.

4.2 ELECTRON MICRO-BEAM PROBE ANALYSES

Samples of pure tantalum, Ta-10W, and Ta-30Cb-7.5V were specially prepared for probe analyses at Advanced Metals Research Company, Somerville, Mass. The samples were slurry coated with (Sn-25Al)-10TaAl₃ and examined in the as-coated condition and after oxidation exposure at 2800°F for two and eight hours for the Ta and Ta-10W and two and four hours for the Ta-30Cb-7.5V. Complete scans were made from the base metal through the coating to the oxide at a 45 degree angle to the coating to magnify the thickness of individual layers in the coating. A separate scan was made for each of the metallic elements of interest in the system being examined. Charts of each scan

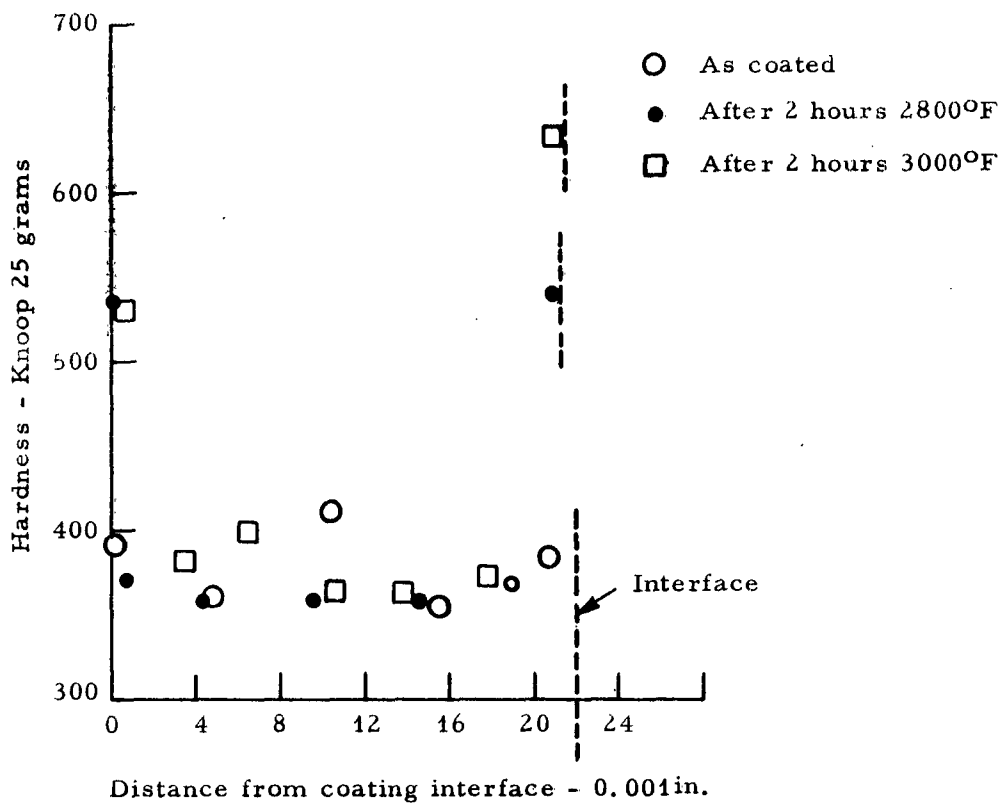
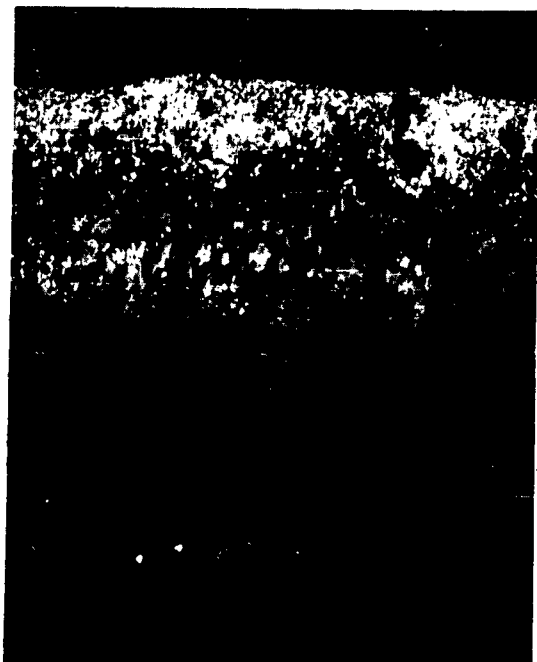


Fig. 40. Microhardness traverses on Ta-30Cb-7.5V coated samples. Samples of Ta-30Cb-7.5V coated with (Sn-25Al)-10TaAl₃.



(a) Average coating thickness 0.003"



(b) Average coating thickness 0.006"

Fig. 41. Sn-50(Al-Si)-10TaAl₃ coatings on Ta-30Cb-7.5V samples (polarized light). (500X)



(a) 2500°F - 2 hrs



(b) 2800°F - 2 hrs



(c) 3000°F - 2 hrs



(d) 2800°F - 8 hrs

Fig. 42. Ta-30 Cb-7.5V samples coated with (Sn-50Al-Si)-10TaAl₃ after oxidation tests.



(a) After 100 hrs at 2500°F



(b) Same as (a), but under polarized light



(c) After 24 hrs at 2800°F

Fig. 43. Ta-30Cb-7.5V samples coated with (Sn-50Al-Si)-10TaAl₃ (250X)

TABLE 32

Coating-Substrate Interface Penetration for Furnace
 Oxidation Tested Samples of Ta-10W and Cb-5Zr
 Coated with (Sn-25Al)-10TaAl₃ and Ta-30Cb-7.5V
 Coated with (Sn-50Al-Si)-10MoAl₃

Alloy	Test temp. (°F)	Time (hours)	Coating weight (mg/cm ²)	Penetration (mils)	Weighted penetration (mils/mg/cm ²)
Ta-10W	2800	6	55	1.1	0.020
Ta-10W	2800	15	84	2.1	0.025
Ta-30Cb-7.5V	2500	87	48	4.0	0.083
Ta-30Cb-7.5V	2500	100	69	6.5	0.094
Ta-30Cb-7.5V	2800	9	40	4.3	0.107
Ta-30Cb-7.5V	2800	24	73	6.9	0.096
Cb-5Zr	2400	4	24	1.0	0.042
Cb-5Zr	2400	23	49	2.0	0.041



Fig. 44. Cb-5Zr coated with (Sn-25Al)-10TaAl₃ after
furnace oxidation tests at 2400°F for 23 hours.
(250X)

were returned to the GT&E Laboratories together with background counts and intensity measurements on standards of each of the pure elements of interest which were run concurrently.

