NASA CR-54529

DEVELOPMENT OF COATINGS FOR TANTALUM ALLOY NOZZLE VANES

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-7276

SOLAR

DIVISION OF INTERNATIONAL HARVESTER COMPANY

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RDR 1396-3

FINAL REPORT

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TECHNICAL MANAGEMENT
NASA LEWIS RESEARCH CENTER
CLEVELAND, OHIO

ROBERT E. OLDRIEVE, PROJECT MANAGER
SALVATORE J. GRISAFFE, RESEARCH ADVISOR

SOLAR
DIVISION OF INTERNATIONAL HARVESTER COMPANY
2200 PACIFIC HIGHWAY, SAN DIEGO, CALIFORNIA 92112

FOREWORD

This Final Summary Report covers the work performed under NASA Contract NAS3-7276 during the period 1 May 1965 through 31 January 1967. The Solar internal number RDR 1396-3 has been assigned.

This contract was initiated between NASA Lewis Research Center and the Solar Division of International Harvester, for the Development of Coatings for Tantalum Alloy Nozzle Vanes. Technical direction was supplied by Robert E. Oldrieve, Project Manager, of the Lewis Research Center, Cleveland, Ohio. Salvatore J. Grisaffe served as NASA Research Advisor.

A. R. Stetson was the Program Director and R. T. Wimber was the Principal Engineer. Mr. O. M. Stansfield and F. J. Hodnick were contributing engineers.

The coatings were applied by D. H. Creighton, Jr. and G. T. Moyers. The metallography was performed by R. Hutting. The electron microprobe work was done by C. H. Saucer, and the electron micrographs were obtained by J. M. Stice. T. L. Johnson obtained the X-ray diffraction patterns.

SOLAR PUBLICATION REVIEW

Approved by: John V. Long

John V. Long
Director of Research

ABSTRACT

A group of silicide coatings developed for the T222 tantalum-base alloy have afforded over 600 hours of protection at 1600 and 2400 F during cyclic exposure in air. These coatings were applied in two steps. A modifier alloy was applied by slurry techniques and was sintered in vacuum prior to siliciding by pack cementation in argon. Application of the modifier alloy by pack cementation was found to be much less effective. The addition of titanium and vanadium to molybdenum and tungsten yielded beneficial modifier alloys, whereas the addition of chromium showed no improvement. After siliciding, the 15Ti-35W-15V-35Mo modifier alloy exhibited the best performance; one sample survived 1064 hours of oxidation at 2400 F. This same coating was the only coating to reproducibly provide 600 hours of protection at both 1600 and 2400 F; in the second and third of three experiments, involving oxidation of three to five specimens at each temperature in each experiment, no failures were observed in 600 hours of testing. The slurry coatings were also shown to protect the Cb752 and D43 columbium-base alloys.

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INTRODUCTION

The efficiency and thrust of turbojet engines can be improved by increasing their operating temperatures. However, as turbine temperatures are increased, the number of materials suitable for use as turbine nozzle vanes decreases rapidly. Above the temperatures where the iron-, nickel-, and cobalt-base superalloys lose long-term strength, the mechanical properties of the refractory metals attract interest. Specifically, the tantalum alloy designated T222 (Ta-9.6W-2.4Hf-0.01C) is one of the more promising nozzle vane materials, if a suitable oxidation-resistant coating can be developed. This report summarizes the results of a research program having as its goal the development of a coating that will prevent oxidation and interstitial contamination of the T222 tantalum alloy when exposed to static air at 2400 F for a minimum of 600 hours, with an ultimate goal of 3000 hours. To be fully effective, the coating must also provide protection at lower temperatures and under cyclic conditions. The approach taken to the solution of the coating problem involved silicide-type coatings. At the outset of the subject program, the best silicide coatings for tantalum alloys provided 30 to 50 hours of protection at temperatures in the range of 1600 to 2400 F.

Simple siliciding does not adequately improve the oxidation resistance of the unmodified T222 alloy. In less than thirty hours at 2300 F silicided, unmodified samples failed in oxidation testing. Thus, modification of the composition of the silicide coatings was necessary and was accomplished by alloying the surface of the T222 before siliciding.

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TECHNICAL APPROACH

2.1 STATEMENT AND ANALYSIS OF THE PROBLEM

Turbine nozzle vanes are subject to high-velocity gases that cause a high aerodynamic shear stress on the surface. To this condition must be added the erosive effect of particulate matter such as finely divided carbon resulting from local fluctuations in the combustion conditions. Viscous coatings flow under such conditions, and coatings containing liquid can be stripped from the substrate by a high-velocity flame. Consequently, one of the first requirements of a coating is that it be able to resist the shear and erosion encountered in service. This criterion eliminated many of the fluid and partially fluid coatings from consideration. The Al/Sn-type coatings and the high boron content coatings were eliminated because of this requirement. Tests of the Al/Sn and Cr/Ti-Si/B coatings in a plasma torch at only 2500 F have shown these types of coatings to perform inadequately even though the shear forces were far lower than on a turbine vane (Ref. 1). Silicide-type coatings which are solid at operating temperatures appeared to offer the most potential for protection of tantalum alloy nozzle vanes. In general, silicide coatings have presented the most successful approach to the coating problem for temperatures of 3000 F and less (Ref. 2).

The brittle silicide coating is usually subject to craze cracking because normally there is a significant mismatch in thermal expansion of the coatings and the substrate. Defects can also arise because of external influences such as creep, impact, or thermal shock. Minimizing the possibility of catastrophic oxidation at coating defects was considered the most significant problem to be solved.

The coefficient of expansion of T222 alloy and some of the important coating disilicides are contained in Table I. The expansivity of T222 is so low that all disilicides will be in tension at any temperature below the application temperature. Aluminides with higher thermal expansions present an even more severe problem. In general, all potential coating materials have expansivities greater than the substrate. Experience has shown that the high-expansion coatings exhibit a craze pattern of cracks

TABLE I

EXPANSION COEFFICIENT OF REFRACTORY SILICIDES AND THE T222 ALLOY (REF. 3)

Alloy	Composition in Atomic Percent							Coefficient of Expansion $X10^{-6}$/degrees F	
	Ti	V	Cb	Cr	Mo	W	Si	400 F	1800 F
T222	--	--	--	--	--	--	--	3.00	3.85
-	19	--	--	--	15	--	67	5.56	5.56
-	13	--	--	--	7	--	80	3.92	3.92
-	9	--	11	--	11	--	69	5.38	5.38
-	19	--	13	--	9	--	59	4.29	7.85
-	--	--	--	--	32	--	68	4.54	4.54
-	21	--	--	--	--	15	64	5.50	5.50
-	11	--	--	--	--	12	77	3.84	3.84
-	10	--	7	--	--	11	72	5.44	5.44
-	16	--	14	--	--	5	65	5.80	5.80
-	--	--	--	--	--	31	69	4.36	4.36
-	17	--	--	17	--	--	66	6.00	8.56
-	12	--	--	9	--	--	79	5.44	5.44
-	10	--	--	23	--	--	67	6.48	8.54
-	14	--	10	11	--	--	64	6.65	6.65
-	2	--	11	6	--	--	81	4.82	4.82
-	7	--	11	15	--	--	67	6.03	7.68
-	--	--	--	100	--	--	--	5.0	6.7
-	--	--	--	--	--	100	--	2.65	2.65
-	--	--	--	--	100	--	--	3.35	3.35
-	--	14	--	18	--	--	68	5.68	11.32
-	--	8	--	25	--	--	67	6.26	8.55
-	--	25	--	8	--	--	67	5.74	7.33
-	--	10	10	11	--	--	69	6.53	6.53
-	--	5	10	17	--	--	68	6.15	7.46
-	--	15	10	10	--	--	65	5.92	5.92
-	--	14	17	--	--	--	69	5.98	5.98
-	8	8	--	17	--	--	67	7.25	7.25
-	6	12	--	15	--	--	68	7.30	7.30
-	3	5	10	17	--	--	65	6.45	6.45
-	--	30	--	--	--	--	70	7.25	7.25

on cooling down from the coating temperature. These cracks, although they tend to heal at elevated temperatures, can severely decrease the low-temperature protection afforded by the coatings. For example, work at Solar has shown that the silicide-coated T111 alloy with an 0.004-inch thick coating has a longer 2800 F oxidation life (12 hours) than 1800 F life (1 hour); whereas, diffusion kinetics predict a life several orders of magnitude greater at the lower temperatures. The problem may, in part, be due to pest type oxidation failure, but it is thought to be primarily the result of oxidation within the differential expansion cracks. The growth of substrate oxide in cracks stresses the coating with consequential spalling and rapid failure.

2.2 PROPOSED APPROACH

The most promising approach for successfully coating the T222 alloy was considered to be modification alloying of the surface to improve the basic oxidation resistance of the alloy, followed by siliciding only part of the modified layer. The unsilicided alloy layer beneath the oxidation resistant silicide layer was expected to serve two purposes:

- The unsilicided alloy might act as a ductile layer of intermediate thermal expansion that might mitigate the high shear stress resulting from differential expansion between the substrate and the silicide coating.
- By improving the basic oxidation resistance of the substrate, alloying might mitigate oxidation at the base of cracks resulting from differential expansion and other damage, giving the silicide coating time to repair itself by diffusional processes.

At the outset of the experimental program, pack cementation was investigated as a means of accomplishing the modification alloying. However, as the program developed, it became apparent that pack cementation modification has serious limitations and that the modification alloying can be much more effectively accomplished by slurry coating followed by vacuum sintering. Throughout the entire program siliciding was accomplished by pack cementation.

2.3 SELECTION OF THE BASIC COATING SYSTEM

A review is presented of the factors which influenced selection of the coating systems. The effects of alloy additions on the oxidation resistance of tantalum alloys and the effect on the silicide developed therefrom are covered.

2.3.1 Effect of Alloying Additions on the Substrate

A simplified picture of the effects of various alloying metals on the oxidation weight-gain behavior of tantalum is shown in Figure 1 for oxidation at 1832 to 2192 F in air (Ref. 4).

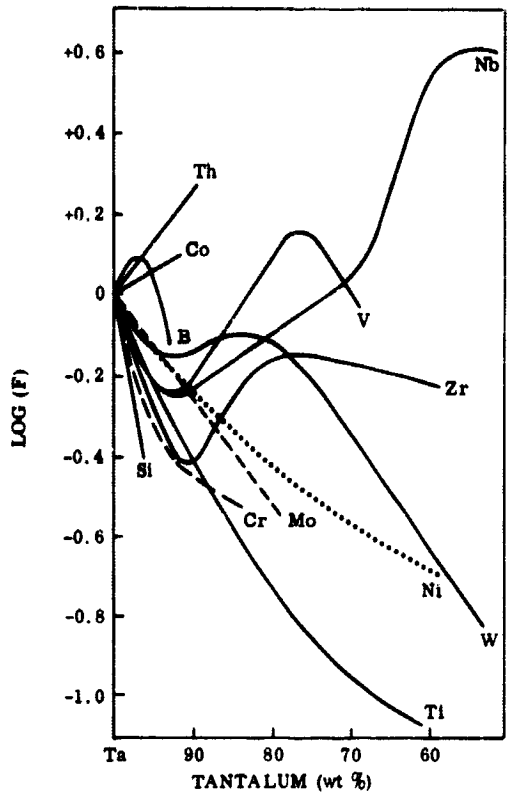
Alloying additions which significantly improve the oxidation resistance of tantalum include titanium and zirconium. The reductions in oxidation rate are on the order of five to twentyfold, with titanium being the more beneficial of the two elements.

The Ta-60 and -80Ti alloys oxidize considerably slower than the tantalum-rich alloys in this system (Ref. 4). Both alloys formed thin, protective scales and oxidized parabolically for six hours at 2550 F. The weight gain versus composition curves are characterized by sharp decreases in weight gain from zero to 20 titanium as shown in Figure 1, with more gradual decreases to minima in the range of 60 to 80 titanium. The initial improvement on adding titanium is attributed to the formation of protective complex oxides of Ta_2O_5-TiO_2. The minimum oxidation rate in the titanium-rich alloys appears to be associated with the higher valence of tantalum dissolved in the TiO_2-rich scale. Titanium dioxide is classed as an oxygen-deficient semiconductor through which diffusion occurs by movement of oxygen ions. Substitution of higher valence cations such as Ta^{5+} for Ti^{4+} would be expected to reduce the number of anion vacancies and thus reduce diffusion through the oxide.

Additions of 5 to 10 percent vanadium or columbium reduce the 2190 F oxidation rates as much as 50 percent, but are ineffective at 2500 F. Improvements in the oxidation behavior at 2190 F are also effected by tungsten (30 to 50 percent), chromium (about 5 percent), and molybdenum (about 5 percent). Ternary alloys based on Ta-30Cb are less oxidation resistant than binary alloys based on tantalum alone. This is consistent with the observation that the addition of 30 percent columbium increases the oxidation rate of tantalum markedly at 2190 F.

Ternary additions of chromium improve the oxidation resistance of Ta-30Ti. However, linear oxidation behavior (at low rates) is observed with the ternary chromium alloys.

The rate of contamination hardening of tantalum during oxidation is reduced significantly by additions of titanium, zirconium, hafnium, silicon, thorium, rhenium, tungsten, vanadium, and molybdenum. The first five elements, titanium through thorium, react with the diffusing oxygen to form stable oxides which segregate to form



$$F = \frac{\Delta m_{alloy}}{\Delta m_{base\ metal}}$$

Δ m = weight change

FIGURE 1. EFFECT OF ALLOYING ELEMENTS ON THE OXIDATION OF TANTALUM IN AIR AT 1832 TO 2192 F

an internal precipitate. The four elements, rhenium through molybdenum, have smaller atomic radii than tantalum and are believed to reduce contamination by contracting the tantalum lattice, thus hindering the inward diffusion of oxygen.

Based on the foregoing discussion, titanium was considered to be the most outstanding additive to improve the oxidation resistance. Adding a Group VIB element to the tantalum/titanium system appears to further increase the oxidation resistance. Chromium appears to be a good ternary additive but molybdenum and tungsten, by decreasing the oxygen solubility and diffusion, also are important additives. Of the Group VB elements, some appear to have little effect while others are deleterious to the oxidation resistance of tantalum.

The use of titanium as a coating material can have a significant effect on the mechanical properties of certain refractory alloys. For example, duplex annealed 0.012-inch D43 foil (Cb-10W-1Zr-0.1C) loses approximately half its strength at 2200 F after being coated with the TiCr-Si coating.

The low interstitial content of the T222 alloy should minimize the effect of the coating on substrate properties. This conclusion was based on experience at Solar with (Ti-W)-Si coating on the T111 alloy which is similar to the T222. The (Ti-W)-Si coating (primarily a titanium subcoat of approximately 20 mg/cm^2 overlayed with silicon) was applied to the T111 alloy and its strength was measured and compared with the uncoated T111 alloy. The results shown in Table II indicate that even with the fairly high interstitial content of T111 alloy, the change in strength was nil.

TABLE II

EFFECT OF (Ti-W)-Si COATING ON ULTIMATE TENSILE STRENGTH OF T111 ALLOY AT 2600 F

Alloy Condition	Ultimate Tensile Strength (ksi)	Sheet Thickness (in.)
Uncoated (Ref. 5)	33.0	0.012
Coated (Ref. 6)	36.4	0.012

2.3.2 Effect of Alloying Additions on the Silicides

Using an alloy approach to minimize oxidation at the base of cracks at the lower temperature can be a satisfactory concept only if the alloy layer can be silicided to develop the resistance to oxidation and oxygen diffusion required for the full range of operating temperatures. Fortunately, the element exhibiting the greatest improvement in oxidation resistance when alloyed with tantalum, i.e., titanium, forms an oxidation-resistant disilicide. Other potential additives, vanadium, molybdenum, and tungsten also form more oxidation-resistant disilicides than does tantalum.

Oxidation tests performed at Solar, under Contract AF33(615)-1598, on massive silicides resulting from titanium additives to chromium, tungsten, and molybdenum disilicides showed outstanding results at 1500 F with tungsten exhibiting some pest failure. Oxidation tests at 2400 F showed that titanium/tungsten and titanium/molybdenum silicides were superior to titanium/chromium silicides in oxidation resistance. The titanium/chromium silicide was somewhat deteriorated by apparent liquation. Addition of columbium to the system increased the refractoriness and also the oxidation resistance. In oxidation tests of simple disilicides at 1500 F (VSi_2, WSi_2, $MoSi_2$, $CbSi_2$, and $TaSi_2$), VSi_2 was the only one that did not exhibit pest-type failure.

The preceding discussion has pointed out the various factors that can be affected by prealloying the surface prior to siliciding, and also the resultant properties of the silicide produced by alloying. In summary, it can be concluded from the preceding discussion that:

- Silicides have higher thermal expansivities than that of the T222 alloy substrate.
- The coatings are expected to craze crack on cooling from the application temperature.
- Prealloying of the substrate seems desirable to provide oxidation resistance for the substrate by preventing gross oxidation at the base of the fissures.
- The disilicide formed on unmodified T222 alloy is expected to suffer from pest oxidation and have relatively poor oxidation resistance at high temperatures.
- Alloying of the silicide is thus required to minimize pest-type oxidation and to improve the high-temperature oxidation resistance of the silicide.
- Titanium appears to be the most effective alloying element in improving the oxidation resistance of tantalum.
- Tungsten and molybdenum are the most effective additives in decreasing the thermal expansion of the disilicide coatings.
- Titanium combined with a Group VI element such as molybdenum, tungsten, or chromium appears to offer the greatest potential for modifying the silicide while retaining an oxidation-resistant alloyed substrate.
- Additions of vanadium can be expected to minimize pest-type oxidation failure of silicides.
- Complex disilicides appear to offer better overall oxidation resistance than simple silicides.

Table III shows the compositions of the alloy packs selected for the pack-cementation modification of the surface of the T222 alloy. In selecting the pack alloy compositions, it was assumed that the different elements in a given alloy would transfer to the surface of the T222 alloy at equal rates to accomplish the desired alloying effects (this assumption was later shown to be invalid; slurry coating techniques were subsequently observed to allow greater control of the composition of the alloyed surface layer). The basic coating is (Ti-W)-Si and all other coatings are modifications.

TABLE III

MODIFICATIONS OF BASIC Ti-W-Si COATING

Solar Coating Designation	Composition (wt %)					Remarks
	Ti	W	V	Mo	Cr	
TNV-1	90	10	--	--	--	Composition variations of standard Ti-W pack; increase tungsten to decrease expansivity.
TNV-2	60	40	--	--	--	
TNV-3	30	70	--	--	--	
TNV-4	60	--	--	40	--	Expansion same as (Ti, W)Si_2, but better 1500 F oxidation resistance.
TNV-5	30	35	--	35	--	Same as (TNV-4), but Ti reduced and W added to decrease expansivity.
TNV-6	30	40	30	--	--	Replace Ti in (TNV-2) with V to reduce expansion and improve low-temperature oxidation resistance of silicides.
TNV-7	15	35	15	35	--	Combine benefits of (TNV-5) and (TNV-6)
TNV-8	30	35	--	--	35	Modification of standard (Ti, Cr)-Si coating to reduce expansivity by lower titanium and higher tungsten. Chromium improves low-temperature oxidation resistance of silicides, and Ta-Ti-Cr alloys have good oxidation resistance at 1800 F.
TNV-9	30	--	--	35	35	Molybdenum analog of (TNV-8) to give better low-temperature oxidation resistance to silicide.
TNV-10	30	--	30	--	40	Vanadium modification of (Ti, Cr)-Si coating to improve low-temperature oxidation resistance of silicide.

Titanium is retained in all coatings to improve the oxidation resistance of the tantalum alloy, but the amount is reduced compared with the standard 90Ti-10W pack to decrease the expansivity of the disilicide formed on this prealloyed layer. Most of the coatings contain tungsten, but where this element is removed it is replaced by one of the other Group VI metals. Table I shows that in the series $(Ti, W)Si_2$, $(Ti, Mo)Si_2$, and $(Ti, Cr)Si_2$, the expansivities of the chromium-containing silicides are markedly higher than those of the molybdenum- or tungsten-containing silicide. On the other hand, the molybdenum- and chromium-containing disilicides are better in oxidation resistance at 1500 F. Better performance throughout has been found for the titanium/molybdenum modified disilicides than for the other Group VI metals. This is the reason for the inclusion of four modifications with molybdenum.

Each coating element can be ascribed a certain characteristic that appears to accompany this element under all conditions. Accordingly, coating compositions were selected to obtain contributions from each element in an effort to provide refractoriness of the silicide, viscosity control of silica glass, less disparity in expansivity of substrate and silicide, oxidation resistance of the alloy modified unsilicided substrate, low-temperature oxidation resistance of the silicide, high-temperature oxidation resistance of silicide, and resistance to pest failure.

The ideal coating process was considered to correspond to deposition of a two- to six-mil (0.002- to 0.006-inch) thick modifier layer which, upon siliciding, would produce an outer silicide layer of two-mil minimum thickness on top of an unsilicided modified alloy zone of one- to two-mil minimum thickness. This structure is shown schematically in Figure 2.

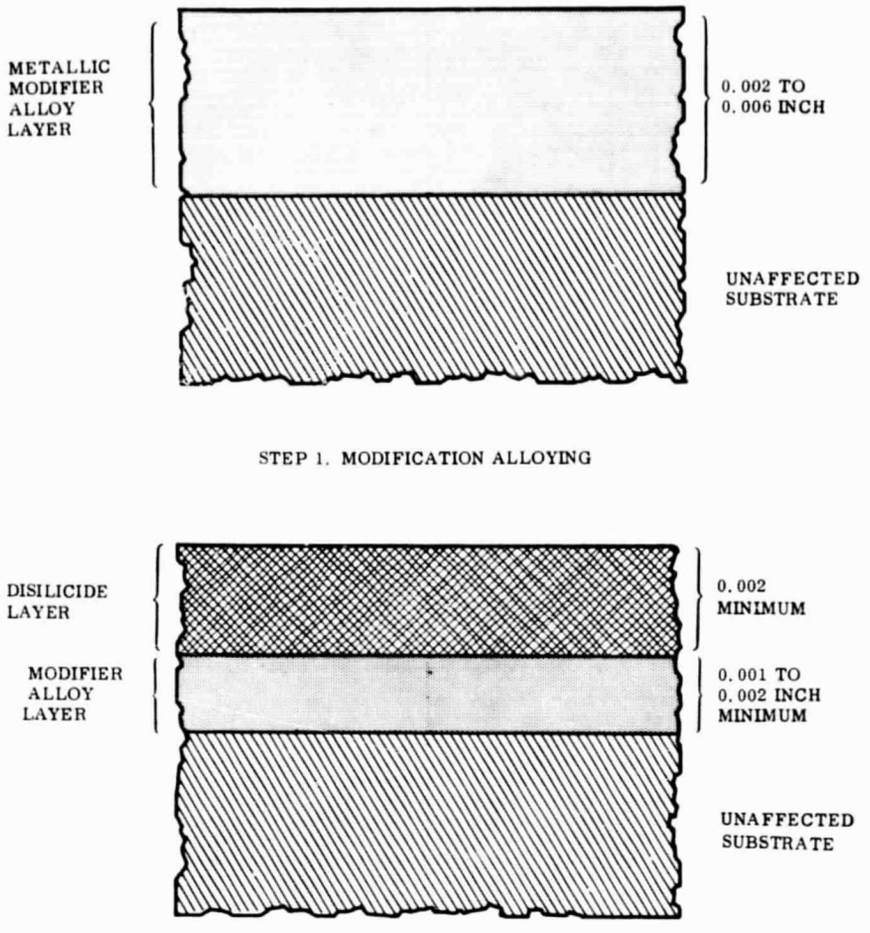


FIGURE 2. SCHEMATIC OF MICROSECTION THROUGH THE IDEALIZED COATING SYSTEM

3

EXPERIMENTAL

3.1 MATERIALS

3.1.1 Substrate

T111 Alloy

The T111 alloy, which was on hand at Solar, was used in initial optimization work while awaiting delivery of the T222 alloy. This action was taken to expedite the program under the reasonable assumption that the T111 substrate was comparable to the T222 for coating purposes. The T111 alloy was supplied by the Westinghouse Corporation as 0.012-inch thick sheet from Heat No. DX570. The ingot analysis is shown in Table IV.

TABLE IV

INGOT ANALYSIS OF T111 TANTALUM ALLOYS

Ingot	W (wt %)	Hf (wt %)	Fe (ppm)	O (ppm)	N (ppm)	C (ppm)
Top	8.5	2.32	20	42	16	17
Bottom	8.6	2.20	20	37	13	10

T222 Alloy

The T222 alloy was supplied by the Wah Chang Corporation in accordance with the specification shown in Appendix A. A total of 171 pounds of 0.0625-inch thick sheet (12 in. by 36 in.) and 14 pounds of 0.250 inch plate (1 in. by 36 in. or 17 in.) was obtained. The sheet and plate were fabricated from a single heat (65041-T222). A typical ingot analysis and the mechanical properties of the finished product, as determined by the Wah Chang Corporation, are shown in Table V. Figures 3 and 4 are photomicrographs of sections of T222 sheet.

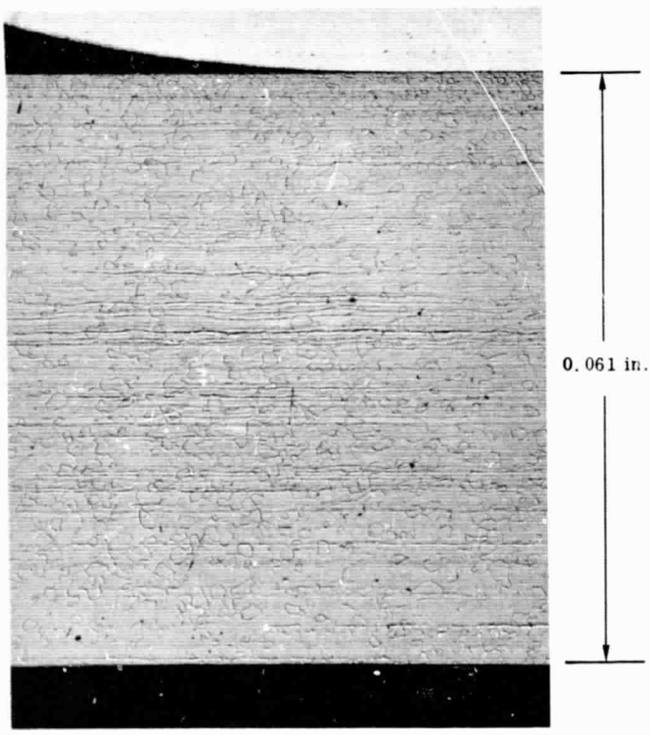
FABRICATION STEPS

1. 83 Percent Reduction from Slab
2. Vacuum Anneal 1 Hour at 3000 F, P $<10^{-5}$ Torr
3. 96 Percent Reduction
4. Vacuum Anneal 1 Hour at 3000 F, P $<10^{-5}$ Torr
5. 70 Percent Reduction
6. Vacuum Anneal 1 Hour at 3000 F, P $<10^{-5}$ Torr

Vendor: Wah Chang Corp.

Magnification: 250X

FIGURE 3. T222 ALLOY SHEET AS RECEIVED FROM VENDOR; Showing Hardness Traverse



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4. Vacuum Anneal 1 Hour at 3000 F, P $<10^{-5}$ Torr
5. 70 Percent Reduction
6. Vacuum Anneal 1 Hour at 3000 F, P $<10^{-5}$ Torr

Vendor: Wah Chang Corp.

Magnification: 50X

FIGURE 4. CROSS SECTION OF T222 ALLOY SHEET AS RECEIVED FROM VENDOR; Showing Precipitation Bands Parallel to the Surface

TABLE V

TYPICAL INGOT ANALYSIS AND MECHANICAL PROPERTIES OF T222 ALLOY (Ta-9.6W-2.4Hf-0.01C) PLATE AND SHEET (Wah Chang Heat No. 65041-T222)

Ingot Analysis									ASTM Grain Size	Tensile Strength (psi)	Yield Strength 0.2% Offset (psi)	Product Hardness	
W (wt%)	Hf (wt%)	Cb (ppm)	Ti (ppm)	Fe (ppm)	O (ppm)	N (ppm)	C (ppm)	H (ppm)				BHN	KHN (50-gram load)
9.0	2.7	525	50	40	50	20	110	3.1	8	115,000	100,000	288 to 297	245 to 274

The plate was fabricated by an 83 percent cold work reduction from the slab followed by a one-hour anneal at 3000 F in a vacuum of less than 10^{-5} Torr. The sheet was fabricated by a 96 and 70 percent cold work reduction with each reduction followed by a one-hour anneal at 3000 F. Fluorescent dye penetrant inspection of each piece of alloy at Solar revealed no significant surface defects. There was evidence of preferred alignment of precipitates parallel to the surface of the sheet. This alignment is particularly evident in Figure 4.

3.1.2 Pack Materials

The starting pack materials were titanium, chromium, vanadium, molybdenum, tungsten, silicon, and NaF activator. The respective sources and chemical analyses are given in Table VI. The chromium briquettes and silicon were crushed in a laboratory size pulverizer, screened to -20 +50 mesh, and leached in a 40 percent HCl solution in an attempt to remove iron introduced during crushing. The vanadium and tungsten (0.25 inch and smaller) were screened and only particles 0.125 inch in diameter and smaller were used. The titanium, molybdenum, and -325 mesh tungsten were used as received.

The pack alloys, contained in Table III, were prepared in 1500-gram batches. The alloying was accomplished by mixing the individual components, dry compacting at 5 to 10,000 psi, and arc melting twice. Five compacts of approximately 100 grams each were simultaneously inserted into the arc-melting apparatus and individually melted.

The arc-melted buttons were crushed to -20 + 50 mesh in a laboratory crusher. Alloys TNV-1, -2, -3, -4, -6, and -10 of Table III were not brittle enough for crushing. They were, therefore, hydrided prior to the crushing operation by holding them

TABLE VI

MATERIALS USED IN PACK CEMENTATION - SOURCE AND CHEMICAL ANALYSIS

Material	Vendor	Particle Size	Chemical Analysis																	
			Ti (wt%)	Cr (wt%)	V (wt%)	Mo (wt%)	W (wt%)	Si (wt%)	Ni (wt%)	Mn (wt%)	Fe (wt%)	Co (wt%)	Co (wt%)	Na (wt%)	Cl (wt%)	Cu (wt%)	H (ppm)	C (ppm)	N (ppm)	O (ppm)
Titanium Sponge	Oregon Metallurgical Corporation	-20 + 50 Mesh	99.6	----	----	----	----	----	----	----	0.04	----	---	0.09	0.11	----	30	200	400	1000
Chromium Briquettes	Union Carbide Corporation (Elchrome VG)	1.25 by 1.0 inch	----	99.5	----	----	----	----	----	----	0.26	----	----	----	----	----	--	---	---	1300
Vanadium	Vanadium Corporation of America	0.25 inch and lower	----	----	99.8	.025	----	0.03	----	----	.015	----	----	----	----	----	12	270	60	770
Molybdenum	Wah Chang Corporation	-20 + 60 Mesh	----	0.02	----	99.5	0.02	.013	0.05	.001	0.01	.001	.001	----	----	----	--	20	---	2000
Tungsten	Wah Chang Corporation	-325 Mesh	----	----	----	0.01	99.8	----	0.01	----	0.03	----	----	----	----	----	--	---	---	300
Tungsten	Oregon Metallurgical Corporation	0.25 inch and lower	----	----	----	----	99.0	----	----	----	----	----	----	----	----	----	--	---	---	40
Silicon	Union Carbide Corporation	1 inch to 8 Mesh	----	----	----	----	----	99.1	----	----	0.34	----	----	----	----	0.03	--	--	---	190
NaF	Mallinckrodt Chemical Works	Powder	Analytical Reagent Grade (99.8 %)																	
60Cr-40Ti Alloy	Oregon Metallurgical Corporation	0.25 inch and less	39.4	58.8	----	----	----	----	----	----	0.21	----	----	----	----	----	--	---	---	830
Chromium Briquettes	Union Carbide Corporation (Elchrome VG)	1.25 by 1.0 inch	----	99.7	----	----	----	----	----	----	0.24	----	----	----	----	----	--	---	---	1190

at 1250 F for one hour in titanium-gettered hydrogen (App. B). After crushing and screening to -20 + 50 mesh, the TNV-5, -7, -8, and -9 alloys were dehydrided by heating them at 1800 F in a vacuum of about one Torr for two hours.

The crushed alloys were leached in a 40 percent aqueous HCl solution for one hour at room temperature to remove iron introduced during crushing. A magnetic probing of the leached alloys yielded no particles. However, chemical analysis of the pack alloys revealed that some particles of high iron content remained. This condition was discovered after most of the high-pressure pack experiments were completed; however, it is doubtful that the iron content was high enough to be deleterious.

In the vacuum pack cementation work careful magnetic scanning of pack materials was conducted. In the major portion of this work, the materials were thoroughly scanned with a magnet in the as-received condition and after any crushing operation to reduce iron content to a minimum. An acid leaching process preceded and followed magnetic separation.

An 80Cr-20Ti pack alloy was prepared and should be described as a pseudo-alloy as it corresponded to a mixture of the crushed chromium briquettes and the arc-melted 60Cr-40Ti alloy characterized in Table VI.

3.1.3 Slurry Coating Materials

Typical analyses of the -325 mesh molybdenum, tungsten, and titanium are shown in Table VII. Titanium hydride, obtained by hydriding titanium sponge, was used in the coatings containing less than 10 percent titanium. The coarse vanadium used in the pack studies was partially hydrided and ball milled to produce a -325 mesh product. The procedures used in hydriding the titanium and vanadium are outlined in Appendix B. The chromium used in the slurry coatings was the -325 mesh fraction of the Elchrome VG material characterized in Table VII, and thus may have higher impurity levels than are indicated in the table.

TABLE VII

MATERIALS USED IN SLURRY COATINGS
SOURCE AND TYPICAL CHEMICAL ANALYSIS

Material	Vendor	Particle Size	Chemical Analysis[a]																	
			Al	Ca	Si	Fe	Cr	Ni	Cu	W	Mn	Mg	Sn	Mo	Na	K	S	C	N	O	H
Molybdenum	General Electric Company	5-micron average	<10	<5	<15	<15	<10	<5	<5	88	<10	<10	12	--	--	--	--	<10	--	610	--
Tungsten	General Electric Company	5-micron average	<6	5	<7	10	3	10	<3	--	<6	3	<6	110	7	30	--	<10	--	220	--
Titanium	Metals Disintegrating Corp. (MD301)	-325 microns	--	--	--	560	--	--	--	--	--	--	--	--	--	--	--	430	230	3100	--
Chromium	Union Carbide Corp. Elchrome LG	100 mesh and lower	--	--	--	40	--	--	--	--	--	--	--	--	--	--	230	200	10	5500	300

a. Analysis expressed in ppm.

3.2 PREPARATION OF SPECIMENS

Oxidation tests on coated refractory alloys, in general, have shown that failures are predominantly initiated at the edges, and are probably the result of uneven deposition of the coating over the sharp edges of the substrate. In general, frequency of edge-type oxidation failure is reduced considerably by rounding the edges of the test specimens to obtain a more uniform coating thickness (Ref. 7). One of the most successful and reproducible methods of rounding the edges prior to coating is tumbling the specimens in an abrasive compound until a continuous radius of the edges is obtained. The T111 and T222 sheet material was sheared into either 0.5 by 0.75-inch or 1.0 by 2.0-inch pieces preparatory to radiusing the edges. The smaller samples were used in the earlier part of the program in the pack-cementation work. At the very outset

of the program (in the single-modifier cycle high-pressure pack work) the samples were provided with a 3/32-inch diameter drill hole. This practice was discontinued after the initial experiments because coating defects tended to develop at the edges of the holes. Initially, the corners of the specimens were rounded using alumina grinding wheels and bonded paper/pumice polishing wheels before tumbling was started in a two-quart ball mill containing milling pebbles and distilled water; however, it was later discovered that tumbling the as-sheared specimens for a period of 64 hours in a ball mill charged with arrowhead-shaped deburring media was found to adequately radius the corners while properly rounding the edges at the same time. After tumbling, the specimens used in the pack cementation modification studies were cleaned in a one-percent Pennsalt-45 solution, rinsed several times in distilled water, and etched in $30HNO_3$-$60H_2SO_4$-10HF (volume percent). After being rinsed in water and acetoned, the specimens were dried in a nitrogen blast before being weighed and measured.

The specimens used in the slurry coating experiments received a slightly different treatment. Following tumbling in the deburring media and rinsing in trichloroethylene, the specimens were sandblasted and etched in $45HNO_3$-$45H_2SO_4$-10HF. Water and acetone rinses preceded drying, weighing, and measuring the specimens.

3.3 DEPOSITION STUDIES

3.3.1 High-Pressure Pack Cementation

Apparatus and Procedure

The retort used in the single-modifier cycle high-pressure pack work consisted of an Inconel shell with a graphite liner. The covered graphite liner (Great Lakes Carbon Co., HLM Grade) was employed to contain the vapors generated by the pack and to prevent interaction of the pack with the retort walls. The retort walls were constructed of 0.125-inch Inconel 600 sheet. Between the liner and the retort walls an alumina-5 percent Bentonite wash coat was used to prevent reaction of the Inconel and graphite. This same wash coat was applied to the outside of the retort to help control oxidation of the Inconel.

The specimens were imbedded in either the pack alloy (-20 + 50 mesh) mixed with 0.1 percent NaF (used as an activator) or silicon (-20 + 50 mesh in the single-modifier cycle work, -200 mesh in the subsequent work) mixed with 0.1 to 1.0 percent NaF. After the retort was sealed by fusion welding, it was alternately evacuated to

approximately 50 microns and backfilled to 800 Torr with argon before being placed in an electrically-heated box furnace preheated to the specified temperature. Although the evacuation-backfill cycle was conducted six times when -20 + 50 mesh pack materials were used, only two cycles were employed when -200 mesh silicon was used because of the slow evacuation rates resulting from the need to prevent expulsion of silicon which attacks the Inconel retort walls. A thermocouple placed in the center of a -200 mesh silicon pack indicated that approximately one hour was required for that region to reach the furnace temperature.

In the high-pressure pack cementation work involving multiple modifier cycles preceding the siliciding cycle, the procedure was modified. The samples and modifier pack alloys were contained in small B66 or Cb-1Zr alloy boots placed inside the larger, double-wall, Cb-1Zr box shown in Figure 5 where the 0.25-inch space between the outer two walls was packed with titanium sponge. The addition of a tray containing titanium sponge provided a nearly closed titanium gettering envelope around the pack. Specimens and silicon powder were placed directly in the double-wall box (dimensions of inner box - 3.0 inches by 10.5 inches by 3.25 inches deep). In the experiments

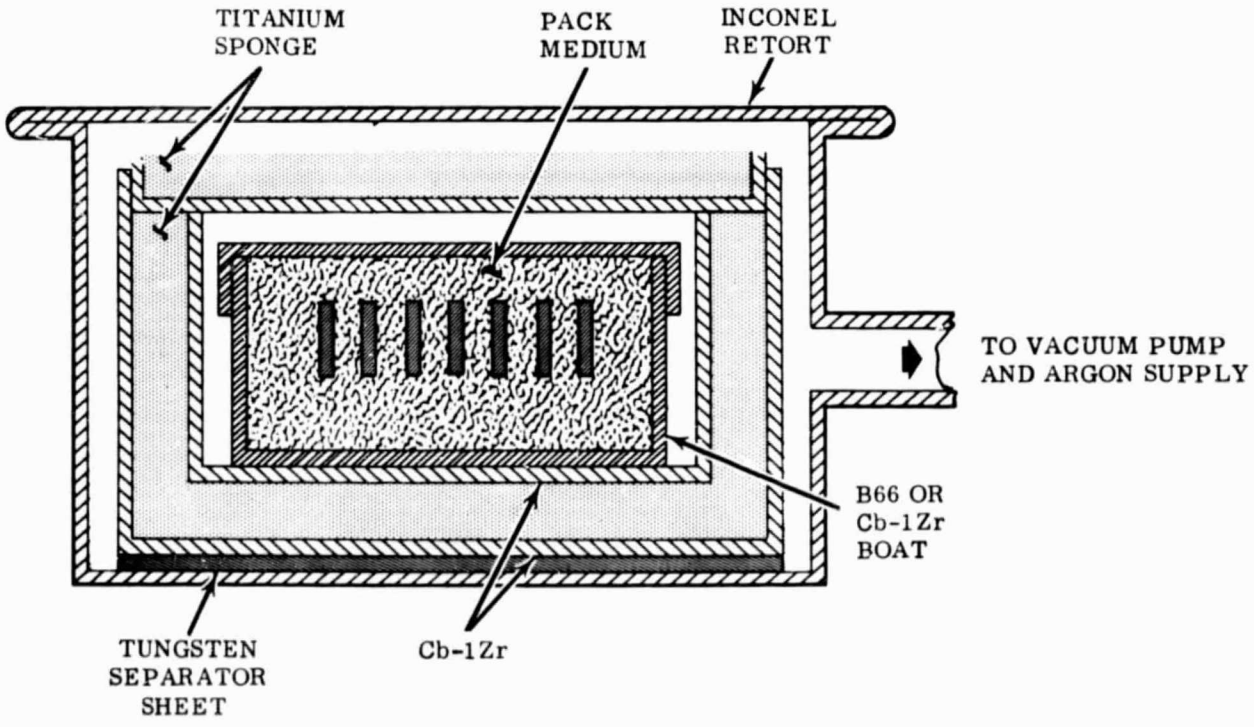


FIGURE 5. SCHEMATIC OF A HIGH-PRESSURE RETORT

where TNV-2, TNV-3, or silicon packs were used, the columbium alloy double-wall box assembly was placed in the tungsten-sheet-lined Inconel retort. When vanadium packs were used, the columbium alloy box assembly was placed on a tungsten-sheet resting on the graphite dowel framework of a graphite-cloth element vacuum furnace, which was subsequently operated just below atmospheric pressure (cycle purging was completed with a final backfill of argon or helium).

Results of Single-Modifier-Cycle High-Pressure Pack Cementation Studies

At the outset of the program, the temperature dependence of the rate of deposition from the ten pack alloys was investigated. This phase of the program was initiated using T111 alloy specimens, but was concluded with T222 specimens; no significant difference in the deposition rates of the two substrate alloys was apparent. None of the T111 specimens were subjected to siliciding or to subsequent oxidation.

Attempts at obtaining a 0.002-inch thick modifier alloy zone before siliciding resulted in utilization of the highest practical temperatures. In the case of TNV-1, -2, and -3, the upper temperature was limited by the tendency for pack particles to sinter to the specimen surfaces. With pack alloys TNV-4 through -10, the maximum process temperature was limited to 2300 F, the maximum temperature allowed by the Inconel retorts. The weight gains for the different deposition cycles and the total coating thickness volumes are summarized in Table VIII. Typical defects resulting from the adherence of pack particles are shown in Figures 6 and 7.