Areas had to be selected on each scan which represented the same location on the sample, the relative intensities calculated, an approximate composition assumed, absorption corrections made, and the exact compositions calculated. Figure 45, which shows pure tantalum before and after oxidation testing, is illustrative of the types of structure encountered and the position and nature of the scans made. Unfortunately, the scans did not appear to traverse the identical location for each element. In addition, the complex and broken-up nature of the structures examined also made quantitative analysis of the data difficult. Quantitative analyses for the alloying additions in the base metals appear to be reasonably accurate in comparison with the nominal composition, as shown in Table 33. However, owing to the wide difference in absorption properties between aluminum and tantalum and its alloying additives and to the nature of the coating structure, only a qualitative summary of the results can be made.

TABLE 33

Electron Micro-Beam Probe Analyses of Alloy Base Metal Compositions

<u>Alloy</u>	<u>Nominal composition (w/o)</u>	<u>Probe composition (w/o)</u>
Ta-10W	W-10	9.8
	Ta-90	90.2
Ta-Cb-V	V-7.5	6.9
	Cb-30.0	31.3
	Ta-62.5	61.8



(a) As coated

(300X)



(b) After 2 hrs at 2800°F (300X)



(c) After 8 hrs at 2800°F (200X)

Fig. 45. Pure tantalum coated with (Sn-25Al)-10TaAl₃ showing probe location.

4.2.1 Pure Tantalum

Although calculations indicate the as-coated intermetallic present to be $TaAl_4$, it must be assumed that $TaAl_3$ is formed since this compound has been identified by x ray and its existence is well substantiated in the literature. The compound appears to have a fairly uniform composition. The excess Sn-Al phase varies in composition somewhat but is approximately 10% Al. There is evidence of a much higher aluminum composition at the extreme surface of the sample.

After two-hours oxidation at 2800°F, the intermetallic has been converted to a lower aluminum compound, probably Ta_2Al , although calculations indicate $TaAl$. This compound has a very thin layer of $TaAl_3$ interposed between it and the Sn-rich layer in some areas. Some tantalum is apparently in solution in the tin, approximately 1%, together with about 10% aluminum. The tin composition varies considerably, decreasing in going from adjacent to the substrate to the outer surface. There is a possibility of a small amount of tin present in the Ta_2Al compound. An aluminum-rich zone is at the coating surface which is probably Al_2O_3 , but by calculation appears much too high in aluminum.

After 8 hours at 2800°F the outer structure is broken up considerably. The aluminide compound has slightly less aluminum in it and its tin composition increased somewhat. Both the aluminum and tantalum composition in the tin appear to be equivalent to that after 2 hours, i.e., 10% and 1%, respectively. Again, an aluminum-rich region is found at the surface which calculates to be higher than that in Al_2O_3 .

4.2.2 Ta-10W Alloy

In the as-coated condition there is an aluminide compound, probably $TaAl_3$, which appears to change gradually in tantalum composition from inner to outer edge; there may be a small area adjacent to the substrate which is of constant composition. In addition there may be a broad diffusion zone and a very thin aluminide layer of lower aluminum composition next to the substrate. The tin composition in the Sn-Al layer changes sharply in composition, reaching a sharp peak of practically 100% Sn at or near the center. The aluminum composition varies inversely with the tin but then rises to about 45 to 80% near the surface. Tungsten appears to follow tantalum quite closely in compositional changes in the aluminide compound.

The aluminide intermetallic layer is broken up considerably after two hours at 2800°F and the aluminum composition is much lower than as-coated. There is an increase in aluminum in the compound going from the substrate to the tin-rich overlay. There may be a small amount of tin which diffused into the compound. The tin composition increases from compound to surface with an extremely sharp peak just below the surface, again approximating over 90% Sn. It appears that just above it is an aluminum-rich peak which may be Al_2O_3 . Calculations indicate that the Sn peak may correspond to SnO_2 . There appears to be little or no tantalum or tungsten in the tin-rich region; again the tungsten composition correlated with the tantalum.

After 8 hours at 2800°F the aluminide compound layer appears similar in appearance to that after 2 hours, but there is a composition gradient such that the aluminum is higher at the center of the layer and lower in contact with the tin-rich phase and with the substrate, indicating loss by diffusion in both directions. The overall aluminum composition is lower than at 2 hours and some tin, probably several percent, is found in the compound, decreasing towards the substrate. There is very little aluminum in the tin phase and a thick broken up aluminum-rich phase at the surface which may be impure Al_2O_3 since the aluminum concentration appears low; there are also indications that both tungsten and tantalum are in the oxide layer.

4.2.3 Ta-30Cb-7.5V Alloy

On the as-coated sample the MAl_3 (probably) aluminide compound appears to have two separate zones indicated mainly by two plateaus in each of the Ta, Cb and V charts. In addition there appears to be a ~~diffusion zone in the substrate. Both plateaus appear flat for the vanadium.~~ The Ta and Cb in the inner zones appear to have a smooth concentration gradient, whereas the outer zones have a tendency to "peak." In general, there appears to be no tendency toward segregation of the Ta, Cb or V. There is a tin-rich region which has a very sharp peak approximating over 95% tin; there is on top of this a broad aluminum-rich zone which peaks at over 80% aluminum.

After two hours at 2800°F the aluminide layer is quite broken up, but there is also an unusual distribution of Ta, Cb, and V. There are apparently several compound layers adjacent to the substrate consisting of aluminides lower in Al than MAl_3 . However, there is also a region above this where columbium and vanadium have concentrated and which may be an aluminide or tin compound, or a complex compound containing both. The tin trace

is very simple, having a small and large peak, and therefore it is difficult to state what kind of compound is present. Some tin is present in the aluminide layers next to the substrate. The surface layer appears to be Al_2O_3 .

After four hours at 2800°F the traces of the individual elements become quite complex and difficult to correlate. It is apparent that both columbium and vanadium, particularly vanadium, have become depleted in the inter-metallic zone nearest the substrate and predominate in a complex Ta-Cb-V aluminide nearer the surface. This compound also appears to be higher in aluminum than the two zones adjacent to the substrate. Again there appear to be Al-rich and Sn-rich zones intermixed in regions surrounding the intermetallics. There is also evidence of intermixed Al_2O_3 layers.

4.3 X-Ray Analyses

In the past, x-ray examinations have been made on samples that have been oxidation tested at 2500°F or higher. To obtain information relating to a broad temperature range, a number of Ta-10W samples were coated with Sn-25Al and tested at 1100, 1400, 2000, 2500 and 2800°F and then subjected to x-ray diffraction studies. The results are shown in Table 34. It is interesting to note that, after low temperature oxidation exposure, the Al_2O_3 film is not fully formed, is exceedingly thin, or is amorphous. At 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 is not found after higher temperature oxidation. It is quite probable that it exists beneath the Al_2O_3 film but cannot be detected because of the thickness of the film. The fact that tin oxide forms at all is somewhat surprising because of the relative thermodynamic stability of Al_2O_3 .

It had been noted in samples heated with an oxyacetylene torch at one end that a dark black band was formed on the surface of the sample in the somewhat cooler regions. As shown schematically in Fig. 46, one of these samples which had been heated at 2600°F for 26 hours formed this black band in the apparent region of 1500 to 1650°F . Qualitative x-ray scans taken across this region showed that the area was SnO_2 . Metallographic examination at this point showed that there was a general thickening in the coating because of an overlay of oxide which had formed. It is possible that SnO is formed in the hotter regions or volatilizes therefrom, oxidizes to the SnO_2 state, and deposits in a colder area.

TABLE 34

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

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

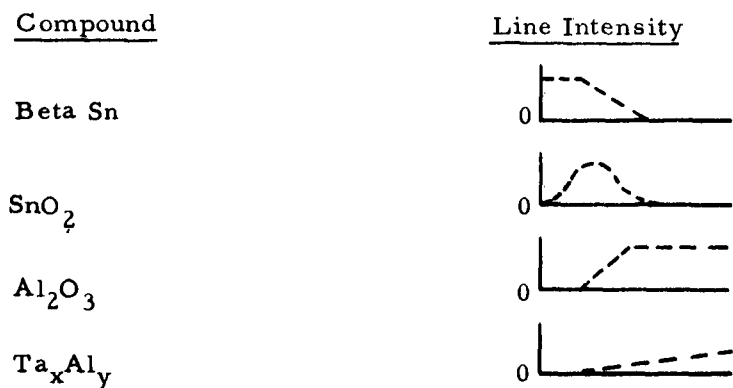
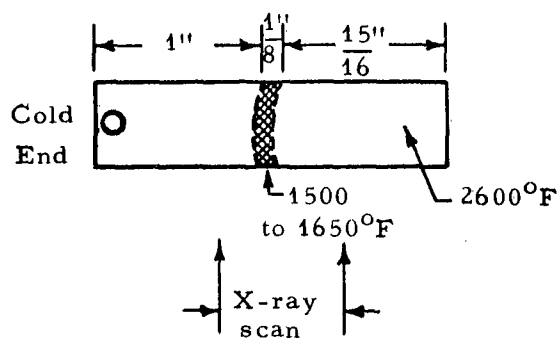


Fig. 46. Qualitative x-ray analysis of Ta-10W sample coated with (Sn-25Al)-10TaAl₃ and tested in an oxyacetylene torch at 2600°F for 26 hours. Dark area is SnO_2 growth.

To study oxide formation more carefully in its initial stages, a similarly coated sample was analyzed by the hot camera technique. The heating procedure and results of the analysis are shown in Table 35. The presence of a strong aluminum line and the absence of beta tin on the as-coated sample indicates that the starting point for the initial x-ray scan was in an aluminum-rich region. However, subsequent heating to temperatures of 1100°F and above changes the pattern completely. It is significant that in the vicinity of 1400°F, SnO is starting to form and after a half-hour at this temperature has converted to SnO₂, with Al₂O₃ forming and growing concurrently. The SnO₂ continues to increase on heating to 1800°F and becomes stronger with increased exposure at this temperature. Since the SnO₂ is not seen after hours of exposure at 2500 and 2800°F, as shown in Table 34, it is quite probable that the Al₂O₃ film is growing thick enough and is on the outside and thereby masks out the presence of SnO₂. Therefore the region of 1800°F appears to be a temperature range of preferred growth of the SnO₂. This evidence appears to refute the idea previously speculated upon that SnO₂ is deposited from a volatilized form of tin oxide created in the high-temperature region of the sample which was heated by oxyacetylene torch.

TABLE 35

Hot Camera X-ray Analysis of Ta-10W Sample
Coated with (Sn-25Al)-10TaAl₃

Step No.	Condition	X-ray scan temp. (°F)	Analysis
1	As coated	R. T.	Al, TaAl ₃ , + unidentified lines
2	Heated up	1100	Al, probably TaAl ₃ , high background
3	After 1.3 hours	1100	Al, TaAl ₃ , possibly Al ₂ O ₃ (weak pattern)
4	Heated further	1400	Al ₂ O ₃ , possibly SnO, + unidentified lines, possibly Ta-Al compounds
5	After 0.5 hours	1400	Al ₂ O ₃ (stronger), SnO ₂ , + weak lines
6	Cooled down	R. T.	Al ₂ O ₃ , SnO ₂ , Beta Sn, + weak lines
7	Reheated	1800	Al ₂ O ₃ , SnO ₂ , (stronger), + weak lines
8	Cooled down	R. T.	Al ₂ O ₃ , SnO ₂ , Beta Sn
9	Reheated	1800	Al ₂ O ₃ , SnO ₂ , (stronger than Step 8)
10	After 2.5 hours	1800	Al ₂ O ₃ , SnO ₂ , (stronger than Step 9)

5. SILICIDE COATINGS

It was not within the scope of this work to develop silicide coatings for tantalum alloys. However, in view of certain promising results with other work at the Laboratories, a limited contribution of GT&E silicide experience to the program was made, and no further work in the way of development was carried out.