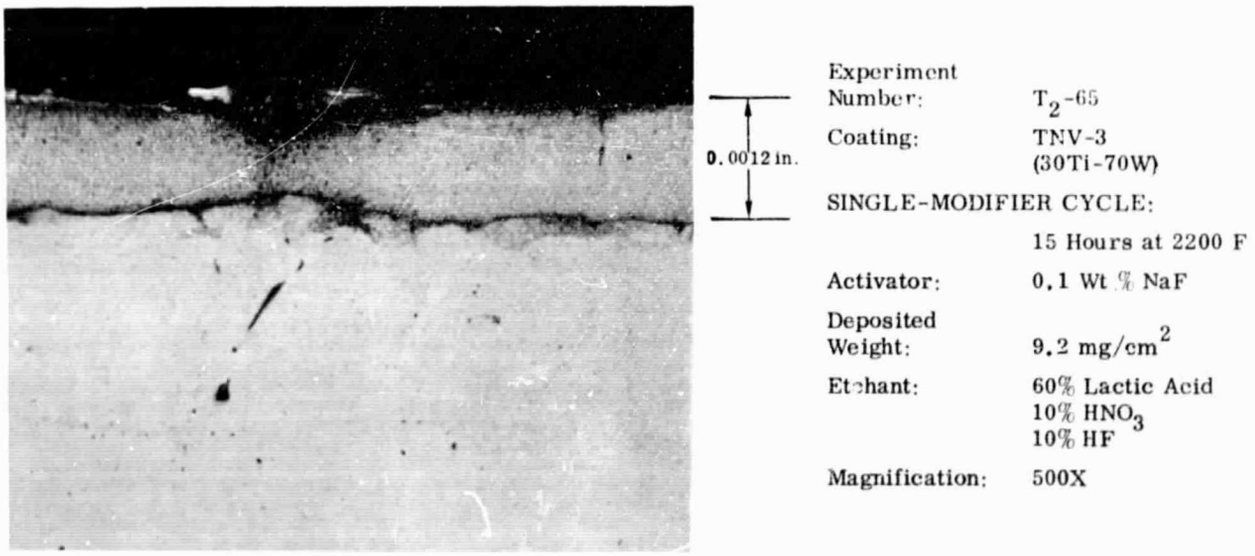


FIGURE 6. DEFECT IN MODIFIER COATING DEPOSITED FROM PACK ALLOY TNV-3 ON T222 ALLOY

Experiment Number: T_2-47
Coating: TNV-2 (60Ti-40W)
SINGLE-MODIFIER CYCLE:
15 Hours at 2000 F
Activator: 0.1 Wt % NaF
Deposited Weight: 9.5 mg/cm^2
SILICIDE CYCLE:
Activator: 0.1 Wt % NaF
Deposited Weight: 9.6 mg/cm^2
Etchant: 2% HF
3% HNO_3
95% H_2
Magnification: 250X

FIGURE 7. DEFECT IN SILICIDED COATING DUE TO INCLUDED PACK PARTICLE IN THE MODIFIER COAT ON T222 ALLOY

TABLE VIII

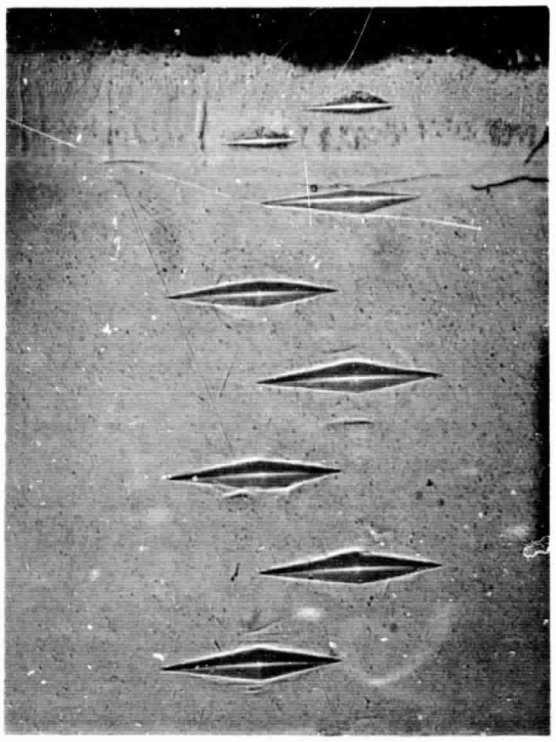
INITIAL COATING OF BASIC PACK COMPOSITIONS BY SINGLE-MODIFIER CYCLE HIGH-PRESSURE PACK CEMENTATION

Alloy Number	Nominal Composition (wt %)	Modifying Alloy Coating Cycle (15-hr)		Silicide Coating Cycle (2100 F)		Total Coating Thickness
		Temperature (F)	Deposited Weight (mg/cm^2)	Time (hr)	Deposited Weight (mg/cm^2)	(mil)
TNV-1	90Ti-10W	1900	9.6	1	4.7, 5.5*	1.4
		1900	6.8	2.5	10.9	2.5
TNV-2	60Ti-40W	2000	9.5	1	4.3, 5.5*	1.4
		2000	8.4	2.5	10.8	2.5
TNV-3	30Ti-70W	2150	8.4	1	3.9, 4.6*	1.0
		2200	9.2	2.5	10.9	2.5
TNV-4	60Ti-40Mo	2300	2.9	3	10.3	2.0
TNV-5	30Ti-35W-35Mo	2300	1.2	4	10.7	2.1
TNV-6	30Ti-40W-30V	2300	1.1	4	10.1	2.1
TNV-7	15Ti-35W-15V-35Mo	2300	0.5	6	11.4, 11.7*	2.3
TNV-8	30Ti-35W-35Cr	2300	2.8	3	11.6	2.1
TNV-9	30Ti-35Mo-35Cr	2300	1.6	6	16.2	3.1
TNV-10	30Ti-30V-40Cr	2300	2.8	3	10.0	1.8
	T222 Alloy	NA	NA	6	10.6	2.0

*Modifier-alloyed specimens divided into two groups for siliciding in separate experiments under same conditions.

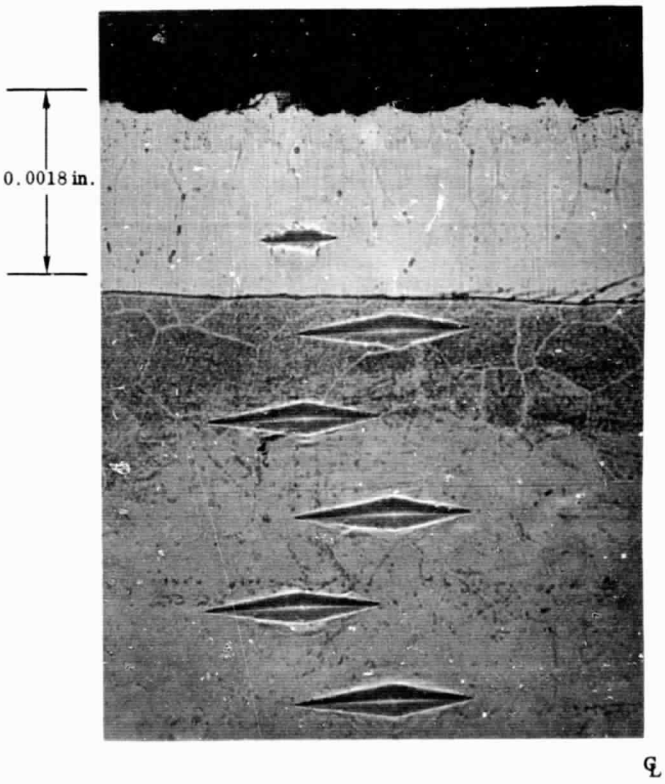
Even though the 0.002-inch goal for the thickness of the modifier layer was not achieved, the specimens were silicided under conditions (determined by experimental trial) where it was hoped that only partial siliciding of the modifier layer would be accomplished. However, partial siliciding was not attainable as is indicated by the microstructures shown in Figures 8, 9, and 10. Figure 8 is typical of the microstructures of the coatings on the T222 alloy modified with TNV-1, -2, and 3. At least four distinct layers with a total thickness in the range from 1.4 to 2.5 mils were developed on the specimens during siliciding. Craze cracking of the silicide was evident with cracks extending into the diffusion zone adjacent to an apparently unaffected T222 substrate. Figure 9 shows the microstructure typical of the specimens modified in packs of TNV-4, -5, -6, and -7. With each of these modifier alloys, a very small deposition was experienced and, thus, in subsequent siliciding complete penetration of the prealloyed layer resulted. All of the coatings in this group had the common feature of only one sharp phase boundary, which presumably separated the T222 substrate from the silicided layer. All of the coatings showed craze cracks which penetrated to the substrate. Figure 10 shows the microstructure typical of the specimens modified in packs of TNV-8, -9, and -10. With this group of coatings, there were two sharp boundaries in the layered coating structure. The apparent difference in the microstructure of this group and the preceding group may simply have been a slight variation in the etching characteristics of the two groups.

To determine whether or not the modification alloying was of any benefit, unmodified T222 specimens were silicided to provide control specimens. Table VIII shows that a weight gain of 10.6 mg/cm^2 was obtained by holding the specimens at 2100 F for six hours in a silicon pack containing 0.1 weight percent NaF. The resultant 0.002-inch thick silicide layer was observed to have a columnar structure and a hardness of 1680.



Experiment Number: T_2-49
Coating: TNV-1 (90Ti-10W)
SINGLE-MODIFIER CYCLE:
15 Hours at 1900 F
Activator: 0.1 Wt % NaF
Deposited Weight: 9.6 mg/cm^2
SILICIDE CYCLE:
1 Hour at 2100 F
Activator: 0.1 Wt % NaF
Deposited Weight: 5.5 mg/cm^2
Etchant: Krolls
2 Vol % HF
3 Vol % HNO_3
95 Vol % H_2O
Magnification: 500X

FIGURE 8. TYPICAL SILICIDE COATING ON T222 PREALLOYED WITH TNV-1, -2, OR -3 IN A SINGLE MODIFIER CYCLE



Experiment Number: T_2-55
Coating: TNV-7 (15Ti-35W-15V-35Mo)
SINGLE-MODIFIER CYCLE:
15 Hours at 2300 F
Activator: 0.1 Wt % NaF
Deposited Weight: 0.5 mg/cm^2
SILICIDE CYCLE:
2 Hours at 2100 F
Activator: 0.4 Wt % NaF
Deposited Weight: 11.7 mg/cm^2
Etchant: 60% Lactic Acid
10% HNO_3
10% HF
Magnification: 500X

FIGURE 9. TYPICAL SILICIDE COATING ON T222 PREALLOYED WITH TNV-4, -5, -6, OR -7 IN A SINGLE MODIFIER CYCLE

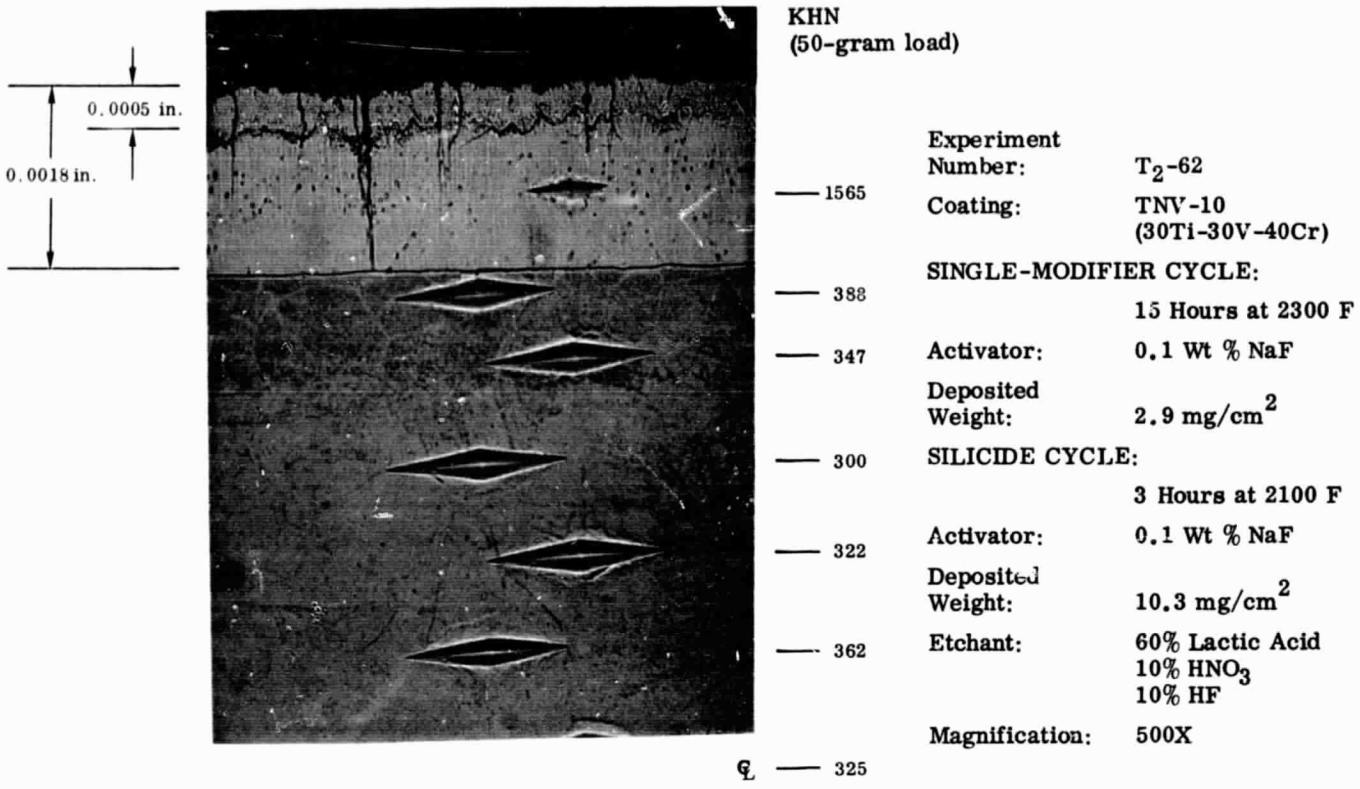


FIGURE 10. TYPICAL SILICIDE COATING ON T222 PREALLOYED WITH TNV-8, -9, OR -10 IN A SINGLE MODIFIER CYCLE

Results of Multiple-Modifier-Cycle High-Pressure Pack Cementation

Because an 0.002-inch thick modifier layer could not be obtained in a single-modifier cycle, multiple cycling was investigated in an effort to obtain the stated goal. Removal of the specimens from the packs between cycles had the effect of reducing the extent of sintering of the pack particles to the specimens.

As the multiple-cycle work progressed, it became apparent that the elements in a given pack alloy do not transfer to the specimens at equal rates (thus, the desired modification of the T222 specimens was not being accomplished). Accordingly, an investigation was made of the process in which samples were modified first in a pack of one composition (unalloyed vanadium in each case), and were subsequently modified in another pack (TNV-3 or 80Cr-20Ti alloys) prior to siliciding. These experiments corresponded to an attempt to apply the modifying elements contained in the alloys designated as TNV-6 and TNV-10.

Coatings Based on Modification of T222 Alloy in TNV-2 Packs

Specimens were exposed to eight, 12- to 15-hour cycles in a TNV-2 alloy pack at 1950 to 2000 F. In all but one cycle, the activator corresponded to 0.1 percent NaF; in the one cycle where 1.0 percent NaF was used, the weight gain was nearly the same as when 0.1 percent NaF was used. At the conclusion of the eight coating cycles, the specimens had accumulated a weight gain of 22.0 mg/cm^2, but because the sintering of the pack particles to the specimens was considered to be excessive, a decision was made not to silicide or oxidize the specimens.

Coatings Based on Modification of T222 Alloy in TNV-3 Packs

During the six high-pressure pack cementation cycles of Experiment No. T_2-103, samples of T222 accumulated a 20.0 mg/cm^2 weight increase; the conditions of each of the cycles are indicated in Table IX. These specimens were then subjected to the annealing and siliciding processes described in the flow chart of Figure 11. Half of the high-pressure pack modified samples were vacuum annealed at 2540 F for 15 hours in a TNV-3 pack containing no activator. The TNV-3 pack was used to prevent evaporative losses, and the samples showed a small weight gain of 0.8 mg/cm^2. Subsequent siliciding under the conditions shown in Figure 11 resulted in a weight gain of 12 mg/cm^2 and left the specimens with detached, wrinkled coatings. Before proceeding with the annealing and siliciding of the other half of the samples modified by high-pressure pack techniques, the problem of wrinkling during siliciding was studied by siliconizing specimens of unalloyed titanium, B120VCA (a beta-stabilized titanium alloy), and unalloyed vanadium; a decreasing tendency toward wrinkling in the aforementioned order was noted. Thus, it was concluded that through beta-stabilization of the titanium alloy (accomplished by extensive alloying of the titanium), the wrinkling problem might be diminished. During the course of solving the wrinkling problem, mottling of the samples was observed. Replacing the -20 + 50 mesh silicon (used in all the previous work) by -200 mesh silicon (used in all the subsequent work) resulted in elimination of the mottling problem. As is indicated in Figure 11, the second half of the specimens modified in high-pressure pack Experiment No. T_2-103 were vacuum annealed in a TNV-3 pack at 2760 F for 15 hours, and experienced a 9.0 mg/cm^2 weight gain. But, because the largest portion of this weight gain was thought to be titanium (based on electron microprobe results obtained in another program at Solar), the samples were not siliconized without further annealing in an effort to avoid wrinkling of the silicided coating. Accordingly, a second vacuum anneal at 2760 F was

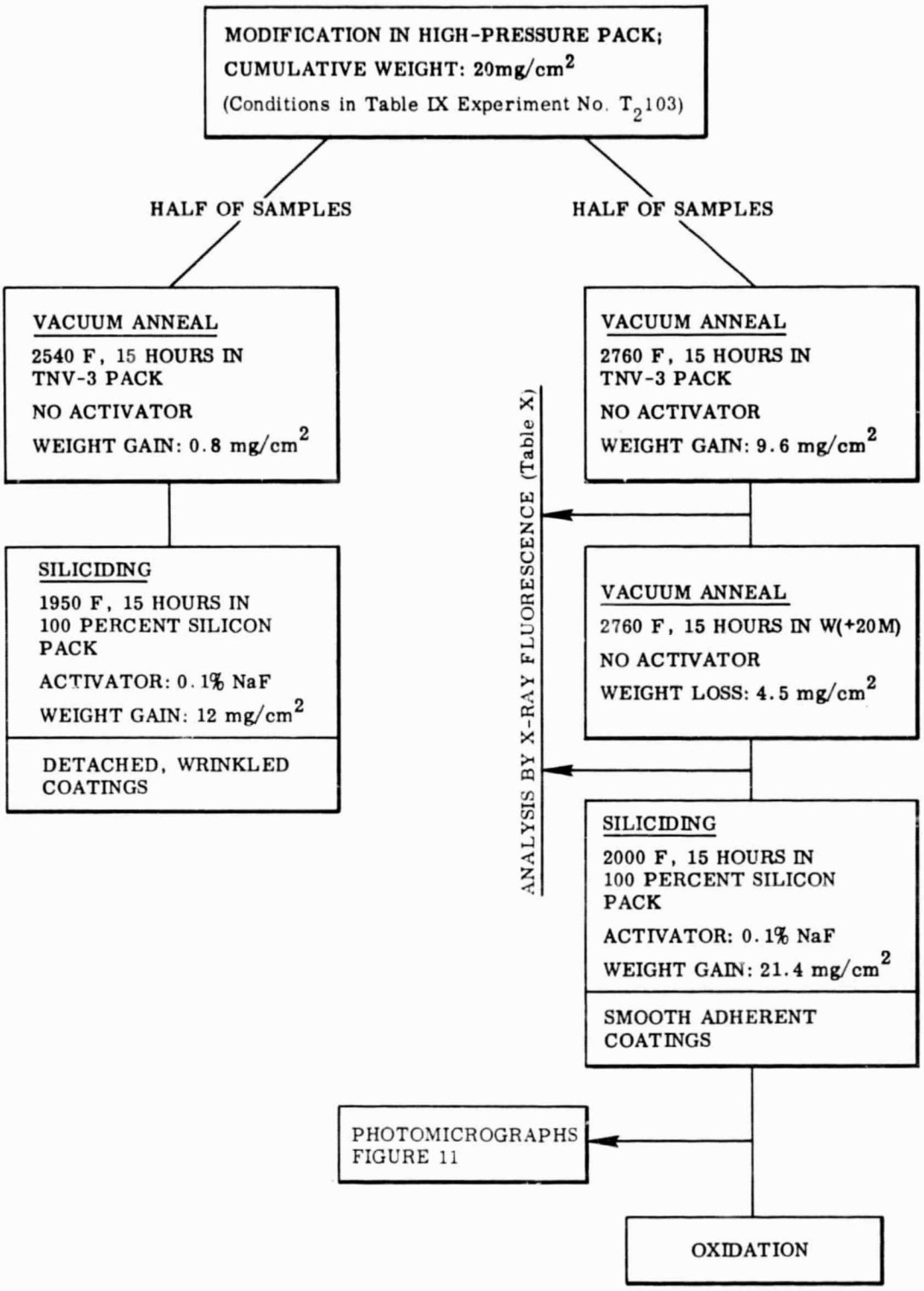


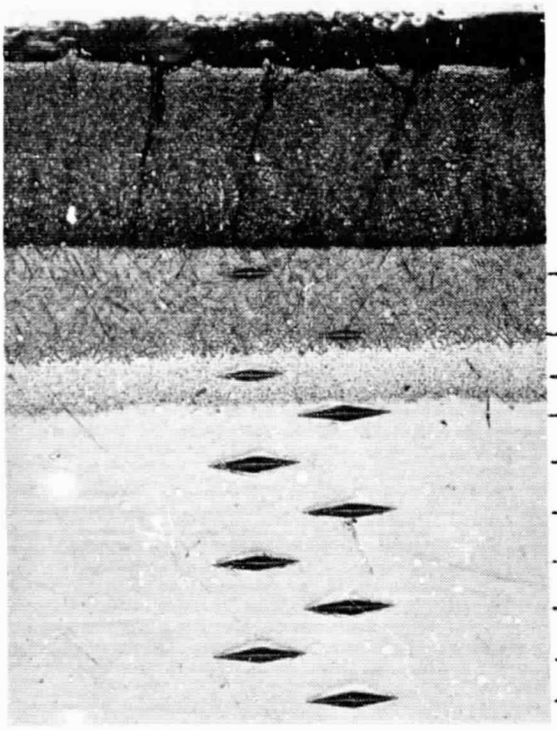
FIGURE 11. FLOW CHART FOR ANNEALING AND SILICIDING PROCESSES: Following Multiple Cycle High-Pressure Pack Modification in TNV-3 Pack

performed with the specimens packed in +20 mesh tungsten particles. It appears that interdiffusion of the titanium-rich coating layer and the T222 substrate proceeded significantly as is suggested by the results of an X-ray fluorescence analysis shown in Table X. In addition to indicating significant interdiffusion, the X-ray fluorescence data suggests that titanium transfers from the pack to the specimens considerably more readily than does the tungsten during the coating cycle. The concentration of tungsten in the annealed coating appears to be comparable to the 9.6 percent contained in the T222 alloy rather than the 70 percent contained in the TNV-3 pack alloy. Figure 11 shows the samples were subsequently siliconized with a weight gain of 21.4 mg/cm^2 of silicon; the resultant coatings were smooth and adherent and were considered to be of sufficient quality for oxidation testing. The microhardness values shown in Figure 12 suggest that the silicon did not completely penetrate the modified layer. The second photomicrograph shown in Figure 12 shows a crack running through all three layers of the coating.

TABLE IX

HIGH-PRESSURE PACK MODIFICATION IN TNV-3 PACKS
(Experiment T_2-103)

Cycle No.	Time (hr)	Temperature (F)	Activator (wt% NaF)	Weight Gain (mg/cm^2)
1	5	2300	0.1	5.9
2	15	2000	0.1	0.8
3	5	2300	0.1	4.4
4	5	2300	0.1	3.3
5	5	2300	0.1	2.4
6	6.5	2300	0.1	3.2
			Total Weight Gain	20.0



Magnification: 250X

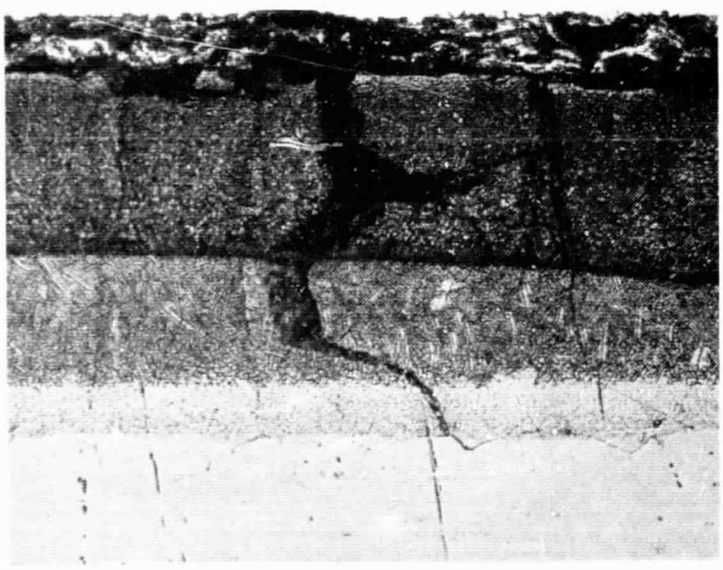
Experiment Number: T_2-103

Substrate: T222

Coating: TNV-3 followed by Silicon

Processing Conditions: Refer to Flow Chart, Figure 11

Etchant: 60% Lactic Acid (85% solution)
20% Concentrated HF
20% Concentrated HNO_3



Magnification: 250X

FIGURE 12. SILICIDED COATING OBTAINED BY MULTIPLE-CYCLE HIGH-PRESSURE PACK MODIFICATION IN TNV-3 PACK

TABLE X

X-RAY FLUORESCENCE ANALYSIS OF T222 HIGH-PRESSURE PACK MODIFIED IN TNV-3
(Experiment T_2-103, Figure 11)

Sample Condition	Counts per Second (above background)				
	Hf	Fe	Ti	W	Ta
Uncoated T222	453	18	34	385	1392
As-coated (29.6 mg/cm^2)	--	15	4000	300	644
Coated and annealed in W pack	91	25	2447	330	876

Coatings Based on Modification of Vanadized T222 Alloy in TNV-3 Packs

An attempt was made to vanadize specimens of T222 alloy in the graphite-cloth element vacuum furnace in a helium atmosphere (710 Torr) under the experimental conditions shown in Table XI. Because the samples appeared to have been contaminated by the furnace atmosphere (suggested by the golden color of the samples) during the first cycle, and because the depositions were relatively small, no further work was performed with this particular set of samples; rather, a new set of samples was coated by means of the cycles characterized in Table XII. Some particle inclusion was noticed at the conclusion of the third cycle in the vanadium pack, and the sintering during the second cycle in the TNV-3 pack was so excessive that the experiment was discontinued completely.

TABLE XI

HIGH-PRESSURE PACK MODIFICATION IN UNALLOYED VANADIUM (-20 +50 MESH) PACKS*

Time (hr)	Temperature (F)	Activator Type and Concentration	Weight Gain (mg/cm^2)
5	2300	0.1% NaF	0.65
5	2400	0.1% NaF	3.30
5	2300	0.1% K_2VF_5	0.72
5	2400	0.1% K_2VF_5	3.20
5	2400	0.5% K_2VF_5	3.20
5	2400	1.0% K_2VF_5	3.20

* Samples exposed to only one cycle

TABLE XII

HIGH-PRESSURE PACK VANADIZATION AND
SUBSEQUENT MODIFICATION IN TNV-3 PACKS

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	V(-20 +50M)	15	2400	0.1	710	2.1
2	V(-20 +50M)	15	2400	0.1	710	2.9
3	V(-20 +50M)	15	2700	None	$<10^{-4}$	9.4
4	TNV-3	15	2200	0.1	800	7.2
5	TNV-3	15	2250	0.1	800	6.0

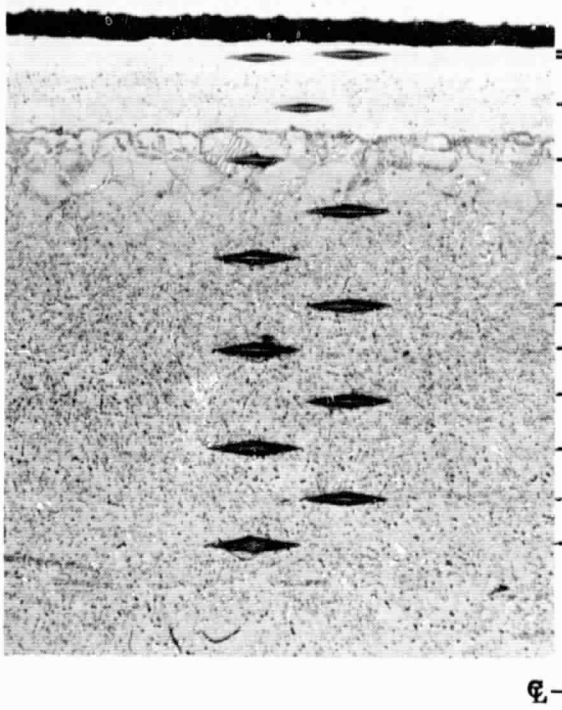
Coatings Based on Modification of Vanadized T222 Alloy in 80Cr-20Ti Packs

Exposure of T222 specimens to vanadium packs during the three cycles of Experiment No. T_2-121-A2 characterized in Table XIII resulted in a total accumulation of 14.4 mg/cm^2 of vanadium. A photomicrograph (Fig. 13) of the vanadized surface of the modified specimens reveals what appears to be the TaV_2 intermetallic compound both in the grain boundaries of the T222 alloy and also in a band of lamellar structure. The presence of the TaV_2 phase has not had any apparent effect on the coherency of the vanadized layer however. Following an accumulated weight gain of 19.1 mg/cm^2 during two cycles of modification in 80Cr-20Ti packs at 2375 F (Table XIII), the specimens were siliconized at 2000 F with the resultant weight gain of 27.2 mg/cm^2 and were considered to be of sufficient quality to merit oxidation testing.

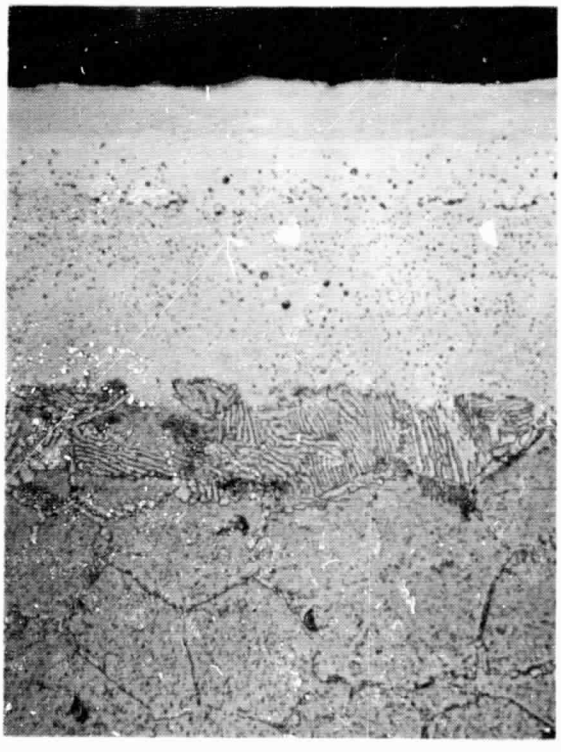
TABLE XIII

HIGH-PRESSURE PACK VANADIZATION AND
SUBSEQUENT MODIFICATION IN 80Cr-20Ti AND Si PACKS
(Experiment T_2-121-A2)

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	V(-20 +50M)	15	2400	0.1	710	2.1
2	V(-20 +50M)	15	2400	0.1	710	2.9
3	V(-20 +50M)	15	2700	None	$<10^{-4}$	9.4
4	80Cr-20Ti	15	2375	0.1	710	9.9
5	80Cr-20Ti	15	2375	0.1	710	9.2
6	Si(-200M)	15	2000	0.1	800	27.2



Magnification: 250X



Experiment Number:	T_2-121-A2
Substrate:	T222
Coating:	Vanadium
Processing Conditions:	First 3 steps of Table XIII
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3

Magnification: 750X

FIGURE 13. T222 ALLOY VANADIZED BY MULTIPLE-CYCLE HIGH-PRESSURE PACK CEMENTATION

3.3.2 Vacuum Pack Cementation

Pack cementation in a vacuum environment was investigated experimentally to obtain greater deposition rates than were obtainable at the 2300 F maximum operating temperature of the Inconel retorts used in the high-pressure work and to take advantage of the cleanliness of the vacuum environment.

Apparatus

Two vacuum furnaces were employed in this work. One had carbon cloth heating elements and the other had a tantalum element.

Vacuum Furnace - Carbon Cloth Heating Elements. The carbon cloth heating elements of the vacuum furnace were resistance heated. The elements enclosed, on six sides, a working space about 11 by 11 by 5 inches. Carbon felt was used as a heat shield. With continuous pumping by a conventional six-inch diameter oil-diffusion pump and a 30-cfm forepump, pressures of less than 10^{-4} Torr were possible during operation at 2700 F. Temperature was determined by a Pt/Pt-13Rh thermocouple sheathed in Al_2O_3 and inserted into the retort. Normally temperature was manually controlled during heatup to maintain a pressure of 10^{-4} Torr or less. Temperature was controlled automatically (±15 degrees F) with a proportional band controller after the process temperature was attained.

A 4- by 5- by 2-inch Cb752 alloy (Cb-9W-2.7Zr) retort held the pack alloys. It rested on a tungsten sheet placed on a graphite dowel framework at the center of the furnace hot zone. Figure 14 shows the retort in place with the top section of the furnace removed. The pack alloys and T222 specimens were held inside the Cb752 retort in B66 alloy (Cb-5Mo-5V-1Zr) boats provided with loose fitting covers.

Vacuum Furnace - Tantalum Heating Elements. A vacuum furnace with a split-cylinder type tantalum resistance heating element was used for some vacuum pack cementation when no activator was used. The furnace was a nine-cubic foot cold-wall vacuum furnace with a four-inch oil diffusion pump and a 30-cfm forepump capable of producing a pressure of $<10^{-6}$ Torr in the chamber.

The furnace had an effective working space five inches in diameter and five inches in height into which up to two 4- by 1- by 1-3/4-inch B66 alloy boats, filled with pack alloy, could be placed at one time. The furnace had a temperature capability of 3000 F for extended periods. The temperature was controlled by manual operation of an autotransformer. Temperature measurement was accomplished by sighting an

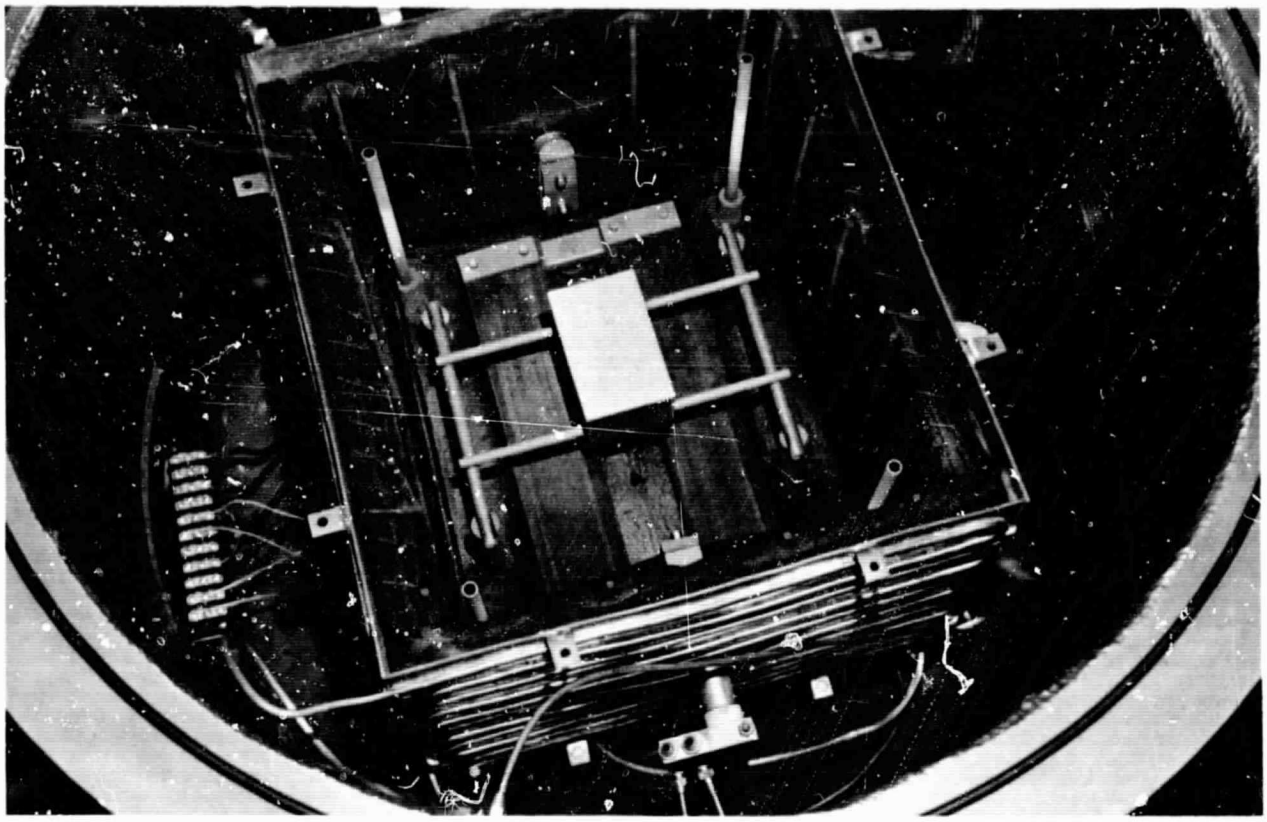


FIGURE 14. COLD WALL VACUUM FURNACE WITH GRAPHITE CLOTH HEATING ELEMENTS; Top Heating Elements Removed for Access and Retort in Place

optical pyrometer through a hole in the tungsten heat shield onto a tungsten hearth plate in the work chamber. Temperature correction for absorption of the sight glass was made, but no correction was made for the small variation of the hot zone from black body conditions. Figure 15 shows the cold-wall vacuum furnace with the tantalum heating element.

Procedure

The vacuum pack cementation experiments may be divided into groups designated as open pack and closed pack. The open-pack experiments involved the use of retorts with or without loose fitting covers. In the closed-pack experiments, the samples, along with the pack and activator, were placed in Cb752 alloy retorts which were TIG welded closed except for a small hole in the lid. This hole was later sealed in an evacuated EB welding chamber. The closed-pack experiments were considerably more laborious, and occasional weld cracks were a problem. The largest majority of the vacuum pack cementation experiments were performed in open packs; unless stated

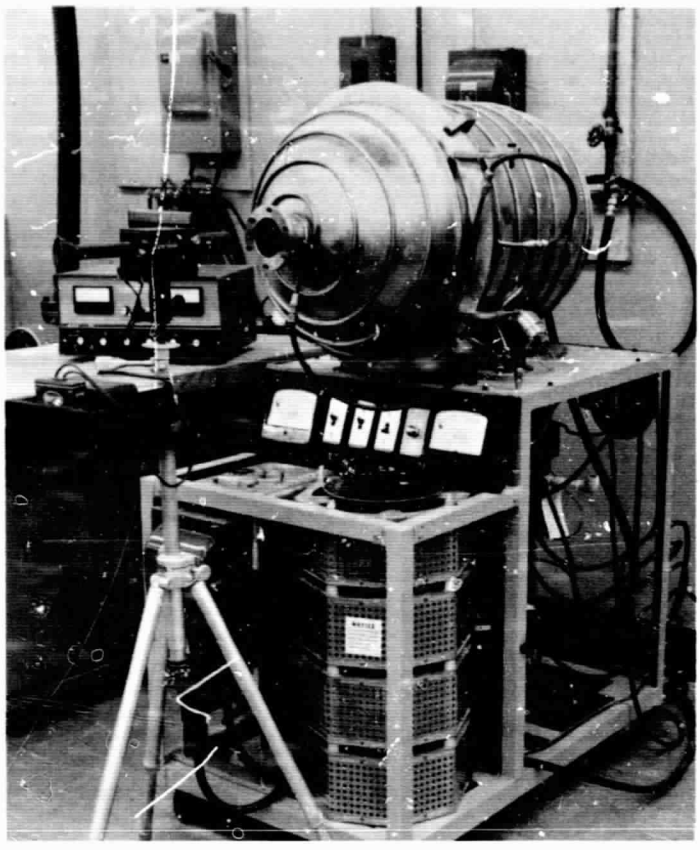


FIGURE 15.

COLD WALL VACUUM FURNACE WITH A TANTALUM HEATING ELEMENT

to the contrary it may be assumed that the work was done under open-pack conditions. No siliciding experiments were performed in a vacuum environment; all siliciding involved the use of high-pressure pack techniques.

The procedure for preparation of pack alloys and specimens was the same for vacuum packs as for the high-pressure pack cementation. Up to 15 specimens were placed vertically in the B66 alloy boats with approximately 0.25-inch separation. Pack alloy, which was either thoroughly mixed with 0.01 weight percent NaF activator or free of activator, was poured into the boat to completely enclose each specimen. A loose fitting B66 alloy lid was placed on the filled boat. When the furnace with carbon heating elements was used, the boats were inserted into a Cb752 retort. The retort could hold two boats at one time. A lid was placed on the retort and the entire assembly was placed in the furnace so that the control thermocouple passed through a hole in the bottom of the retort into the chamber containing the boats filled with the pack alloy. The retort was not used when the run was made in the furnace with a tantalum heating element. In that situation the boats were placed directly on the tungsten hearth.

The vacuum furnace containing the pack was evacuated at room temperature overnight (15 hours) at pressures of less than 10^{-5} Torr. Heating to the desired temperature was usually accomplished in 1.5 to 2.0 hours. The heating rate was controlled to maintain a pressure of less than 2×10^{-4} Torr. Cooldown from the operating temperature was effected by turning the power off and filling the furnace with helium. Thirty to 45 minutes were required for cooling to about 200 F, at which time the pack could be removed from the furnace.

3.3.3 Results of Vacuum Pack Cementation

Coatings Based on Modification of T222 Alloy in TNV-1 Pack

A closed-pack cementation run was made using TNV-1 pack alloy with 0.1, 1.0, and 5.0 weight percent NaF activator; the cycle was 15 hours at 1915 F. Excessive sintering of the pack particles to the specimens occured with all three activator concentrations so that no meaningful weight gain data were obtained. Because of the tendency of TNV-1 alloy to sinter at coating temperatures high enough for practical deposition rates, no further work with TNV-1 was performed.

Coatings Based on Modification of T222 Alloy in TNV-3

An initial vacuum pack experiment corresponded to three 4-hour cycles at 2500 F and one 5-hour cycle at 2700 F. The resultant accumulated weight gain of 5.7 mg/cm^2 corresponded to a modified layer less than 0.001 inch thick. Because the desired modified layer thickness was less than the stated 0.002-inch goal, the samples were neither silicided nor oxidized.

The experimental conditions employed in a second vacuum-pack experiment (T_2-131) are summarized in Table XIV. During the three modifier application cycles and subsequent anneal in a tungsten pack, the specimens displayed a net accumulation of 26.8 mg/cm^2. As is indicated in Table XIV, the samples experienced an 18.9 mg/cm^2 weight gain during siliciding at 2000 F. The samples were subsequently submitted to oxidation testing.

TABLE XIV

VACUUM PACK MODIFICATION IN TNV-3 PACKS AND SUBSEQUENT SILICIDING
(Experiment T_2-131)

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	TNV-3 (30Ti-70W)	15	2625	Zero	$<10^{-4}$	9.8
2	TNV-3 (30Ti-70W)	15	2700	Zero	$<10^{-4}$	12.3
3	TNV-3 (30Ti-70W)	15	2700	Zero	$<10^{-4}$	11.3
4	W(+20M)	15	2700	Zero	$<10^{-4}$	-6.6
5	Si(-200M)	15	2000	0.1	800	18.9

Coatings Based on Modification of T222 Alloy in TNV-5, -6, and -7 Packs

Both open and closed vacuum-pack techniques were employed in an attempt to satisfactorily modify the T222 alloy in pack compositions TNV-5, -6, and -7. The experiments performed are characterized in Tables XV and XVI. Because the thickness of the modified layer was less than 0.001 inch in each of the experiments, the specimens were neither silicided nor oxidized.

TABLE XV

VACUUM PACK MODIFICATION IN TNV-5, -6, AND -7 PACKS
(Open-Pack Process)

Pack Alloy No.	Pack Alloy Composition (wt %)	Weight Gain (mg/cm^2) With Indicated Coating Cycle Time and Temperature			
		Cycle 1	Cycle 2	Cycle 3	Cycle 4
		4 Hours 2500 F 0.01 wt % NaF	5 Hours 2700 F No Activator	4 Hours 2500 F No Activator	4 Hours 2500 F No Activator
TNV-5	30Ti-35W-35Mo	0.43	1.50	Not Performed	Not Performed
TNV-6	30Ti-40W-30V	0.30	1.30	Not Performed	Not Performed
TNV-7	15Ti-35W-15V-35Mo	0.20	1.50	0.00	0.00

TABLE XVI

VACUUM PACK MODIFICATION IN TNV-5, -6, AND -7 PACKS,
FOUR-HOUR CYCLES AT 2500 F
(Closed-Pack Process)

Pack Alloy No.	Pack Alloy Composition (wt %)	Weight Gain (mg/cm^2) With Indicated Activator		
		NaF		K_2VF_5
		0.02 wt %	0.10 wt %	0.10 wt %
TNV-5	30Ti-35W-35Mo	0.67	---	----
TNV-5	30Ti-35W-35Mo	----	1.1	----
TNV-6	30Ti-40W-30V	0.59	---	----
TNV-7	15Ti-35W-15V-35Mo	----	---	0.70

Coatings Based on Modification of T222 Alloy in Unalloyed Titanium Packs

Investigation of modification of the T222 alloy in unalloyed titanium packs involved use of CaF_2 and K_2VF_5 activators under the experimental conditions summarized in Table XVII. Calcium fluoride was employed as an activator on the basis that is vapor pressure is lower than that of sodium fluoride, and thus calcium fluoride would be expected to be retained for greater periods of time in a vacuum environment at a given temperature. The K_2VF_5 was investigated as an activator on the basis that the material has the potential for reduction by titanium to possibly produce active volatile titanium fluoride. Although reasonable deposition rates were experienced, excessive sintering of the titanium sponge to the specimens took place at both 2300 and 2650 F; as a result, the samples were neither silicided nor oxidized.