5.1 Sn-Si SLURRIES

Samples of Ta-30Cb-7.5V were coated with various Sn-Si slurries by spray diffusion. In the initial attempts to insure wetting, diffusion was carried out at 2100°F under a vacuum of 30 microns. During the half-hour treatment, however, a good deal of the coating material evaporated, with a resultant thickness of only 0.25 mils per side. Samples so treated had very dark coatings and failed within 10 minutes at 2800°F. Nevertheless, it was of interest to note that wetting could be accomplished without aluminum in the mix.

Further attempts were made to spray coat Sn-10Si and Sn-25Si by diffusing at 2100°F for 1/2 hour in a vacuum of 0.1 micron. Small areas of the samples did not wet with the Sn-10Si mix. The Sn-25Si coating appeared metallic and had good coverage but peeled off readily, exposing a powdery layer of what probably was silicon. It was noted that the premixed slurry, when allowed to settle and separate, had a discolored lacquer layer which was not present in the Sn-Al slurries. Therefore a fresh batch of silicon powder was used to make up another series of coated samples. From the previous results it appeared that higher pressures during the diffusion treatment would be preferable at the 2100°F diffusion temperature. Therefore the samples were diffusion treated at 30 microns for 1/2 hour. The resultant coatings had rough surfaces and were not wetted around the wire suspension holes and were powdery in these areas. From these results it does not appear that tin is a proper slurry base for applying silicon coatings.

5.2 Ti-Si COATING

In view of promising results with other work in the Laboratories, samples of Ta-10W and Ta-30Cb-7.5V alloys were titanized at 2200°F for 16 hours and then silicided at 1900°F in argon, using a NaF-activated silicon powder pack. Coating data are shown in Table 36 and oxidation data in Table 37. It was found that the equivalent of 1.5 to 3 mils of

TABLE 36

Coating Data for Pretitanized Tantalum Alloy
 Samples Packed in a NaF-Activated Si-Al₂O₃
 Pack and Fired in Argon for 2 to 17 Hours

Siliciding time (hrs)	Average coating on					
	Ta		Ta-10 W		Ta-30 Cb-7.5V	
	(mg/cm ²)	(Mils Si)	(mg/cm ²)	(Mils Si)	(mg/cm ²)	(Mils Si)
2	7.8	1.3	6.9	1.2	7.4	1.3
4	11.9	2.0	11.1	1.9	10.7	1.8
17	19.4	3.3	17.6	3.0	17.3	2.9

TABLE 37

Furnace Oxidation Data for Ti-Si Coated Alloys

Run No.	Alloy	Coating wt. (mg/cm ²)	Test temp. °F	Time to failure (hrs)	Comments
<u>U160-70-1</u>	Ta-Cb-V	7.4	2800	1	Contact Marks
-2	Ta-Cb-V	10.7	2800	5-6	Contact Marks
-3	Ta-Cb-V	17.3	2800	3-4	Contact Marks
-1	Ta-10 W	17.6	2800	8	O.K.
<u>U160-73-4</u>	Ta-Cb-V	7.4	1800	213	Corner
-3	Ta-10 W	11.1	1800	221	Corner
-2	Ta-Cb-V	10.7	1100	221	Corner
-1	Ta-10 W	6.9	1100	24-28	Corner

silicon are deposited in 2 to 17 hours at 1900°F. Only a few samples of each alloy had been coated. Therefore oxidation test data are not extensive. The Ta-Cb-V alloy was not as well protected at 2800°F as was the Ta-10W alloy. Although there was evidence of interaction, mechanical or chemical, between the W-Si₂ pads used to support the samples and the Ta-Cb-V samples, failure occurred at other sites. Both alloys showed excellent resistance at 1800°F and both looked excellent after 1100°F exposure. However, a small corner failure was noted in the Ta-10W sample between 24 and 28 hours at 1100°F.

An oxyacetylene torch test was made to determine the maximum capability of the silicide coating on a Ta-10W sample with 17.6 mg/cm² of silicon coating. The sample was heated to 3100°F, held for five minutes, cooled slightly, and then reheated to 3150°F, at which time failure occurred at a point somewhat removed from the hottest portion of the sample. Examination of the sample under a binocular microscope showed some evidence of bubbling, which may have been indicative of a molten phase. There is a good probability that an element other than titanium that forms silicides with a higher melting eutectic would boost the maximum temperature capability of the system.

Representative photomicrographs of the Ti-Si structure on the Ta-10W samples before and after testing are shown in Fig. 47. It can be seen that after eight hours at 2800°F there is a fairly thick, glassy oxide film on the surface of the sample, some porosity in the next layer, together with some evidence of internal oxidation in small areas. However, it also appears as though the silicide layers are quite intact and adherent to the substrate.



(a) As coated



(b) After oxidation test at 2800°F
for 8 hours

Fig. 47. Ta-10W coupons Ti-Si coated. (250X)

6. BERYLLIDE COATINGS

Data obtained in previous work³ showed that beryllide coatings formed by a vacuum vapor deposition technique were promising but the brittle nature of the beryllides indicated the need for a diluent similar to that of the Sn-Al system.

The diluent systems explored were Sn-Be, Cu-Be, and Si-Be. The results of initial experiments are listed in Table 38. Coated samples were prepared by blending the metal powders, mixing them with a lacquer slurry, and applying the coatings by painting.

Initial work with Sn-Be and Cu-Be slurries on Ta-10W resulted in coatings which were quite poor and nonwetting after vacuum diffusion treatment. Later, attempts were made to prewet the surfaces with Sn-15(Al-11Si) or Cu-15(Al-Si) in a pretreatment in order to use this thin layer as a diffusion medium through which a beryllide subsurface layer could be built up. Although excellent precoats were obtained, the berylliding treatments at elevated temperatures resulted in evaporation of most of the tin or copper.