Coatings Based on Modification of T222 Alloy in Vanadium Packs

Modification in vanadium packs under the experimental conditions employed in the preceding section for unalloyed titanium packs resulted in the weight gains indicated in Table XVIII, all of which were less than 3 mg/cm^2. Increasing the deposition temperature to 2400 F with 0.1 K_2VF_5 activator increased the weight gain an inadequate amount to only 1.6 mg/cm^2 during the 15-hour modification cycle. Elimination of the activator while increasing the temperature to 2760 F for a 15-hour exposure resulted in excessive sintering so that no weight gain measurements could be made.

TABLE XVII

SINGLE-CYCLE VACUUM PACK MODIFICATION IN VANADIUM PACKS

Pack Composition	Weight Gain (mg/cm^2) With Indicated Activator and Coating Cycle	
	0.1 wt% CaF_2 4.5 Hours 2650 F	0.1 wt% K_2VF_5 15 Hours 2300 F
(Ti sponge 99.7%) -20+50 Mesh	--	2.8
(Ti sponge 99.7%) -20+50 Mesh	10.9	-

TABLE XVIII

SINGLE-CYCLE VACUUM PACK MODIFICATION IN UNALLOYED TITANIUM PACKS

Pack Composition	Weight Gain (mg/cm^2) With Indicated Activator and Coating Cycle	
	0.1 wt% CaF_2 4.5 Hours 2650 F	0.1 wt% K_2VF_5 15 Hours 2300 F
(V Chip 99.8%) -20+50 Mesh	--	0.5
(V Chip 99.8%) -20+50 Mesh	2.8	-

TABLE XIX

VACUUM PACK MODIFICATION IN VANADIUM PACKS AND SUBSEQUENT SILICIDING (Experiment T_2-137)

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	V(-1/4 inch +9M)	17	2700	Zero	10^{-4}	12.4
2	V(-1/4 inch +9M)	17	2700	Zero	10^{-4}	10.5
3	Si(-200M)	5-1/2	2150	1.0	800	9.7
4	Si(-200M)	4	2150	1.0	800	2.9

Work on another program at Solar indicated the use of larger vanadium particles resulted in less coating defects. In Experiment T_2-137, -0.25-inch +9 mesh vanadium granules were employed whereas -20 +50 mesh particles were used in the preceding work. As is indicated in Table XIX, nearly 23 mg/cm^2 of vanadium were deposited on the specimens during the two 1-hour cycles at 2700 F. Although the modified surface had generally good appearance, occasional defects could be seen; these defects were thought to correspond to small patches of the modified layer that were torn from the surface of the specimens when the pack particles were removed. During siliciding in two cycles at 2150 F, the specimens experienced a weight gain of 12.6 mg/cm^2. The samples were submitted to oxidation testing.

Coatings Based on Modification of Vanadized T222 Alloy in TNV-3 Packs

During the course of Experiment T_2-136-A, T222 specimens were coated with 16 mg/cm^2 of vanadium in a single-cycle at 2700 F followed by a weight gain of 10.8 mg/cm^2 during a modification in the TNV-3 pack at 2700 F as is indicated in Table XX. Following siliciding in two cycles at 1975 F, with an accumulated weight gain of 12.7 mg/cm^2, the samples were submitted to oxidation testing.

TABLE XX

VACUUM PACK VANADIZATION AND SUBSEQUENT MODIFICATION IN TNV-3 AND SILICON PACKS (Experiment T_2-136A)

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	V-1/4 inch +9M)	15	2700	Zero	10^{-4}	16.0
2	TNV-3 (-1/4 inch +9M)	15*	2700	Zero	10^{-4}	10.0
3	Si(-200M)	8	1975	0.1	800	10.6
4	Si(-200M)	3-3/4	1975	0.1	800	2.1

* Power failed at unknown time during cycle

Coatings Based on Modification of Vanadized T222 Alloy in 80Cr-20Ti Packs

A summary of Experiment No. T_2-136 is given in Table XXI. Samples were coated with 16 mg/cm^2 of vanadium in a single cycle at 2700 F. In two cycles at 2300 F, an accumulation of 9.6 mg/cm^2 was experienced in 80Cr-20Ti packs. Following the deposition of 18 mg/cm^2 of silicon at 1950 F, the specimens were submitted to oxidation testing.

TABLE XXI

VACUUM PACK VANADIZATION AND SUBSEQUENT MODIFICATION IN 80Cr-20Ti AND SILICON PACKS

Cycle No.	Pack Composition	Time (hr)	Temperature (F)	Activator (wt % NaF)	Pressure (Torr)	Weight Gain (mg/cm^2)
1	V (-1/4 inch +9M)	15	2700	Zero	10^{-4}	16.0
2	80Cr-20Ti (-20 +50M)	15	2300	0.1	800	6.0
3	80Cr-20Ti (-20 +50M)	15	2300	0.1	800	3.6
4	Si(-200M)	4	1950	0.1	800	18.0

3.3.4 Coatings Applied By Slurry Techniques

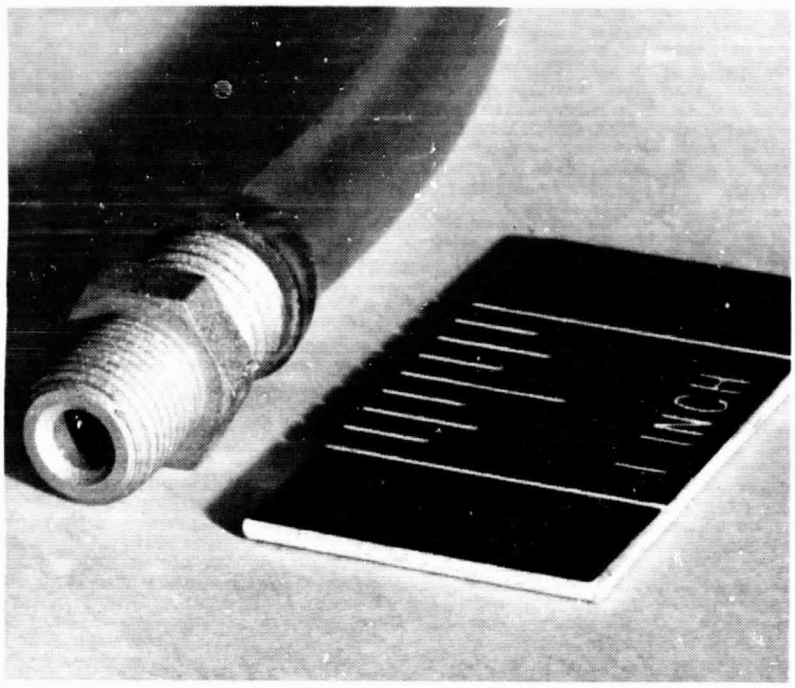
The inability to transfer molybdenum and tungsten from the pack alloys to the substrates, the adherence of pack particles to the specimens, and low deposition rates during pack cementation prompted an investigation of slurry-coating techniques. Two basically different methods of applying coatings by slurry techniques were investigated. In the first of the two processes, a slurry of powders of the elemental modifier metals was sprayed onto the substrate, vacuum sintered, and silicided using activatorless high-pressure pack techniques. (No activator was added intentionally to the siliciding pack; however, trace halide impurities in the silicon may have been present and could have played an important role in the siliciding process.) The second process corresponded to modification of the substrate in a 30Ti-70W pack, spray coating the substrate with a slurry consisting of a mixture of silicon and modifier metal powders, and subsequent sintering (or fusion) to provide consolidation of the coating. The latter process was observed to yield less protective coatings than the first process; accordingly, the bulk of the investigation of slurry-coating techniques involved the first process.

Apparatus and Procedure

The details of the procedure used in suspending the elemental metal powders in an organic vehicle are contained in Appendix C. Originally, a xylene solution of polyisobutelene was used as the vehicle; however, the resultant coatings were quite soft and difficult to handle, and the rubbery nature of the dried coatings allowed the coating to remain intact in areas where it was detached from the substrate. Vistanex LM-MS, L-100, and L-200 grades of polyisobutylene (Enjay Chemical Company, New York, N. Y.) dissolved in xylene in concentrations of 0.5 to 4.0 percent were investigated. Polymethylmethacrylate (transoptic molding powder, Buehler, Ltd., Evanston, Ill.) dissolved in a mixture of amyl-acetate and ethyl acetate was investigated as a vehicle as was a xylene solution of both polyisobutelene and polymethylmethacrylate. The vehicle which gave the best results and was used throughout the latter portion of the slurry-coating work, and the one which is described in Appendix C, corresponds to ethyl cellulose dissolved in a mixture of secondary-butyl alcohol, xylene and stoddard solvent. This particular vehicle, designated as E4, allowed the preparation of slips with a minimum tendency towards particle settling, and allowed fluid-to-solid ratios as low as 2.0, even though a ratio of 2.5 was found to be more desirable for spraying.

Specimens sandblasted and etched by the procedures outlined in Paragraph 3.2 were held on the spraying fixture shown in Figure 16 by an aspirator-drawn vacuum. A model TGA-Series 501 DeVilbiss spray gun was used in making a predetermined number of passes (six fast passes were observed to give greater control than a smaller number of slower passes). After spraying the edges and the top surface of the specimen, the sample was allowed to dry and was then turned over and laid on the second spraying jig (Fig. 16) preparatory to spraying the opposite side. After spraying and drying, the samples were placed on the tungsten rods of the firing jig (Fig. 17). The loaded jig was then placed on the hearth of the tantalum element vacuum furnace in all but a few preliminary experiments involving the graphite cloth heating element furnace. Heating the furnace slowly to approximately 1000 F over a period of about one hour allowed gradual decomposition of the organic binder without disrupted effects. Following decomposition of the binder, the furnace was quickly heated to the specified temperature and was held there for the specified period of time before the supply of electrical power was discontinued and the samples were allowed to cool in vacuum.

After sintering, the modifier layers were silicided by conventional high-pressure pack cementation by heating the specimens in a -200 mesh silicon pack (Par. 3.3.1).



A.

Vacuum jig used when spraying edges and first flat surfaces.

B.

Jig used when spraying second flat surface. (Specimen in place)

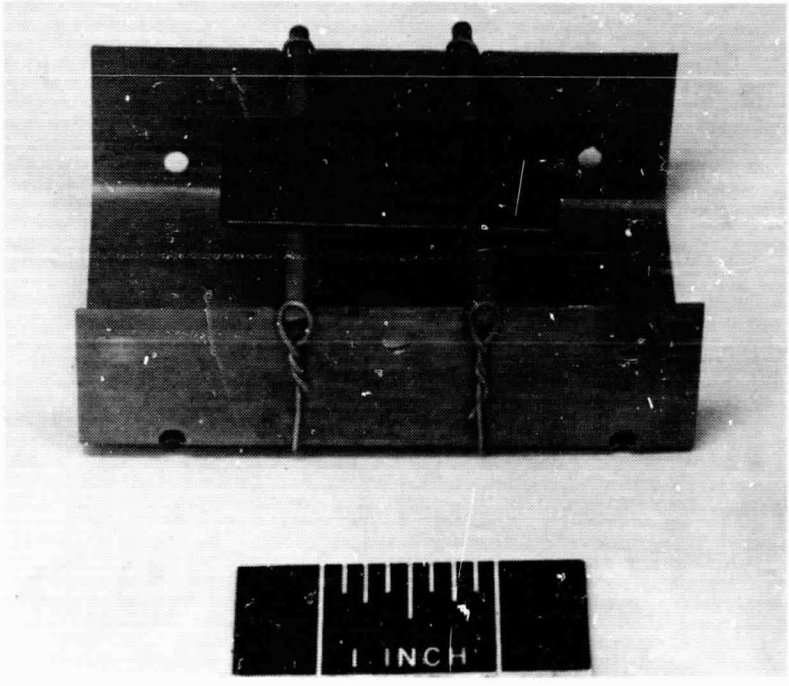


FIGURE 16. JIGS USED WHEN SPRAYING SPECIMENS

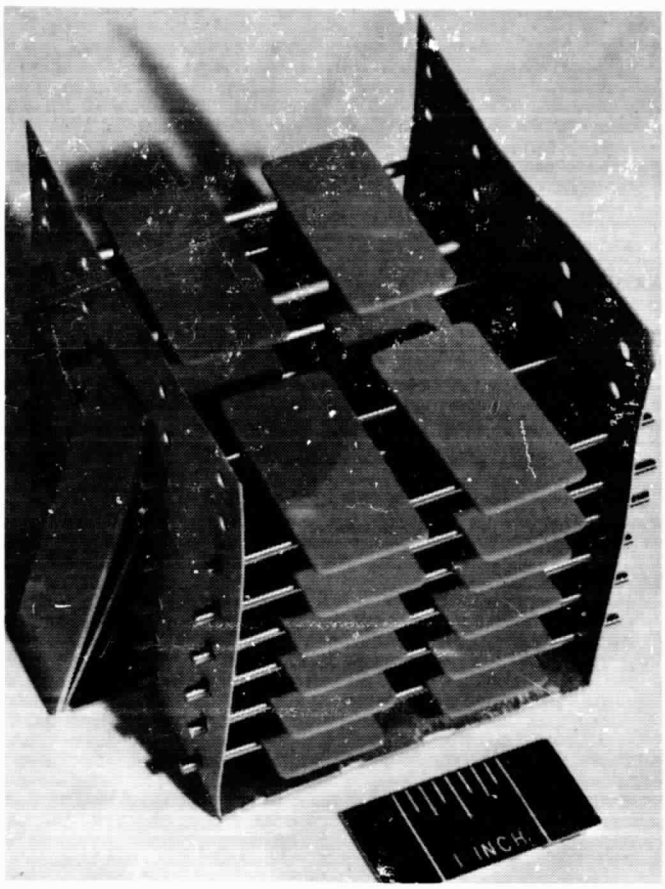


FIGURE 17.
PARTIALLY LOADED FIRING JIG

The use of a phonograph turntable rotating at 78 rpm was investigated as a spraying facility, but was found to yield oxidation lives no greater than those obtained when the specimens rested on stationary jigs. The use of additional passes in spraying the corners of the specimens resting on a fixed jig did not appear to offer an improvement over the normal process of spraying the edges and flat surfaces without giving any special attention to the corners.

3.3.5 Results of Application of Slurry Coatings

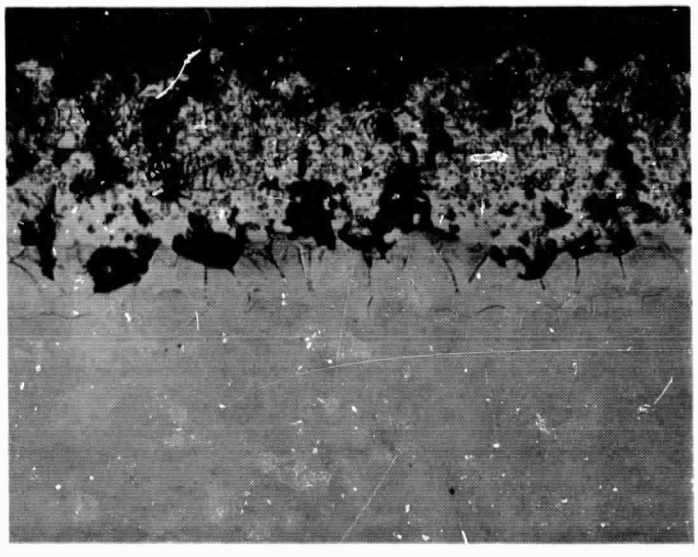
In the early stages of the slurry-coating studies, a cursory investigation of the effects of varying the sintering conditions for the TNV-3, TNV-4, and TNV-9 coatings was conducted. Firing times of 2 and 15 hours, and firing temperatures of 2435 and 2760 F were investigated. In one experiment an argon pressure of 710 Torr was employed during a 15-hour firing at 2760 F in the graphite cloth element furnace.

The evaporation of titanium at the higher temperature was quite noticeable and suggested the use of the 2435 F firing temperature for the titanium-rich coatings. Additional preliminary experiments indicated that it was beneficial to sinter the chromium-containing coatings at 2620 F for 30 minutes to take advantage of the 2535 F minimum in the solidus curve of the Ti-Cr binary system (Ref. 8).

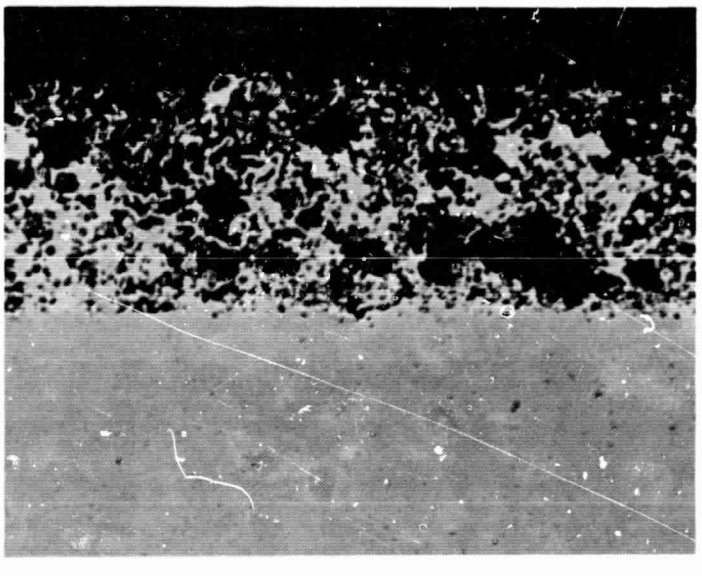
In addition to applying the ten basic chemistries selected at the outset of the program, the slurry-coating process allowed the application of tungsten-rich and molybdenum-rich (containing five percent tiatnium or less) modifier alloys, which upon siliciding yielded nearly unalloyed $MoSi_2$ and WSi_2, both of which are known for their excellent oxidation resistance. While the molybdenum-rich and tungsten-rich coatings were readily applied by the slurry-coating process, these coatings could not be applied by conventional pack techniques.

The microstructure of the as-sintered TNV-3, TNV-7, and TNV-12 (4.7Ti-95.3Mo) modifier alloys are shown in Figure 18, and are representative of the slurry coatings as a group. With the majority of the TNV-1 through TNV-10 coatings (typified by the TNV-3 and TNV-7 microstructures), a light-colored zone within the fully dense substrate was apparent and was attributed to titanium and vanadium diffusion. In the case of the coatings having five percent or less titanium (typified by the TNV-12 coating), the quantity of titanium added appeared to be so small that it did not produce a readily detected zone in the substrate. Application of an alumina-wash coat to the tungsten rods of the firing jig diminished, but did not eliminate, a sticking problem observed with the chromium-containing coatings. Normally, all of the sintered slurry coatings were between 0.004 and 0.006 inch thick and corresponded to a weight gain of about 30 to 135 mg/cm^2.

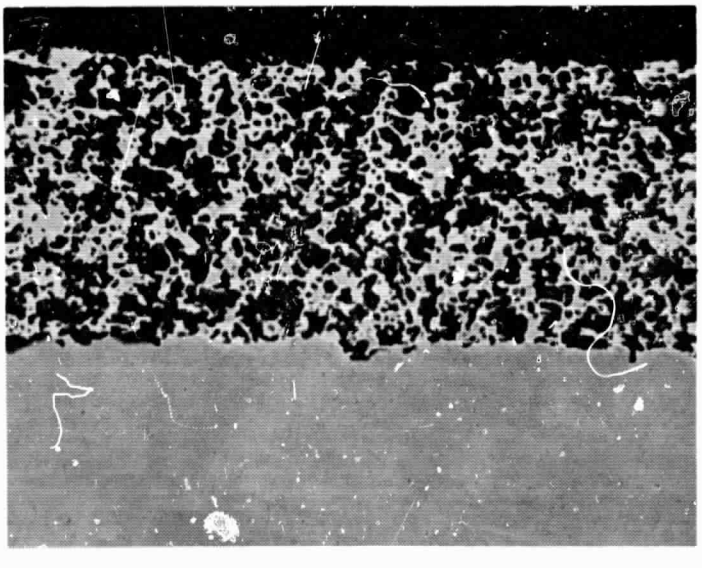
After sintering, the modifier layers were silicided by the conventional high-pressure pack cementation techniques by heating them in -200 mesh silicon powder for sever to eight hours at 2000 to 2250 F. With the exception of a few preliminary experiments with the slurry coatings, no activator was intentionally added to the silicon; however, trace halide impurities may have been present and promoted silicon transfer. Pack siliciding of the slurry coatings resulted in a weight gain of 14 to 48 mg/cm^2, and produced an increase in coating thickness of approximately 0.003 inch with nearly all of the coatings.



Experiment Number: T_2-159
Coating: TNV-3 (30Ti-70W)
Sintered: 15 Hours at 2435 F
Magnification: 250X



Experiment Number: T_2-203
Coating: TNV-7 (15Ti-35W-15V-35Mo)
Sintered: 15 Hours at 2760 F
Magnification: 250X



Experiment Number: T_2-156
Coating: TNV-12 (4.7Ti-95.3Mo)
Sintered: 15 Hours at 2760 F
Magnification: 250X

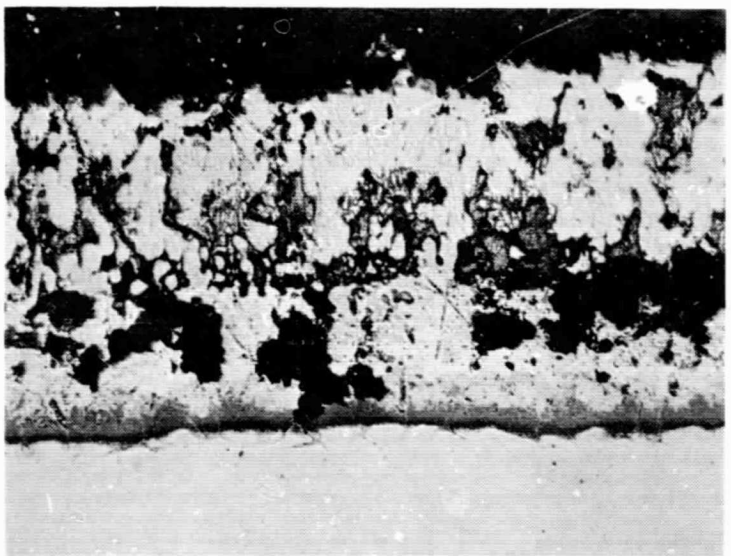
FIGURE 18. AS-SINTERED MICROSTRUCTURES TYPICAL OF SLURRY COATINGS

Siliciding of the TNV-1 coating resulted in spalling with most of the specimens; this was not surprising in view of the problems encountered in siliciding the titanium-rich coatings applied in the pack studies.

The chromium containing coatings (TNV-8, -9, and -10) also had a tendency to spall during siliciding and thus reduced the number of these specimens available for oxidation testing (of this group, TNV-10 had the greatest tendency toward spalling).

The microstructures of the as-silicided coatings which showed some appreciable oxidation resistance are shown in Figures 19 through 22, while the microstructures of the less oxidation-resistant coatings are shown in Appendix D. Significant porosity was apparent in each of the coatings, but this porosity was undoubtedly exaggerated by pullout during metallographic polishing. In some cases the silicon has diffused only part way through the porous coating while, in others, silicon has penetrated well into the substrate. The TNV-7 coating (Fig. 20) is characterized by penetration of the silicon through the porous sintered coating and into the substrate. However, examination of the photomicrograph taken at 40X magnification reveals that the thickness of the porous sintered coating and the fully dense hard sublayer varies appreciably with location on the specimen. Despite this lack of uniformity (resulting from the spraying process), none of the specimens prepared in the experiment for which the metallography is shown in Figure 20 were observed to fail in 600 hours of testing at either 1600 or 2400 F. The silicided porous layer was observed to contain a multiplicity of phases (which are partially characterized in Paragraph 3.4.6). The nonporous light-colored zone of high hardness (KHN 2420) located within the substrate (Fig. 20) was shown by electron microprobe analysis to result from diffusion of silicon into the substrate; however, the silicon concentration was relatively constant throughout the diffused zone. The microprobe traces along with eletron micrographs and X-ray diffraction results are presented in Paragraph 3.4.6 with the analyses of the oxidation specimens.

Examination of the microstructure of the TNV-12 coating (Fig. 21) reveals that silicon did not completely penetrate the porous sintered modifier layer; electron microprobe analysis of the porous ligh-colored zone of intermediate hardness (KHN 623 to 748) revealed that it contained virtually no silicon. The hardness of the as-sintered coating was in the range of 155 to 270; the increase to the range of 623 to 748 was perhaps a result of an accumulation of interstitials during the siliciding process. The



Experiment Number: T_2-159
Substrate: T222
Coating: TNV-3 (30Ti-70W)
Sintered: 15 Hours at 2435 F (79 mg/cm^2 gain)
Silicided: 7.5 Hours at 2150 F (21 mg/cm^2 gain)
Etchant: 60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification: 250X

Experiment Number: T_2-174
Substrate: T222
Coating: TNV-6 (30Ti-40W-30V)
Sintered: 15 Hours at 2760 F (43 mg/cm^2 gain)
Silicided: 7 Hours at 2150 F (31 mg/cm^2 gain)
Etchant: 60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification: 250X

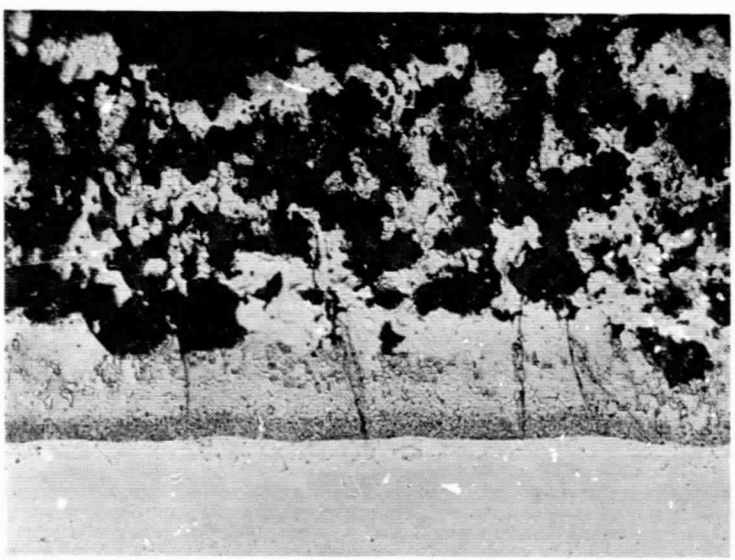
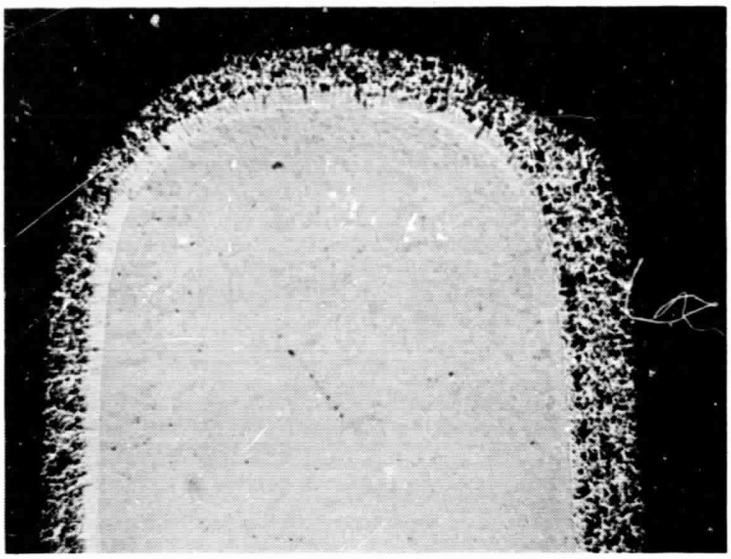


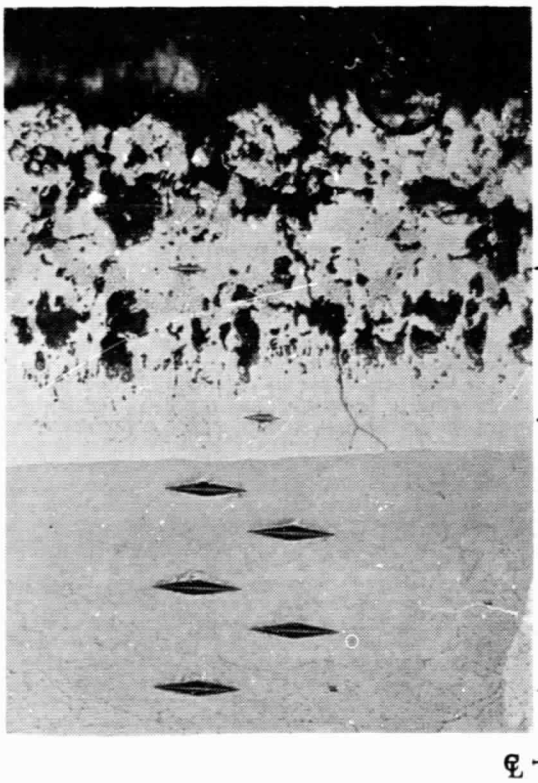
FIGURE 19. AS-SILICIDED MICROSTRUCTURE OF TNV-3 AND TNV-6 COATINGS

cracks in the outer silicided layer of the coating did not traverse the light-colored porous zone adjacent to the substrate. The cracks contained in the TNV-7 coating (Fig. 20) were observed to traverse the coating completely, terminating at the substrate.

Examination of Figure 22 reveals that within the TNV-13 (5Ti-95W) coating prepared in Experiment T_2-170 there were regions in which silicon completely penetrated the porous coating and started into the substrate and other regions where the silicon penetration did not reach the substrate. Electron microprobe analysis confirmed that silicon had not diffused into the substrate in the areas where metallographic examination suggested that it had not.



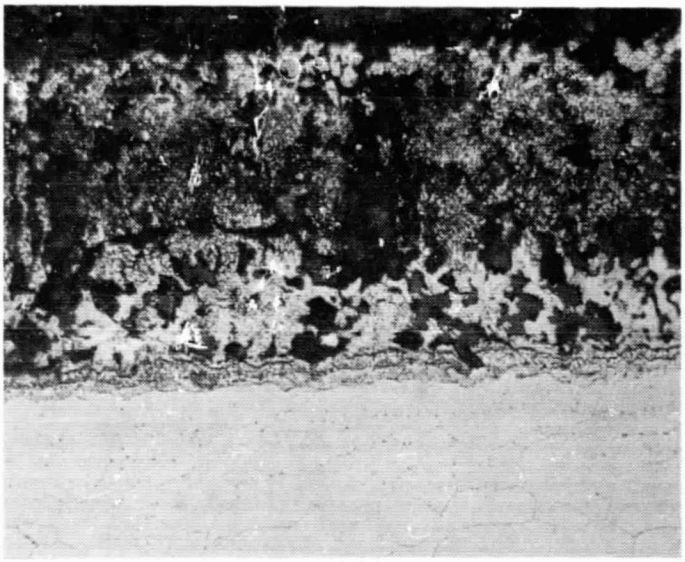
Magnification: 40X



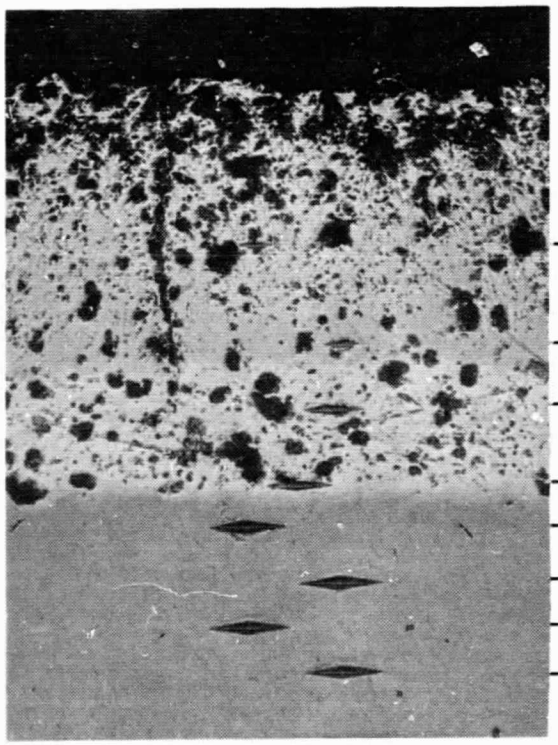
Experiment Number:	T_2-187
Coating:	TNV-7 (15Ti-35W-15V-35Mo)
Substrate:	T222
Sintered:	15 Hours at 2760 F (55 mg/cm^2 gain)
Silicided:	7 Hours at 2150 F (40 mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3

Magnification: 250X

FIGURE 20. AS-SILICIDED MICROSTRUCTURE OF TNV-7 COATING

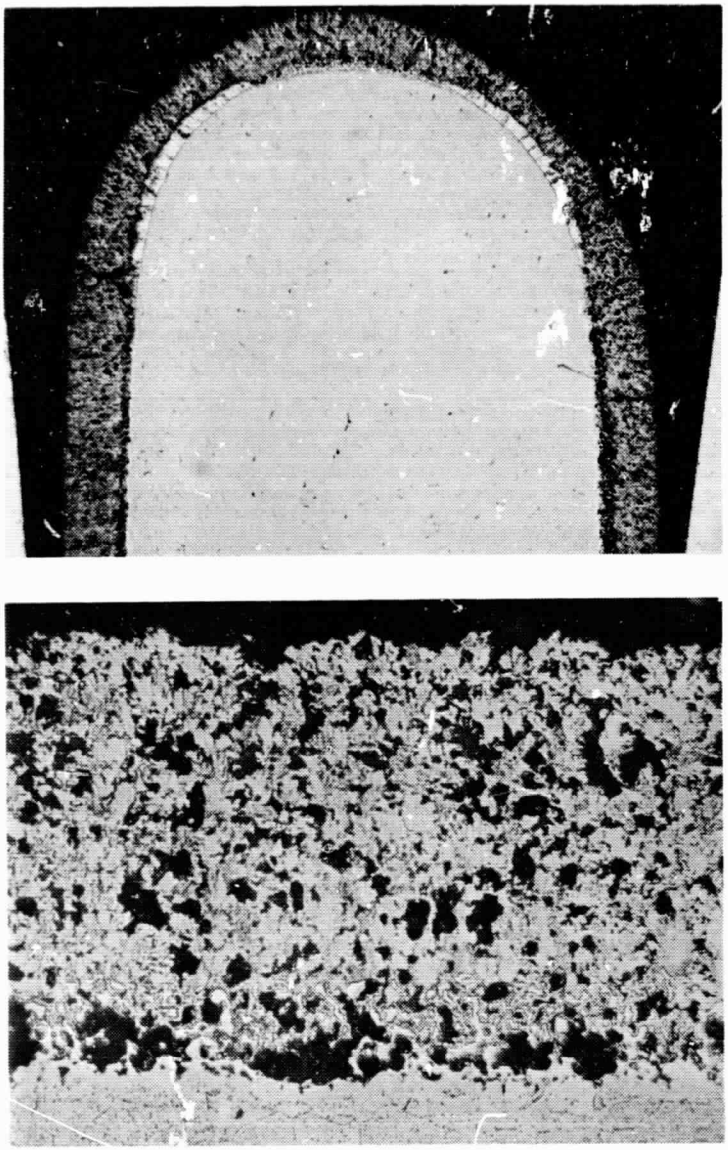


Experiment Number:	T_2-180
Substrate:	T222
Coating:	TNV-9 (30Ti-35Mo-35Cr)
Sintered:	0.5 Hours at 2610 F (43 mg/cm^2 gain)
Silicided:	7 Hours at 2150 F (31 mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20 % Concentrated HNO_3
Magnification:	250X



Experiment Number:	T_2-144
Substrate:	T222
Coating:	TNV-12 (4.7Ti-95.3Mo)
Sintered:	15 Hours at 2760 F (68 mg/cm^2 gain)
Silicided:	7.5 Hours at 2150 F (29 mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification:	250X

FIGURE 21. AS-SILICIDED MICROSTRUCTURE OF TNV-9 AND TNV-12 COATINGS



Magnification: 40X

Experiment Number:	T_2-170
Substrate:	T222
Coating:	TNV-13 (5Ti-95W)
Sintered:	15 Hours at 2760 F (135 mg/cm^2 gain)
Silicided:	7 Hours at 2150 F (35 mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3

Magnification: 250X

FIGURE 2. AS-SILICIDED MICROSTRUCTURE OF TNV-13 COATING

Results of X-ray diffraction and electron microprobe analysis of the TNV-12 and glass-impregnated TNV-13 coatings are presented in Paragraph 3.4.6.

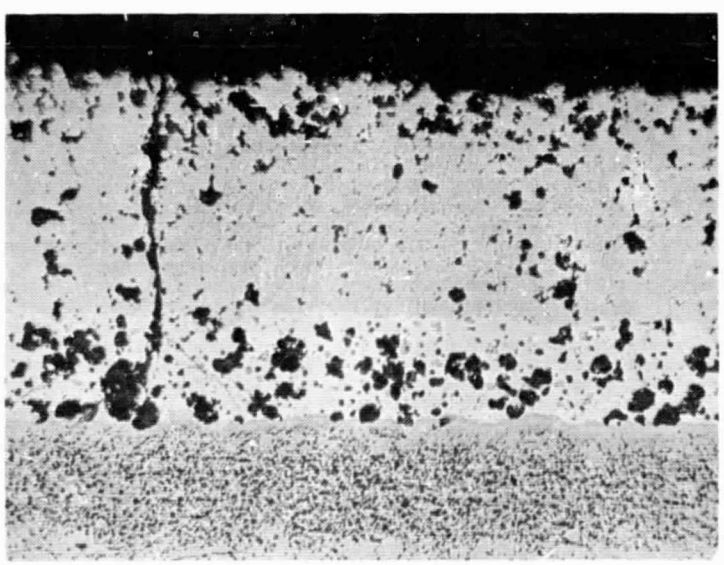
In addition to the ten basic modifier alloys and the TNV-11, -12, and -13 compositions, four additional compositions were investigated by sintering for 15 hours at 2760 F. Two of these corresponded to modification of TNV-12 and were designated as TNV-14 and TNV-15 (2.5Ti-97.5Mo and 10Ti-90Mo, respectively). The as-silicided microstructure of these two coatings was similar to that of TNV-12; however, the width of the porous unsilicided zone appeared to decrease with increasing titanium content. The two compositions designated as TNV-16 and TNV-17 (5Ti-5V-45W-45Mo and 5Ti-5V-90W, respectively) corresponded to modifications of TNV-7 and were observed to have microstructures similar to that of TNV-7.

Investigation of the Effect of Thickness of the TNV-12 Coating

In a single experiment, the thickness of the as-sintered TNV-12 modifier layer was varied intentionally. Siliciding a 0.003-inch thick modifier layer resulted in penetration of the silicon into the substrate; whereas, siliciding the 0.006- and 0.010-inch thick as-sintered coatings resulted in only partial silicon penetration yielding microstructures similar to the microstructure (Fig. 20) corresponding to the normal 0.004 to 0.006 inch as-sintered modifier layer.

Slurry Coatings on Substrates Modified by Pack Cementation

To maximize the extent of an unsilicided modifier alloy beneath the silicided coating, T222 specimens were modified by vacuum pack cementation techniques prior to application of TNV-12 by slurry-coating techniques. A net modifier accumulation of 17 mg/cm^2 was observed when the T222 specimens were given a single vacuum pack cementation cycle in a TNV-3 pack heated to 2760 F for 15 hours prior to an anneal on tungsten rods for the same period of time at the same temperature. The as-sintered TNV-12 slurry coating was a little over 0.004-inch thick and corresponded to a weight gain of 63 mg/cm^2. During siliciding a weight gain of 31.8 mg/cm^2 was observed. The microstructure of the resultant coating is shown in Figure 23.



Experiment Number:	T_2-194
Coating:	TNV-12 on TNV-3 Pack Modified T222
TNV-3 Pack Modification:	15 Hours at 2760 F (26 mg/cm^2 gain)
Vacuum Anneal:	15 Hours at 2760 F (9 mg/cm^2 loss)
TNV-12 Slurry Sintered:	15 Hours at 2760 F (63 mg/cm^2 gain)
Silicided:	7 Hours at 2150 F (32 mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification:	250X

FIGURE 23. TNV-12 SLURRY COATING APPLIED TO SUBSTRATE MODIFIER BY PACK CEMENTATION

Coatings Based on Sintering of Slurries of Silicon and Modifier Metal Powder Mixtures

Blends of elemental powders, corresponding to the TNV-3, -5, -6, and -10 compositions, mixed with 80 atomic percent silicon were sprayed on T222 substrates previously vacuum pack modified in a TNV-3 pack. The pack-modified substrates were taken from the same group as those used in the previously described experiment involving application of the TNV-12 coating to the TNV-3 modified substrates. Sintering a set of specimens provided with the TNV-3Si coating at 2645 F for thirty minutes resulted in a soft porous coating, so a single specimen each of the four compositions was sintered at 2760 F for thirty minutes. Of the group, TNV-10Si was the least porous (Fig. 24); subsequently, a set of samples provided with a 0.005-inch thick TNV-10Si coating was prepared and subjected to oxidation testing.

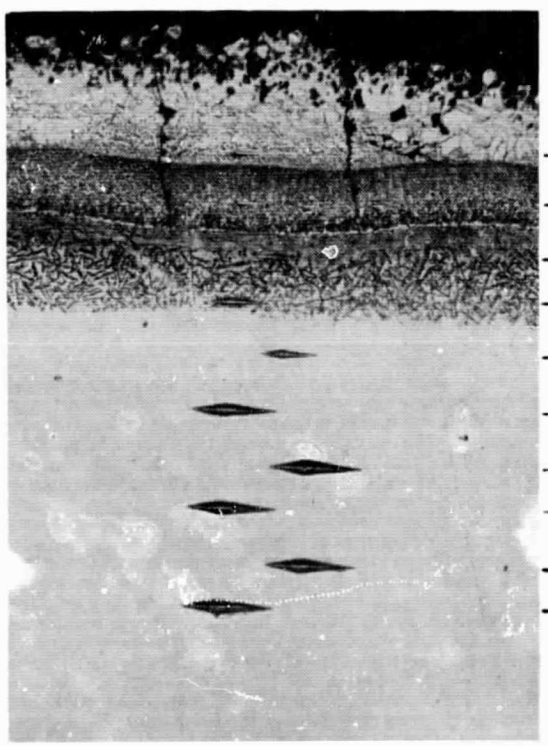


FIGURE 24. TNV-10 Si COATING; Obtained by Sintering Mixture of Silicon and Metal Powders

In a separate experiment, the silicon content of the TNV-6Si coating was increased from 61.7 weight percent silicon (80 at. %) to 80 weight percent silicon. Although the coating was a little more densely sintered, the coating was still quite rough and was observed to fail in the first cycle of oxidation testing. Use of an alumina-wash coat on the tungsten rods of the firing jig tended to diminish, but not eliminate, a problem of sticking of each of the silicon-containir coatings.

Glass Impregnation Studies

The 1600 F oxidation resistance of the tungsten-rich and molybdenum-rich coatings was observed to be poor, and thus prompted an investigation of impregnating the as-silicided coatings with an aqueous slip of finely milled glass frit. In preliminary experiments with the TNV-13 coating, a barium borosilicate glass (Solar Frit No. S-5210) was observed to provide greater improvement in the 1600 F oxidation life then was either Pyrex or a modified barium borosilicate glass (XG201 frit made by the Ferro Corporation). The effects of the S-5210 frit on the TNV-7, -12, -14, -15, -16, and -17 as-silicided coatings were then investigated.

The samples were sprayed with, or dipped in, the finely milled slip and were allowed to dry before the excess frit was removed by brushing. The small quantity of retained frit corresponded to a weight gain of approximately 1 mg/cm^2 or less, except in the case of the TNV-7 coating which picked up approximately 1.7 mg/cm^2. Before the impregnated samples were subjected to the normal oxidation testing, they were air-fired for 10 to 14 minutes at 1800 F, cooled to room temperature, and weighed. Samples impregnated in an aspirator-drawn vacuum were observed to show no greater oxidation resistance than those impregnated in air at atmospheric pressure. The glass impregnating operation (including air firing) produced no detectable change in the coating microstructure.