Attempts were then made to coat samples of columbium and Ta-10W with Si-Be slurries but after diffusion treatment these coatings were flaky and nonadherent. Preberylliding, followed by siliconizing, resulted essentially in a beryllide surface with little evidence of a silicon or Si-Be surface overlay. Similar attempts at coating preberyllided samples of both materials with Cu-Be mixtures indicated that the copper might be reacting appreciably with the outer beryllide layer during the diffusion treatment as shown in Fig. 48.

In checking the Cu-Be system further, samples of columbium and Ta-10W were hot dipped in alloys of Cu-2Be, Cu-5Be, and Cu-6Be at temperatures of 1800-1950°F for times of 2-10 minutes. The Cu-2Be bath did not wet too well, but complete wetting was obtained with the higher beryllium alloys. However, there was considerable dross formation on the bath surface and the sample surfaces were "pebbly" after dipping.

Figure 49 shows that although wetting occurred with Cu-5Be alloy there was no evidence of the growth of a beryllide phase. The Cu-6Be bath was more reactive on the columbium and islands of a beryllide formed and broke away from the surface. However, no beryllide was formed on the Ta-10W. One hour oxidation tests at 2200°F gave poor results with all coatings. Black molten scales were produced which gave

TABLE 38

Berylliding Data for Samples Painted with
Powder Slurries in Lacquer Carrier

Run No.	Alloy	Coating	Vac. D. H. treatment temp time (°F) (hrs)	Comments
-	Ta-10W	Sn-10Be	1900 0.5	Poor wetting
-	Ta-10W	Sn-23Be	1900 0.5	Poor wetting
-	Ta-10W	Cu-17Be	1900 0.5	Poor wetting
-	Ta-10W	Cu-36Be	1900 0.5	Poor wetting
-	Ta-10W	(a) Sn-15(Al-Si)	1900 0.5	-
-		(b) Be	2000 4.0	Sn volatilized
-	Ta-10W	(a) Sn-15(Al-Si)	1900 0.5	-
-		(b) Be	1800 16.0	Spotty
-	Ta-10W	(a) Cu-15(Al-Si)	1900 0.5	-
-		(b) Be	2000 4.0	Cu volatilized
-	Ta-10W	(a) Cu-15(Al-Si)	1900 0.5	-
-		(b) Be	1800 16.0	Spotty
171-14	Ta-10W	Si-20Be	2000 4.0	Flaked
171-14	Ta-10W	Si-30Be	2000 4.0	Flaked
171-14	Cb	Si-20Be	2000 4.0	Flaked
171-14	Cb	Si-30Be	2000 4.0	Flaked
171-22	Ta-10W	(a) Be	2000 4.0	O. K.
		(b) Si	2000 4.0	Spotty
171-22	Cb	(a) Be	2000 4.0	O. K.
		(b) Si	2000 4.0	Spotty
171-24	Ta-10W	(a) Be	2000 4.0	-
		(b) Cu-17Be	1800 0.5	Cu attacks beryllide
171-30	Ta-10W	(a) Be	2000 4.0	-
		(b) Cu-5Be	1650 0.5	Cu attacks beryllide

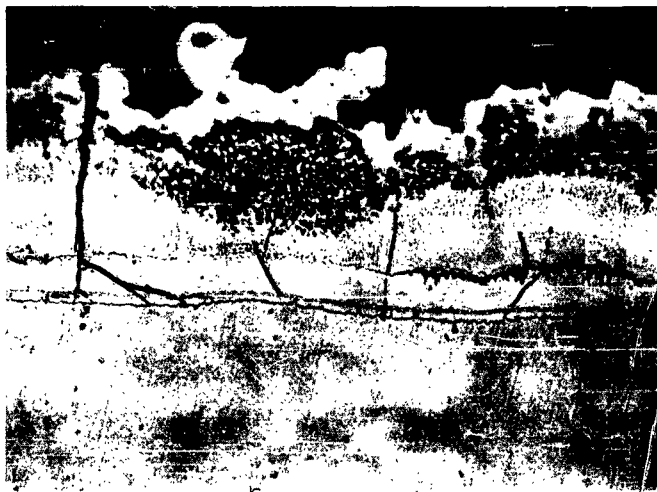
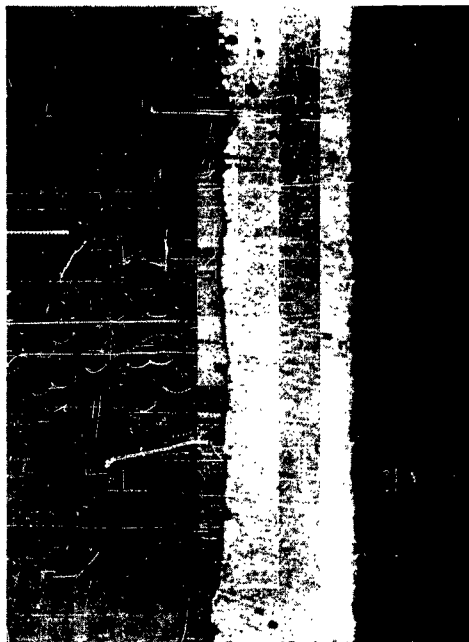


Fig. 48. Preberyllided Ta-10W coated with Cu-17 Be slurry and diffused at 1800°F for 1/2 hour at 1 micron. (500X)



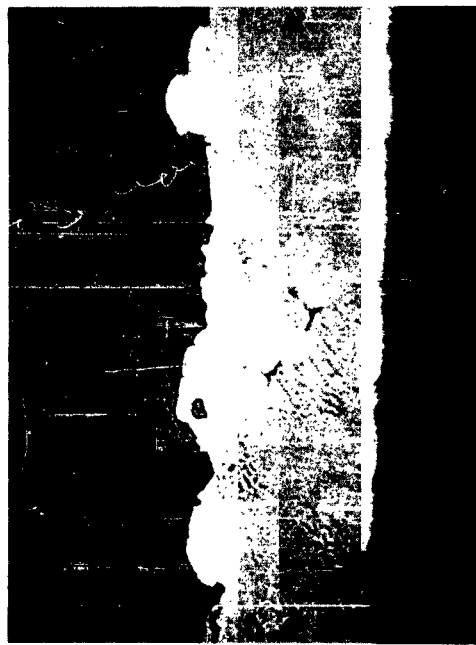
(a) Cb in Cu-5 Be dipped 10 minutes at 1925°F



(b) Ta-10W in Cu-5 Be dipped 10 minutes at 1925°F



(c) Cb in Cu-6 Be dipped 10 minutes at 1950°F



(d) Ta-10W in Cu-6 Be dipped 10 minutes at 1950°F

Fig. 49. Samples hot dipped in Cu-Be alloys. (500X)

no protection. At 1800°F the samples remained bright and relatively unaffected. At 2000°F the samples were covered with what looked like a reddish copper oxide in many areas.

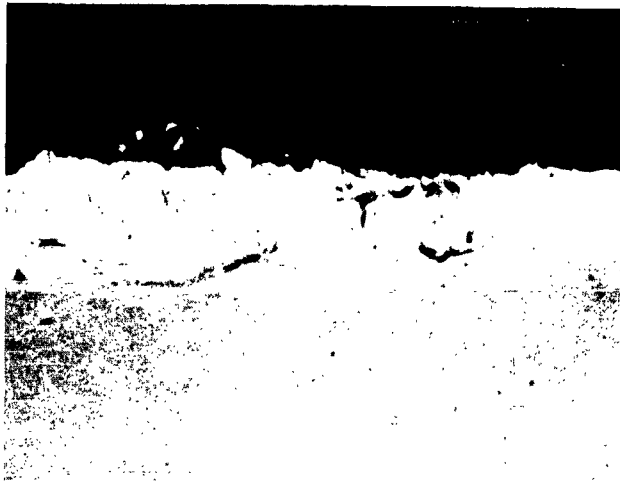
Some promising results were obtained using silver as a diluent. The test runs are listed in Table 39. Attempts to diffuse the slurry-painted coatings in air were partially successful. However, the samples' edges oxidized. The fact that wetting occurred was very promising. Poor coatings were obtained after vacuum treatments due to volatilization of the silver. It should be noted that the vacuum diffusion furnace was large and required relatively long heating and cooling times.

Only partial wetting was obtained on preberyllided samples after painting and diffusing in air. However, excellent looking coatings were obtained by a diffusion treatment in an argon atmosphere. These coatings are shown in Fig. 50. The beryllide layer on the singly treated Ta-10W is fairly thin and the Ag-Be coating on the preberyllided sample is non-uniform. However, the Ag-Be does not appear to attack the outer beryllide as copper does. Initial oxidation tests at 2200°F looked promising. However, work was discontinued on this phase of the investigation to concentrate on Sn-Al.

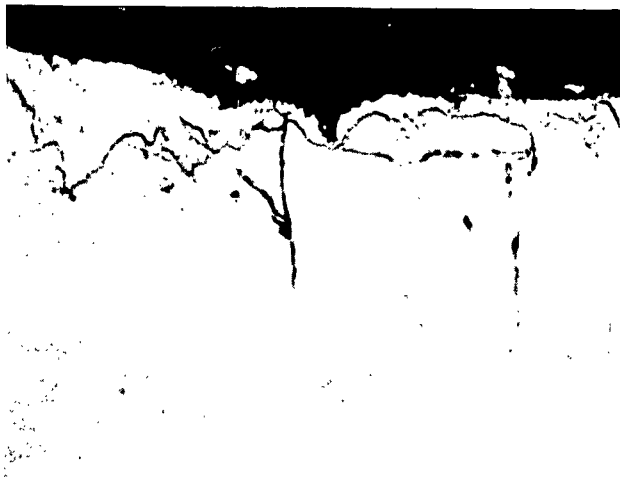
TABLE 39

Silver Diluent Coating Treatments on Ta-10W Samples

Run No.	Coating	Diffusion treatment		Comments
		temp (°F)	time (hours)	
U 171-37	Ag-5Be	1950	0.5 - air	Edge oxidation
U 171-37	Ag-10Be	1950	0.5 - air	Edge oxidation
U 171-37	Ag-5Be	1950	0.5 - vacuum	Ag evaporated
U 171-37	Ag-10Be	1950	0.5 - vacuum	Ag evaporated
U 171-37	(a) Be	2000	2.0 - vacuum	--
U 171-37	(b) Ag-5Be	1950	0.5 - air (2x)	Partial wetting
U 171-37	(a) Be	2000	2.0 - vacuum	--
U 171-37	(b) Ag-10Be	1950	0.5 - air (2x)	Partial wetting
U 171-43	Ag-10Be	2000	1.0 - argon	Smooth - shiny
U 171-43	(a) Be	2000	4.0 - vacuum	--
U 171-43	(b) Ag-10Be	2000	1.0 - argon	Gray - smooth



(a) No preberylliding



(b) Preberyllided at 2000°F for 4 hrs.

Fig. 50. Samples slurry-painted with Ag-10 Be and argon fired at 2000°F for one hour.

7. DISCUSSION

It cannot be emphasized too strongly that Sn-Al is a coating system. In general, changing the relative proportions of tin and aluminum serves mainly to change the thickness of aluminide and, to some extent, the composition of the tin-rich phase which remains at the surface. The most important factor of protection appears to be the thickness of the tin-rich phase, which acts as a sink or reservoir for aluminum, and which apparently diffuses into and through it from the $TaAl_3$ or Ta_2Al inter-metallic compound beneath it. Electron probe data indicate the Ta_2Al phase is stable over a range of aluminum compositions. This case is probably similar to Cb_2Al ¹⁴ which is stable with 33-38 at/o Al. It can be speculated that the tin-rich reservoir cannot be replenished with aluminum where the Ta_2Al composition falls to a critical aluminum level.

The tin-rich phase appears to be particularly important at 2800°F and above. At lower and intermediate temperatures with Ta-10W it appears that the thickness of the $TaAl_3$ intermetallic compound is also important. Therefore prior diffusion temperature should be 1850-1900°F for best low-temperature behavior. In general, any disadvantage which may be attributed to the thicker tin-rich overlay would be in its tendency towards "bleeding" at low temperatures and in wrinkling at high temperatures.