Activated Sintering Studies

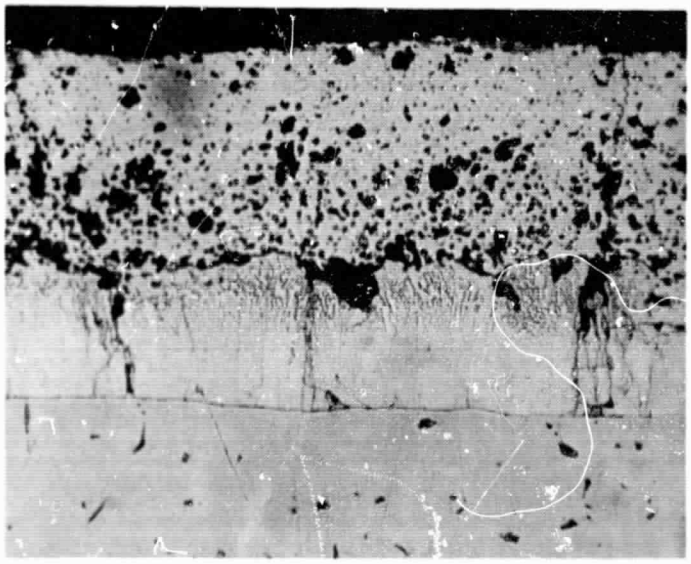
The sintering of tungsten and molybdenum powder compacts was reported to be activated by the addition of very small quantities (0.25 to 1.0 percent) of nickel or palladium, so as to allow the use of greatly reduced sintering temperatures (Ref. 9, 10, and 11). The addition of only 0.25 percent nickel (by an aqueous-solution treatment followed by drying and hydrogen reduction) to tungsten powders allowed sintering to 92 percent of theoretical density in 30 minutes at 2015 F.

The application of activated sintering to slurry-coating technology was successfully investigated in the current program as a means of reducing both the time and temperature for vacuum sintering the TNV-11 modifier alloy. Insufficient time was available to complete preparation and evaluation of a titanium-free tungsten disilicide coating.

Tungsten powder having an average particle size of 0.87 micron was slurried into a dilute nickel nitrate solution before drying, and a subsequent reduction in flowing hydrogen for 1.75 hours at 1470 F was accomplished. Titanium was added to the nickel-coated tungsten powder to yield a modifier alloy characterized as W-2.5Ti-0.25Ni. Specimens spray coated with this composition were vacuum sintered for 2.5 hours at 1925 F to yield a 0.004-inch thick modifier layer (75 mg/cm^2). High-pressure pack siliciding for seven hours at 2150 F resulted in a weight gain of 43 mg/cm^2 and a 0.003-inch increase in coating thickness. The microstructure of the resultant coating (Fig. 25) suggests penetration of the silicon through the coating and into the substrate. The coating was subjected to oxidation testing.

A brief investigation of the dependence placed upon the method of adding nickel to the tungsten powders was made by dipping individual T222 specimens in the slurry remaining from the first activated sintering experiment, as well as preparing a slip by adding nickel powder (as well as titanium powder) directly to the 0.87-micron tungsten powder. After sintering for 2.5 hours at 1925 F, the two coatings were seen to be nearly equal in resistance to abrasion by a pen knife. These results suggested that in the presence of titanium, it made little difference as to whether the nickel was added as a powder or by coating the tungsten powder by hydrogen reduction after treatment with a nickel nitrate solution.

A brief investigation was also made to determine the benefit of nickel coating the tungsten powders relative to the sintering enhancement resulting from use of powders of reduced particle size (while 0.87 micron powder was used for the activated sintering studies, 4- to 6-micron powder was used in the coating program previously). Individual samples of T222 alloy dipped in slurries of uncoated and nickel-coated tungsten powder (0.87 micron average particle size) were vacuum sintered for 2.5 hours at 2230 F. The results indicated that the benefit of reducing the particle size greatly overshadowed the benefit of the nickel when resistance to abrasion by a pen knife was used as an evaluation criterion. However, the nickel coating was seen to have a slight additional benefit by eleiminating any tendency towards chalking during handling of the sintered coatings.



Experiment Number:	ASW-1
Substrate:	T222
Coating:	W-2.5Ti-0.25Ni
Sintered:	2.5 Hours at 1925 F (75 mg/cm^2 gain)
Silicided:	7 Hours at 2150 F (43 Mg/cm^2 gain)
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification:	250X

FIGURE 25. COATING OBTAINED BY ACTIVATED SINTERING OF TNV-11 MODIFIER ALLOY

Slurry Coating of Erosion Bars

The TNV-7 coating (with and without glass impregnation) was applied to T222 erosion bars prepared for testing at the NASA Lewis Research Center after termination of the current research program.

Each erosion bar (Fig. 26) had dimensions of 0.25 by 1.0 by 4.0 inches and was provided with a tapered leading edge and two mutually perpendicular keyways on one end; one keyway had a rectangular cross section while the other had a semicircular cross section. The radius of curvature of the leading edge was 0.030 inch as was the case with the edges of the 1.0 by 2.0 by 0.062-inch specimens used in the slurry-coating development work.

Each erosion bar weighed approximately 225 grams and, thus, was nearly an order of magnitude heavier than the 1.0 by 2.0 by 0.062-inch specimens. Indentations in the as-sintered coatings resulting from the bars resting on the 0.125-inch tungsten rods of the firing jig were approximately 0.001-inch deep and, thus, corresponded to a reasonably small fraction of the 0.005-inch thickness of the as-sintered modifier layer. There was no noticeable tendency for the sintered coating to adhere to the rods. Generally speaking, the as-silicided and glass-impregnated coatings had a good appearance, but some bars displayed unexplainable light-colored wash marks that are barely visible in Figure 26.

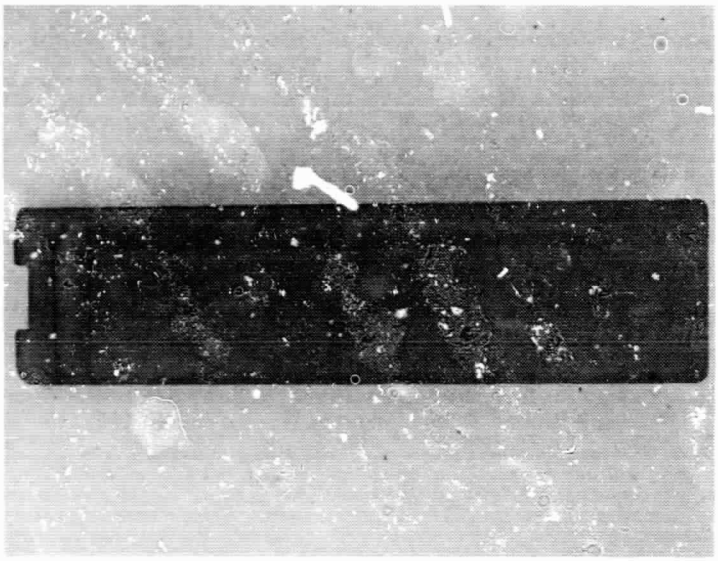


FIGURE 26.

T222 EROSION BAR WITH SILICIDED TNV-7 COATING

Successful coating of the erosion bars indicated the usefulness of the slurry coatings for hardware more complex than the simple 1.0 by 2.0 inch sheet metal specimens.

3.4 OXIDATION TESTING

The specimens coated by the single-modifier-cycle high-pressure pack process were tested at 1500 and 2300 F. The specimens coated by the other processes were tested at 1600 and 2400 F in accordance with the procedures described in Paragraph 3.4.3.

3.4.1 Apparatus and Procedure for Testing Specimens Coated by the Single-Modifier Cycle High-Pressure Pack Process

Resistance heated furnaces were used for oxidation tests at 1500 and 2300 F. A small Hevi-Duty furnace with a rectangular work space four by five by eight inches was used for the 1500 F oxidation tests. The 2300 F tests were conducted in tube furnaces having SiC elements and one-inch ID mullite-muffle tubes. Furnace temperature was controlled to ±10 degrees F. Temperature of the specimens was determined periodically by placing a Pt/Pt-13Rh thermocouple beside the specimens which were placed horizontally on zircon ($ZiSiO_4$) combustion boats. Laboratory air flowed through the combustion tubes and box furnace at a rate that enabled each furnace to have a change of air every minute.

Six specimens were selected from each group of specimens coated under the different conditions. Three of the six specimens were oxidized at 1500 F and three at 2300 F. Each combustion boat held three specimens laid horizontally, and each combustion tube held one boat. Up to four boats could be placed at one time in the box furnace at 1500 F. A random mixture of heating cycles of 7 to 8 and 15 to 16 hours were employed with cooling to room temperature and visual examination performed between cycles. Specimens were turned after each cycle to ensure that each side received similar exposure. Specimens were removed from the test at the first signs of failure.

3.4.2 Results of Testing Specimens Coated by the Single-Modifier Cycle High-Pressure Pack Process

Unsilicided specimens of T222 and T222 prealloyed with TNV-1, -2, and -3 were tested at 1500 and 2300 F as well as silicided specimens prealloyed in packs of the ten basic compositions. The unsilicided specimens were subjected to only a 2- or 3-hour oxidation cycle. Specimens of T222 which were silicided without a prealloying cycle were also tested at 1500 and 2300 F.

The uncoated T222 alloy showed catastrophic oxidation within 30 minutes at both 1500 and 2300 F. Unsilicided specimens prealloyed with TNV-1, -2, and -3 had minimum lives of 14 hours and respective maximum lives of 22, 31, and 46 hours at 1500 F. Failures occurred usually at edges with formation of a soft yellow powder, but failure on the flat portions of the specimens was not uncommon. At 2300 F catastrophic oxidation occurred within 30 minutes in all four cases. These results are shown in Figure 27.

Considerable variation in oxidation life was observed in tests of silicided specimens. Specimens prealloyed in TNV-5, -6, and -7 showed the longest 1500 and 2300 F oxidation life, which ranged from 30 to a maximum of 68 hours. In some cases clear gas bubbles, apparently enclosed by a glass, developed on the specimen surface at 2300 F.

The T222 specimens which were silicided without prealloying, were tested at 1500 and 2300 F. Failures occurred at 37, 60, and 78 hours (1500 F) and at 30 hours (2300 F). Figure 28 shows the results of oxidation tests of silicided specimens which displayed maximum lives of less than 70 hours at 1500 F and less than 60 hours at 2300 F.

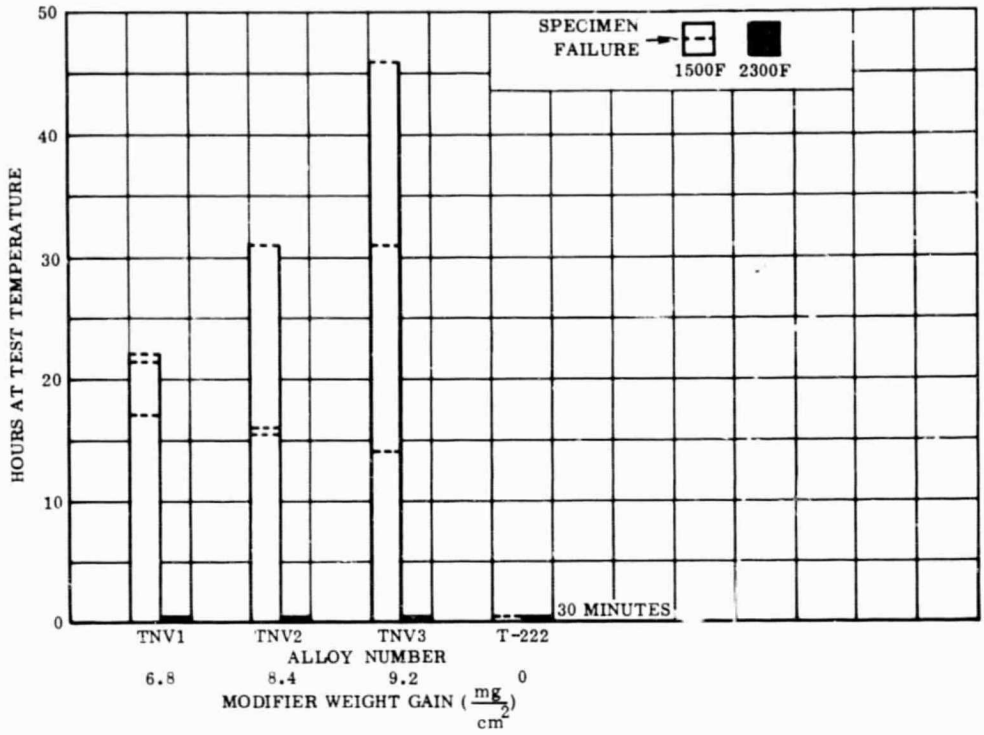


FIGURE 27. CYCLIC OXIDATION OF UNMODIFIED T222 AND T222 MODIFIED IN PACK ALLOYS TNV-1, -2, AND -3; Unsilicided Specimens Coated by Single-Modifier Cycle High-Pressure Pack Process

3.4.3 Apparatus and Procedures Used in General Oxidation Testing

In all but the last few of the pack cementation experiments, 0.5-inch by 0.75-inch specimens were used. The same procedures used in testing at 1500 and 2300 F (Par. 3.4.1) were used for testing these specimens at 1600 and 2400 F, with the exception that fused quartz boats were used at 2400 F.

In the slurry coating experiments and also in the pack cementation experiments numbered T_2-136, T_2-136A, and T_2-137, 1.0-inch by 2.0-inch specimens were coated and oxidized by either the extended 200-hour test procedure or the 600-hour test procedure. Although they were only 0.5-inch by 0.75 inch, the samples used in Experiments T_2-121-A2 and T_2-131 were subjected to the extended 200-hour test.

The 2400 F oxidation testing of 1.0-inch by 2.0 inch specimens was conducted in a Globar-heated, Model G-12248, Hevi-Duty furnace which was new at the outset of the program. The use of a new furnace was considered to be beneficial by providing an uncontaminated oxidation environment. The coated samples were placed on porous

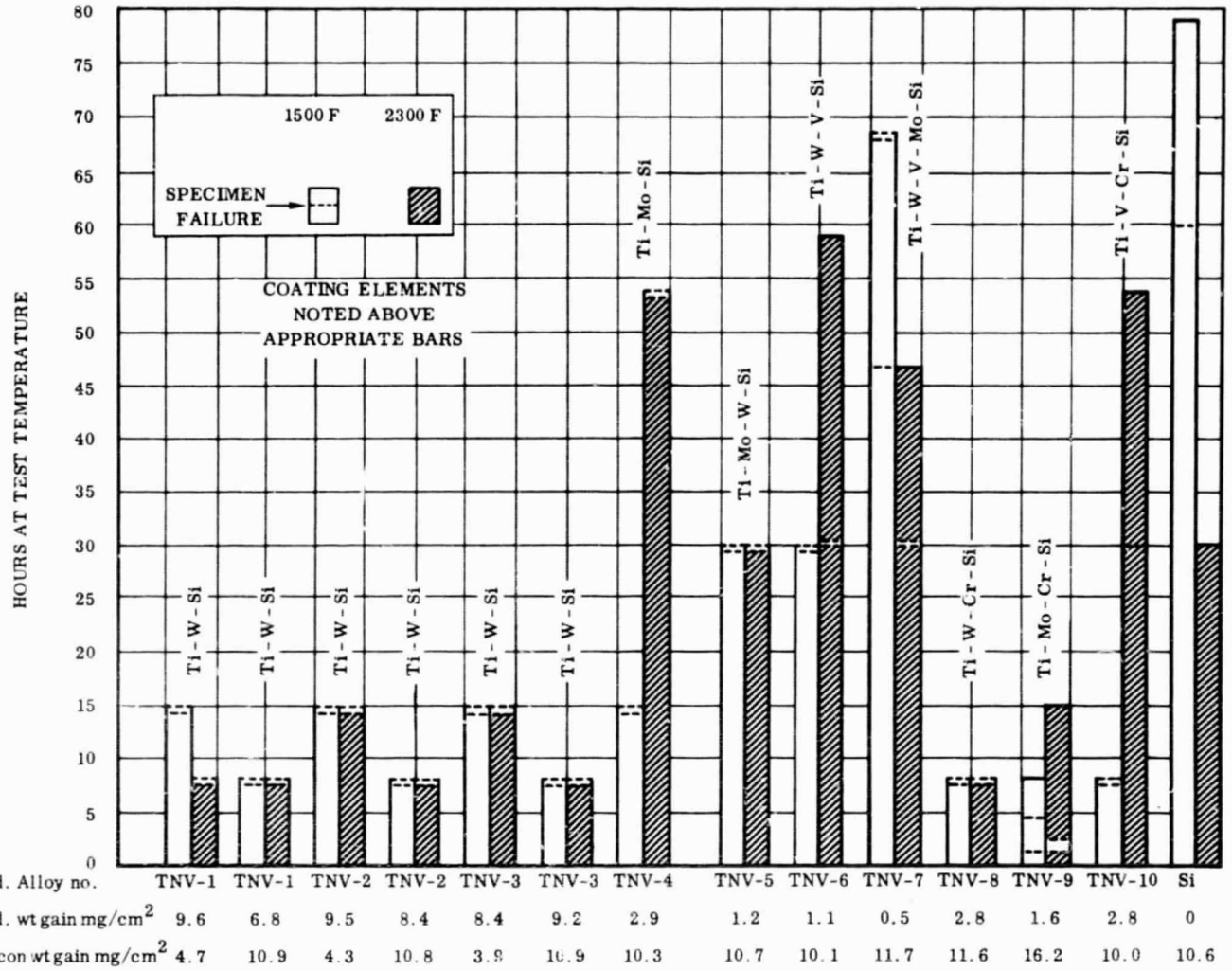


FIGURE 28. CYCLIC OXIDATION OF SILICIDED COATINGS APPLIED BY SINGLE-MODIFIER CYCLE HIGH-PRESSURE PACK PROCESS

Dyna-Quartz plaques resting on bubble-alumina bricks, JM-28 insulating firebricks (product of the Johns-Manville Corporation), or Carbofrax soaps (SiC product of Carborundum Co.), which were then placed in either the 2400 or 1600 F furnace. The Carbofrax soaps lasted longer than the JM-28 bricks, which lasted longer than bubble-alumina bricks. Dyna-Quartz is a fibrous semi-rigid product of the Johns-Manville Corporation and contains 99 percent SiO_2 with Al_2O_3, CaO, and MgO as the major impurities. Although some particles of the Dyna-Quartz tended to adhere to the surface of the specimens, there appeared to be no degradation of the samples as a result of the contract with the Dyna-Quartz. Fiberfrax XLF (45 percent SiO_2, 51 percent Al_2O_3, 3 percent ZrO_2 blanket produced by the Carborundum Co.) reacted with samples, and Micro-Quartz felt (98.5 percent SiO_2 product of the Johns-Manville Corp.) adhered to specimens much more extensively than did the Dyna-Quartz.

The Extended 200-Hour Test Procedure

This test corresponded to eight 15- to 17- hour cycles (overnight) and one 63- to 64-hour cycle (over weekend) in an initial test period, which was extended with a random mixture of 15- to 17-hour and 63- to 64-hour cycles until a total of 600 hours had been accumulated, at which point testing was usually discontinued. The cooled specimens were normally weighed after each of the first few cycles, and before and after each of the weekend cycles.

The 600-Hour Test Procedure

This test consisted of ten 2-hour cycles followed by twenty-nine 20-hour cycles. The specimens were each weighed at the start of the test and at the end of each cycle. One specimen was removed from testing after each 40 hours of oxidation. Twenty specimens of a single coating system were started in testing at each temperature to get a statistical appreciation of the reliability of the coatings.

3.4.4 Results of Extended 200-Hour Oxidation Tests

Coatings Based on Multiple-Modifier-Cycle Pack Cementation

The oxidation lives of samples modified by high-pressure pack and vacuum pack cementation techniques (multiple modifier cycles) are summarized in Tables XXII and XXIII, respectively. Also included in each of the Tables is the weight gain associated with modification in the pack alloys as well as the weight gain experienced during siliciding. The results of Experiment Number T_2-103 are presented in Table XXII even though a random mixture of 5- to 8-hour and 16- to 18-hour cycles were employed rather than the cycles of the extended 200-hour test procedure.

TABLE XXII

RESULTS OF OXIDATION OF SPECIMENS COATED BY MULTIPLE-MODIFIER CYCLE HIGH-PRESSURE PACK TECHNIQUES

Pack Alloy	Experiment Number	Modifier Accumulation (Net Gain: mg/cm^2)	Silicon Accumulation (Gain: mg/cm^2)	Oxidation Lives	
				Hours at 1600 F	Hours at 2400 F
TNV-3 (30Ti-70W)	T_2-103	25.1	21.4	78, 241	78, 83, 114
V followed by 80Cr-20Ti	T_2-121-A2	14.4 + 19.1	27.4	97, 97, 216	17, 17, 17

TABLE XXIII

RESULTS OF OXIDATION OF SPECIMENS COATED BY VACUUM PACK TECHNIQUES

Pack Alloy	Experiment Number	Modifier Accumulation (Net Gain: mg/cm^2)	Silicon Accumulation (Gain: mg/cm^2)	Oxidation Lives	
				Hours at 1600 F	Hours at 2400 F
TNV-3 (30Ti-70W)	T_2-131	26.8	18.9	131, 233, 267	97, 97, 131
V	T_2-137	22.9	12.6	-	-
V followed by TNV-3	T_2-136A	16 + 10	12.7	-	16, 16, 31
V followed by 80Cr-20Ti	T_2-136	16 + 9.6	18.0	-	63[a], 63, 80[b]

a. Single 63-hour cycle

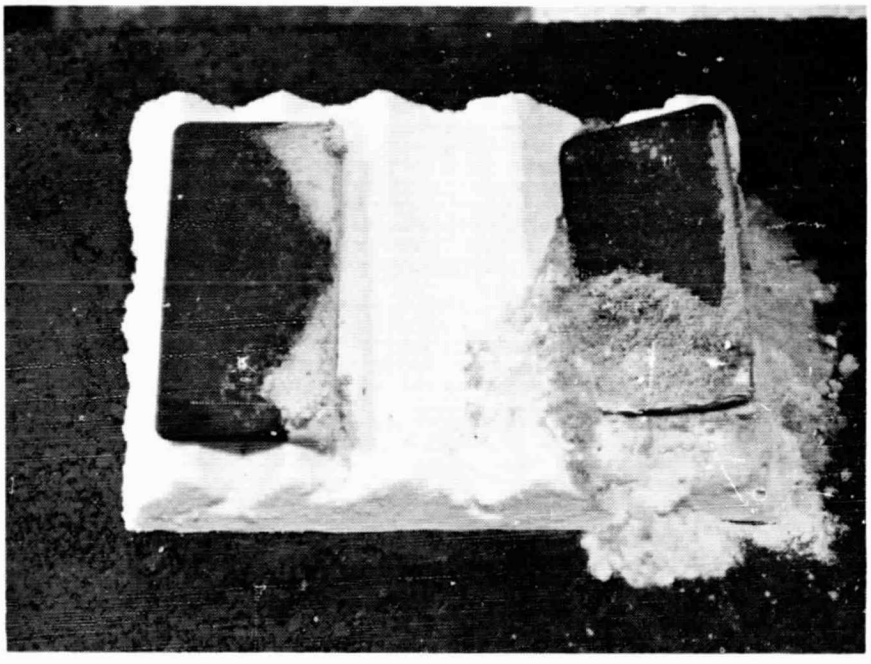
b. Single 63-hour cycle plus 17-hour cycle

Of the multiple-modifier-cycle pack-applied coatings, only the coating resulting from modification in the TNV-3 alloy gave encouraging results at both 1600 and 2400 F; there was no significant difference between the results obtained for samples modified in high-pressure packs and the results for those modified in vacuum packs. The maximum oxidation life at 1600 F obtained for specimens modified in the TNV-3 alloy corresponded to 267 hours while the maximum life at 2400 F corresponded to 131 hours. The only other pack-applied coating that yielded reasonable oxidation life resulted from modification of vanadized T222 alloy in 80Cr-20Ti packs (Experiment No. T_2-121-A2); subsequent to siliciding, the coated specimens showed a maximum life of 216 hours at 1600 F with essentially no life at 2400 F.