The use of refractory metal additives such as tantalum and molybdenum to retain the thick tin-rich overlay appears quite promising. Although these additives appear to be the only ones suitable for maximum temperature use, it is quite possible that where low-temperature long-time service is required, other less refractory metal additives may be more advantageous. Uniform coatings have been obtained on samples up to 10 inches long. However, there have been some erratic tendencies. For example, in isolated cases on test hardware approximately 6 inches long, some run-off has been encountered. The present technique of utilizing refractory metal additives appears to be fairly suitable for slurry spraying. It has also been possible to obtain equivalent coatings by painting the slurry. However, in many practical applications, particularly for large sheet components, it would be preferable to be able to utilize a slurry dipping technique. Present experience has indicated that considerably more work would have to be done to be able to utilize refractory metal additives in slurry dips. It has been found that the additive, because of its higher density, tends to separate out. It will probably also be advantageous to utilize prealloyed Sn-Al powders in order to remove another probable separation variable from the slurry application process.

The base metal composition can have considerable effect on coating behavior with Sn-Al coatings. Alloying additives that form more thermodynamically stable oxides than aluminum can apparently be detrimental to oxidation resistance when present in amounts of 5 to 10 percent. Both zirconium and hafnium are prime examples. It is also possible, however, that at these alloying levels they lead to the formation of low-melting phases. Nevertheless, the severe reaction of the hafnium-containing tantalum alloy with Al_2O_3 at high temperatures strongly indicates that oxide stability is affected.

Both columbium and vanadium appear to be good alloying additives to tantalum from the standpoint of compatibility with the coating. There is some decrease in maximum temperature capability, probably because of the formation of lower melting phases, particularly in combination with the silicon additive to the coating. The major advantages imparted by these additives are the excellent low-temperature oxidation resistance and consistent behavior at high temperatures, including very good cyclic oxidation resistance. In addition, thicker and more uniform coatings can be obtained with this alloy, thereby providing a means for increasing the oxidation life considerably. With thicker coatings, however, diffusion effects are considerably greater than in the Ta-10W alloy. On the other hand, diffusion effects have a more normal relationship with temperature in the Ta-30Cb-7.5V alloy, particularly where localized heating is involved and a temperature gradient exists. In turn, the thinner coatings are more protective to the Ta-10W alloy and apparently have much better self-healing properties.

Temperature gradients in Ta-10W, due to localized heating, also lead to the formation of SnO_2 on the surface. With extended periods of heating and cycling it is likely that this mechanism can be responsible for the gradual loss of tin and eventually limit the full effectiveness of the coating.

The attainment of more uniform coating thicknesses and the large number of samples tested in the extended evaluation part of the program have served to give a better overall picture of oxidation protection. However, considerably more data needs to be obtained, particularly on larger samples and more intricate components. In view of advanced aerospace requirements, there is need to obtain more definitive data regarding behavior in reduced pressure oxidizing environments, particularly with higher velocity gas flow. It would be preferable if a nonresistance type of heating method

could be employed. However, by proper design of sample size and shape, based on existing sample performance, much valuable data could also be obtained with resistance heating.

The limited work done with molybdenum and tungsten indicates that there may be some sort of low-temperature anomalous oxidation behavior which is time and temperature dependent. From the peculiar appearance of sheared edges on molybdenum and tungsten samples after coating, it is felt that edge effects, due to laminations, were probably responsible for any detrimental effects on oxidation resistance during the medium temperature range testing. Yet there are indications that poor oxidation behavior can be alleviated by alloy additives to the coating. For example, it has been found on another program that chromium additives to the Sn-Al slurry increase the coating life considerably at 2500°F. This work was done on resistance-heated samples; the resultant temperature gradient, therefore, included much lower temperatures also. In view of the excellent short-time performance at temperatures above 3000°F previously shown for molybdenum and tungsten with this coating system,³ it would appear desirable to investigate this system further to obtain a more comprehensive evaluation.

8. SUMMARY AND CONCLUSIONS

1. The major effect of increasing aluminum composition in Sn-Al slurry coatings is in the increase of the aluminide phase thickness.
2. The thickness of the Sn-Al phase is more important than the thickness of the aluminide phase for increased protection, particularly at very high temperatures.
3. The amount of Sn-Al phase can be increased and run-off prevented by refractory metal additives to the slurry such as Ta and Mo. About 10% appears to be optimum, and Mo is more effective. Total thickness can be increased by several applications of coating.
4. The Sn-Al coating system is sensitive to substrate composition. Additives which lower melting points appreciably decrease the maximum temperature capability of the coating. Those forming more thermodynamically stable oxides than Al_2O_3 cause a general decrease in coating protection.
5. Coating-substrate interaction reaches an intermediate peak at 2300°F on Ta-10W, whereas there is a normal increase with increasing temperature on Ta-30Cb-7.5V.
6. Ta-10W can be protected for short times by the (Sn-25Al)-10TaAl₃ coating at temperatures to 3350°F (optical), Ta-30Cb-7.5V to 3200°F, and Cb-5Zr to 2500°F. At temperatures up to 2800°F, the (Sn-50Al-Si)-10TaAl₃ coating is more reliable on Ta-30Cb-7.5V.
7. Sn-Al coatings are protective during both rapid and slow short-time deformation at elevated temperatures. They also have self-healing capabilities.
8. Mechanical properties at room and elevated temperature of .02-in.- to .04-in.-thick sheet are not adversely affected by the Sn-Al coatings investigated.
9. Sn-Al coatings have reduced stability in the 1 to 12 mm pressure range. Instability is strongly pressure and temperature dependent and is related to vaporization of the Sn-Al phase and the decomposition of TaAl₃.

10. Ti-Si pack coatings are protective on tantalum alloys but not to as high a temperature as Sn-Al.
11. Silver is a good diluent for beryllium in providing coatings that are analogous to Sn-Al in structural make-up.

9. RECOMMENDATIONS FOR FUTURE WORK

1. The Sn-Al process should be scaled up for coating larger size and more intricate components, aiming at compositions already proven protective and techniques including slurry spraying, dipping, and painting.
2. The Sn-Al system should be evaluated on new tantalum base alloys, particularly those in the Ta-Hf-W system with low hafnium.
3. An extensive investigation should be made into the behavior of Sn-Al coatings in reduced air pressure environment more closely simulating reentry conditions.
4. Further investigation should be made into the feasibility of developing improved Sn-Al base compositions for protecting molybdenum and tungsten for longer times. A more extensive evaluation of known compositions should also be made on these metals.
5. Development of the Ag-Be slurry process should be studied further on a feasibility basis.

10. REFERENCES

1. F.F. Schmidt et al, "Investigation of the Properties of Tantalum and Its Alloys," WADD, TR 61-106, Battelle Memorial Institute to ASD, May 1961.
2. W.D. Klopp et al, "Development of Protective Coatings for Tantalum-Base Alloys," ASD, TR 61-676, Battelle Memorial Institute to ASD, January 1962.
3. D.D. Lawthers and L. Sama, "High Temperature Oxidation Resistant Coatings for Tantalum-Base Alloys," ASD, TR-61-233, Sylcor Division of Sylvania Electric Products Inc. to ASD, October 1961.
4. M. Hausen, "Constitution of Binary Alloys," McGraw-Hill, New York, 1957.
5. R.M. Paine, A.J. Stonehouse, and W.W. Beaver, "An Investigation of Intermetallic Compounds for Very High Temperature Applications," WADC, TR 59-29, Part I, January 1960 and Part II, July 1960.
6. O. Kubaschewski and B.E. Hopkins, "Oxidation of Metals and Alloys," New York Academic Press, 1953, p. 17.
7. Structure Reports, International Union of Crystallography, Vol. 10, 1945-46, p. 118.
8. L.L. Bircumshaw and G.D. Preston, "Studies on the Oxidation of Metals - Part III. The Kinetics of the Oxidation of Molten Tin," Philosophical Magazine, Vol. 21, 1936, pp. 686-97.
9. W. Gruhl and U. Gruhl, Metall., 6 (1952), April, pp. 177-82.
10. H. Nowatny, C. Brukl, F. Benesovsky, "Investigation of the Systems Ta-Al-Si and W-Al-Si," (German) Monatshefte fur Chemie, Vol.92, Part I, 1961.
11. H.R. Ogden et al, "Scale-Up Development of Tantalum Base Alloys," ASD, TR-61-684, March 1962, Battelle Memorial Inst. to Aeronautical System Div. on Contract AF 33(616)-7452.

12. T.E. Tietz and J.W. Wilson, "Mechanical, Oxidation, and Thermal Property Data for Seven Refractory Metals and Their Alloys," Code 2-36-61-1, September 1961, Lockheed Missiles and Space Div.
13. Dupont Metal Products - Product Data Sheet No. 1, Columbium Alloys D-14, D-31, D-36, January 1962.
14. Cb-Al Phase Diagram. Private communication with Denver Research Institute, 1959.

Appendix I

COATING MATERIALS

<u>Material</u>	<u>Designation</u>	<u>Particle Size</u>	<u>Supplier</u>
Aluminum	MD 101 Powder	-200	Metals Disintegrating
Al-11 Si	718 Powder	-200	Alcoa
Tin	MD 301	-325	Metals Disintegrating
Tantalum	Powder	-325	Kawecki
Titanium	Powder (Hydride)	-325	Metals Hydrides
Silicon	Powder	-325 (99.91% Si)	Chas. Hardy
Molybdenum	Powder	-325	Chas. Hardy
Tungsten	Powder	-325	Sylvania Elec. Prod.
Lacquer	L-18 Nitro Cellulose		Raffi & Swanson

1. Refractory metals
2. Oxidation protection
3. Sn-Al coatings
- I. AFSC Project 7312, Task 73120
- II. Contract AF 33 (657)-7339
- III. General Telephone & Electronics Laboratories Inc. Bayside, N. Y.
- IV. L. Sama
- V. Secondary Rpt No. TR 62-460.7
- VI. AVAL IR OTS
- VII. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals & Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr ASD-TDR-63-160. OXIDATION RESISTANT COATINGS FOR TANTALUM ALLOYS AND OTHER METALS. Final report, Feb 63, 141p. incl illus., tables, 14 refs.

Unclassified Report
The effect of coating composition on structure and oxidation behavior was studied using a Sn-Al spray-slurry system with Ta alloys, Co, W and Mo. At 3000°F increased oxidation protection was related to the thickness of the tin-rich surface phase. Refractory metal powder additives served best to

(over)

increase the thickness of this phase. Coating composition was optimized and an extensive evaluation was carried out with Ta-10W, Ta-30Co-7.5V and Co-5Zr. In oxidation tests at 1100 to over 3000°F protective life was significantly affected by substrate composition, coating thickness and thermal cycling. Tensile and stress rupture data on coated samples at 2000 to 3000°F correlated well with data in the literature for uncoated material. Preliminary studies were made of coating stability at air pressures in the micron to millimeter range. Oxidation effects were explored by electron probe. Oxidation data were obtained for several Ta alloys coated with Ti-Si.

1. Refractory metals
2. Oxidation protection
3. Sn-Al coatings
- I. AFSC Project 7312, Task 73120
- II. Contract AF 33 (657)-7339
- III. General Telephone & Electronics Laboratories Inc. Bayside, N. Y.
- IV. L. Sama
- V. Secondary Rpt No. TR 62-460.7
- VI. AVAL IR OTS
- VII. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals & Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr ASD-TDR-63-160. OXIDATION RESISTANT COATINGS FOR TANTALUM ALLOYS AND OTHER METALS. Final report, Feb 63, 141p. incl illus., tables, 14 refs.

Unclassified Report
The effect of coating composition on structure and oxidation behavior was studied using a Sn-Al spray-slurry system with Ta alloys, Co, W and Mo. At 3000°F increased oxidation protection was related to the thickness of the tin-rich surface phase. Refractory metal powder additives served best to

(over)

increase the thickness of this phase. Coating composition was optimized and an extensive evaluation was carried out with Ta-10W, Ta-30Co-7.5V and Co-5Zr. In oxidation tests at 1100 to over 3000°F protective life was significantly affected by substrate composition, coating thickness and thermal cycling. Tensile and stress rupture data on coated samples at 2000 to 3000°F correlated well with data in the literature for uncoated material. Preliminary studies were made of coating stability at air pressures in the micron to millimeter range. Oxidation effects were explored by electron probe. Oxidation data were obtained for several Ta alloys coated with Ti-Si.