Slurry Coatings

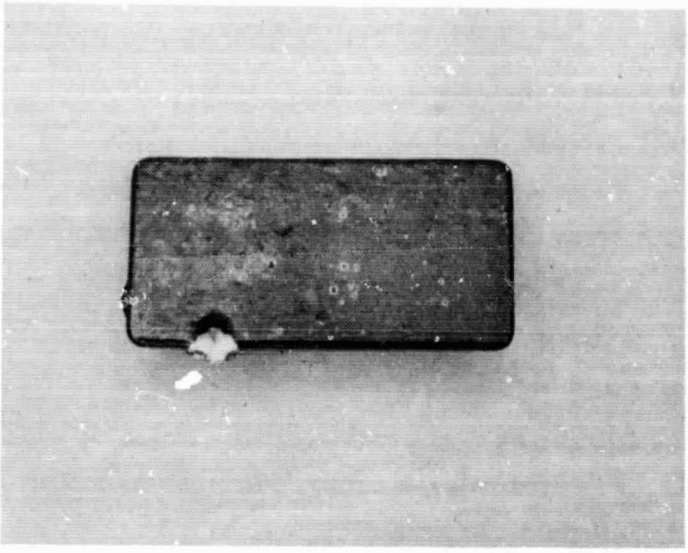
Although a few of the pack-modified specimens were oxidized in the unsilicided conditions, no slurry-coated specimens were oxidized without first being silicided. Figures 29 and 30 show typical failures of slurry-coated specimens oxidized at 1600 and 2400 F.

Failures at 1600 F usually resulted in the formation of a light, powdery oxide while failure at 2400 F resulted in the formation of a hard, more continuous oxide. Failure at either temperature normally occurred at the edge of the slurry-coated specimens, but in something less than five percent of the cases, failure took place on the flat surfaces. The later failures occurred at 2400 F, primarily with the molybdenum-rich and tungsten-rich TNV-12 and TNV-13 alloys, and the TNV-11 alloy with 0.25 percent nickel.

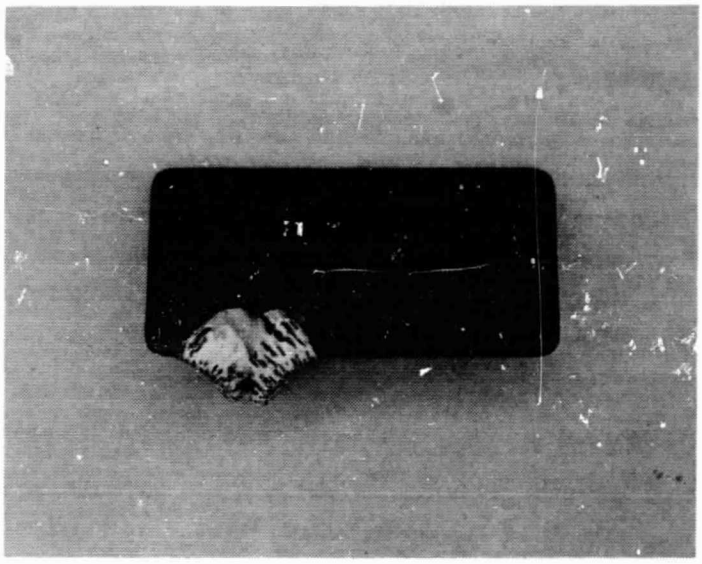


Experiment Number: T_2-170
Coating: TNV-13 (5Ti-95W)
Time: 16 Hours

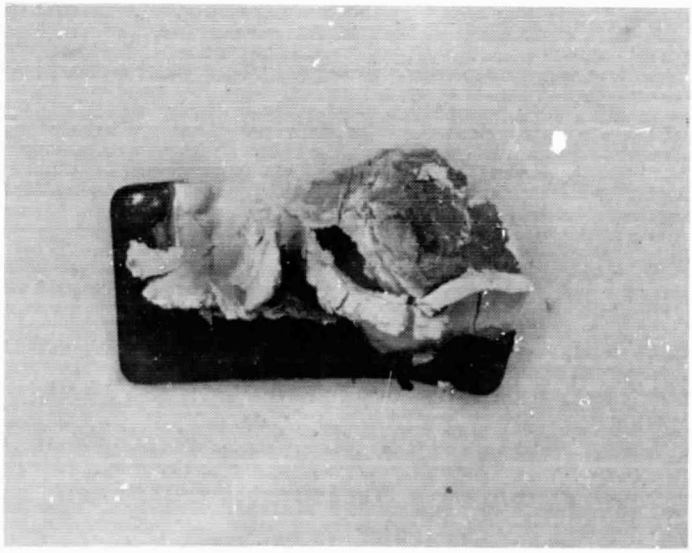
FIGURE 29. TYPICAL FAILURES OF SLURRY COATED SPECIMENS OXIDIZED AT 1600 F



Experiment Number: T_2-190
Coating: TNV-12 (4.7Ti-95.3Mo)
Time: 561 Hours



Experimental Number: T_2-188A
Coating: TNV-12 (4.7Ti-95.3Mo)
Time: 463 Hours



Experiment Number: T_2-200A
Coating: TNV-17 (5Ti-5V-90W)
Time: 16 Hours

FIGURE 30. TYPICAL FAILURES OF SLURRY COATED SPECIMENS OXIDIZED AT 2400 F

Table XXIV summarizes the results of oxidation of slurry coatings for which polyisobutylene and/or polymethylmethacrylate was used as a binder in the spraying vehicle. Table XXV is a tabulation of later results obtained when ethylcellulose was used as the binder in the spraying vehicle. In general, better oxidation lives (as well as better slurry suspension characteristics) were obtained with the ethylcellulose containing venicle, with the possible exception of the TNV-12 coating. The oxidation lives are shown graphically for the better coatings in Figure 31, where an open bar represents oxidation at 1600 F and a shaded bar represents oxidation at 2400 F. Vertical lines on the bars correspond to the times of specimen failures, and a vertical line with an arrow through it indicates the specimen was removed from testing prior to failure, usually for the purpose of metallographic examination.

Examination of the results revealed that the TNV-7 and TNV-12 coatings were the only two coatings to exceed the 600-hour goal at both temperatures. However, no TNV-12 coated samples from a single experiment were good at both temperatures and the experiment that yielded four specimens exceeding the 600-hour goal at 1600 F could not be reproduced.

The TNV-7 coating was of particular interest; in addition to exceeding the 600-hour goal, no specimens failed in less than 200 hours at either test temperature. In the second coating experiment involving the TNV-7 alloy (Experiment T_2-187), none of the specimens failed in less than 600 hours of testing at either temperature, and one specimen was observed to last 1080 hours when failure occurred in the cycle after the slow cooling of the oxidation furnace as a result of an electrical power outage.

The TNV-6 coating was rather interesting in that the 600-hour goal was exceeded at 1600 F; whereas, the oxidation resistance at 2400 F was less satisfactory. None of the TNV-6 coated specimens were observed to fail with less than 95 hours of oxidation. Perhaps, with further effort, the TNV-6 coating could be modified and developed to produce an oxidation-resistant coating.

As is noted in Table XXV, failure of all the specimens provided with the silicided TNV-14 through TNV-17 coatings failed in oxidation testing at 2400 F during the slow cooling of the oxidation furnace following an electrical power outage. Failure under these conditions tended to obscure a comparison of the oxidation resistance of this group of coatings with the other coatings investigated. However, the oxidation resistance of each of these coatings at 1600 F was very poor with the possible exception of the TNV-16 coating (5Ti-5V-45W-45Mo), which allowed one specimen to survive 636 hours.

TABLE XXIV

EXTENDED 200-HOUR TEST RESULTS FOR INITIAL COATINGS BASED ON PACK SILICIDING OF SINTERED SLURRY COATINGS

(Polyisobutylene and/or Polymethylmethacrylate Binder Used in Spraying Vehicle)

Coating	Experiment Number	Modification Gain (mg/cm^2)	Siliciding Gain (mg/cm^2)	Oxidation Lives	
				Hours at 1600 F	Hours at 2400 F
TNV-2 (60Ti-40W)	T_2-150	51	14	3 at 16	2 at 16, 31
TNV-3 (30Ti-70W)	T_2-143	65	24		>611, >627
	T_2-151	77	16	3 at 16	3 at 16
TNV-4 (60Ti-40Mo)	T_2-139	47	13	--	17
	T_2-143	37	21	--	3 at 17, 31
	T_2-152	55	16	3 at 16	3 at 16
TNV-9 (30Ti-35Mo-35Cr)	T_2-145	34	18	3 at 15	15, 142, >610
TNV-11 (2.5Ti-97.5W)	T_2-142	120	48	--	2 at 15, 393[a]
	T_2-144	123	42	4 at 16	3 at 16, 329
TNV-12 (4.7Ti-95.3Mo)	T_2-142	71	40	--	16, >612
	T_2-144	68	29	4 ea >659	2 at 16, 2 at 31
	T_2-146	68	34	3 at 16	2 at 188, 376
	T_2-147	68	31	32, 93, >93[b]	2 at 78, 109
	T_2-148	72	29	3 at 16	31, 126, 141
	T_2-153	67	36	3 at 16, 3 at 31	2 at 31, 142, 298, 474, 764
	T_2-154	61	34	3 at 16, 307	146, 474, 647, 947

a. Al_2O_3 brick broke; sample fell to furnace hearth.

b. Sample to metallography before failure.

TABLE XXV

EXTENDED 200-HOUR TEST RESULTS FOR COATINGS BASED ON PACK SILICIDING OF SINTERED SLURRY COATINGS

(Ethyl Cellulose Binder in Vehicle)

Coating	Experiment Number	Sintering Conditions			Siliciding Conditions			Oxidation Lives	
		Temperature (F)	Time (hr)	Weight Gain (mg/cm^2)	Temperature (F)	Time (hr)	Weight Gain (mg/cm^2)	Hours at 1600 F	Hours at 2400 F
TNV-1 (90Ti-10W)	T_2-149	2435	15	59	2000	7	14	As-silicided Coating Spalled	
TNV-2 (60Ti-40W)	T_2-158			28, 48[a]	2150	7.5	28, 21	3 at 16, 31	62, 126, 173, 332
TNV-3 (30Ti-70W)	T_2-159			54, 79[a]		7.5	24, 23	16, 2 at 31, 111	126, 312, 392, >392[b]
TNV-4 (60Ti-40Mo)	T_2-172	2760	--	51		7	24	3 at 16	3 at 16
TNV-5 (30Ti-35W-35Mo)	T_2-173		--	71			37	2 at 16, 31	2 at 31, >206[b]
TNV-6 (30Ti-40W-30V)	T_2-174		--	43			31	>206[b], >628[b], >653[b]	2 at 95, >206[b]
TNV-7 (15Ti-35W-15V-35Mo)	T_2-175		--	75	--		43	206, >206[b], 316	206, 206[b], 821
	T_2-187		--	55	--	--	40	2 at >630[b]	>622[b], 1,080[d]
TNV-8 (30Ti-35W-35Cr)	T_2-179	2610	0.5	50	--	--	29	2 at 16	2 at 95
TNV-9 (30Ti-35Mo-35Cr)	T_2-180			43	--	--	31	16	95, >252[b]
TNV-10 (30Ti-30V-40Cr)	T_2-181			42	--	--	23	16	16
TNV-11 (2.5Ti-97.5W)	T_2-155	2760	15	119	--	--	43	3 at 16	363, 520, 561
TNV-12 (4.7Ti-95.3Mo)	T_2-156			68	--	--	34	3 at 16	394, 2 at 504
	T_2-195			58	--	--	31	2 at 16	>332[b], 473
TNV-13 (5Ti-95W)	T_2-170	--	--	135	--	--	35	2 at 16, 47	2 at 126, >237[b], >615[b]
	T_2-193	--	--	106	--	--	37	3 at 16	126, 2 at 338
	T_2-196	--	--	84	--	--	33	2 at 16	>332[b], 544
TNV-14 (2.5Ti-97.5Mo)	T_2-197	--	--	66	--	--	35	2 at 16	2 at >338[c]
TNV-15 (10Ti-90Mo)	T_2-198	--	--	57	--	--	38	2 at 16	2 at >338[c]
TNV-16 (5Ti-45W-5V-45Mo)	T_2-199	--	--	72	--	--	40	2 at 16, >636[b]	3 at >338[c]
TNV-17 (5Ti-90W-5V)	T_2-200	--	--	98	--	--	37	3 at 16	2 at 16, >338[c]

a. In experiments T_2-158 and T_2-159, two operators sprayed part of the samples; there was no correlation between operator and oxidation life.

b. Sample to metallography before failure.

c. Sample failed during furnace power outage.

d. Sample failed in first cycle after power outage.

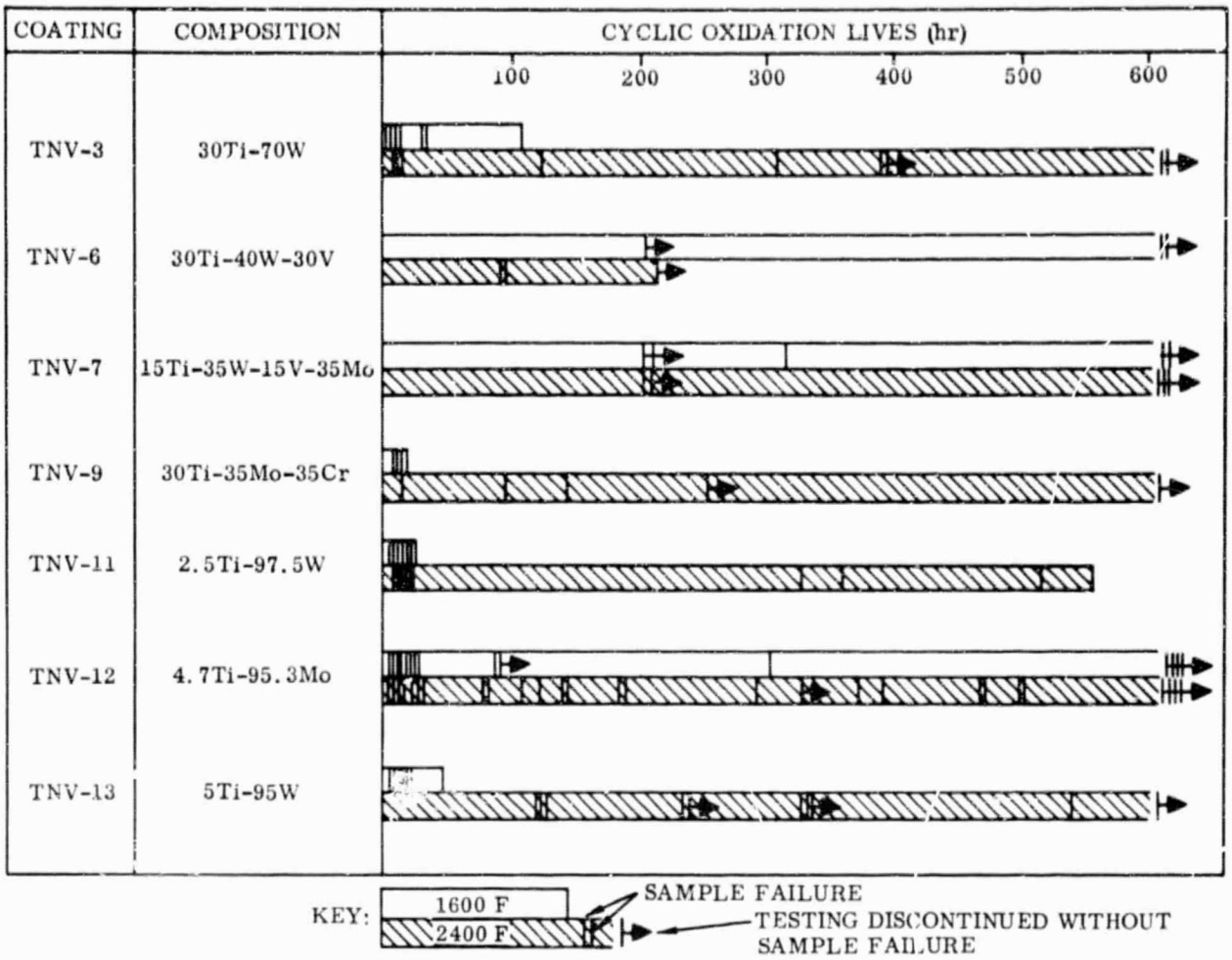


FIGURE 31. EXTENDED 200-HOUR TEST RESULTS OF MORE OXIDATION RESISTANT SLURRY COATINGS

Weight-gain data for oxidation of the more oxidation-resistant coatings at 1600 and 2400 F are plotted in Figures 32 and 33. Oxidation at 2400 F yielded curves having a general parabolic shape with occasional steps suggesting crack formation and healing. Usually the curves for different specimens of a given composition were rather closely grouped; however, the TNV-9 and TNV-13 coatings were observed to be notable exceptions to this rule. Although adherence of small quantities of the Dyan-Quartz support medium to the oxidation samples tended to diminish somewhat the usefulness of the weight-change data, some observations were noted. There appeared to be no correlation between oxidation resistance and weight gain. The TNV-7 coated specimen which survived 601 hours was observed to have a much larger weight gain than the TNV-12 coated specimens that either survived 612 hours of oxidation or were observed to fail early in the oxidation tests. The weight-gain curves for the TNV-12 coated

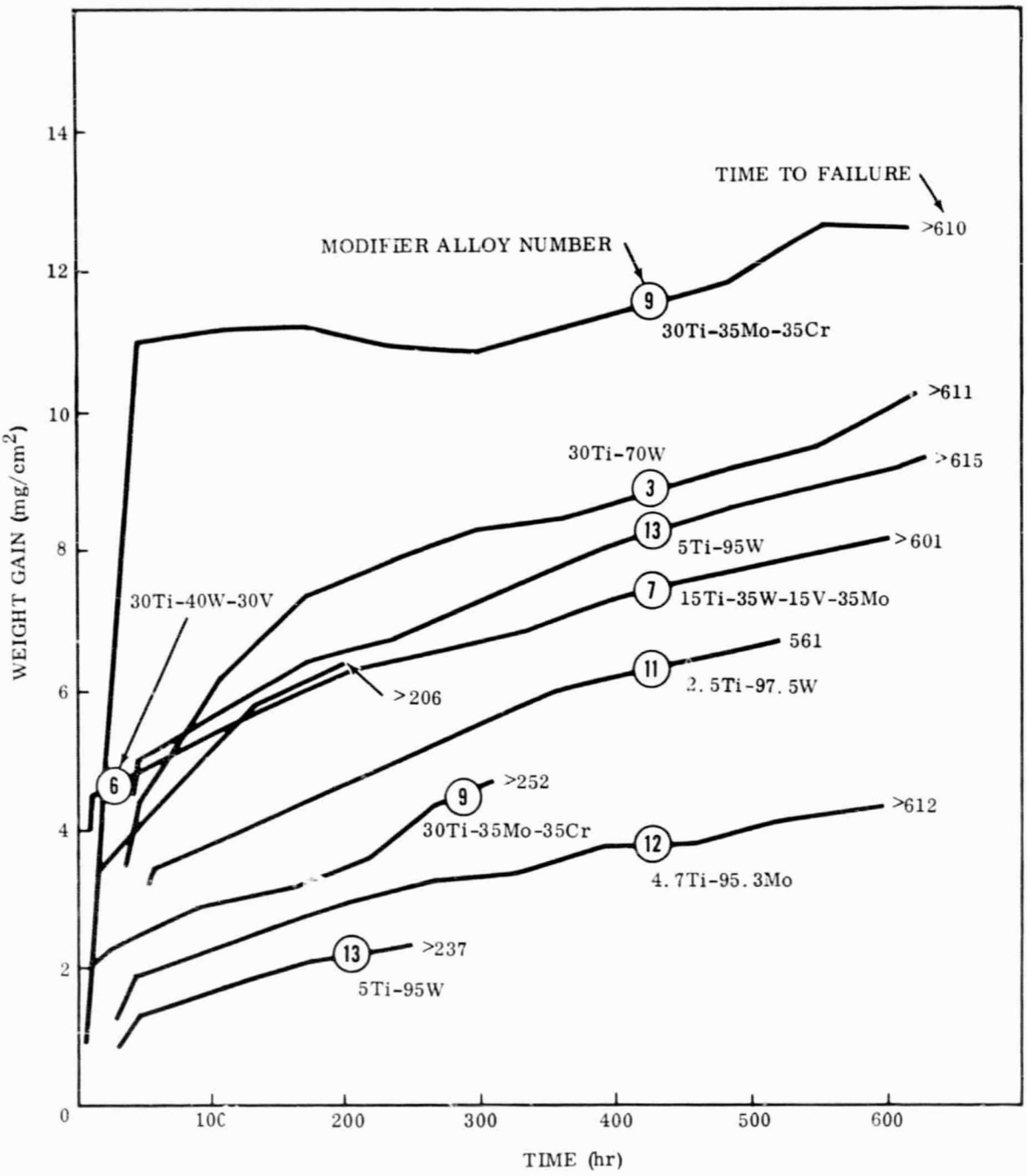


FIGURE 32. WEIGHT GAIN DATA FOR EXTENDED 200-HOUR OXIDATION TESTING OF SLURRY COATED SAMPLES AT 2400 F

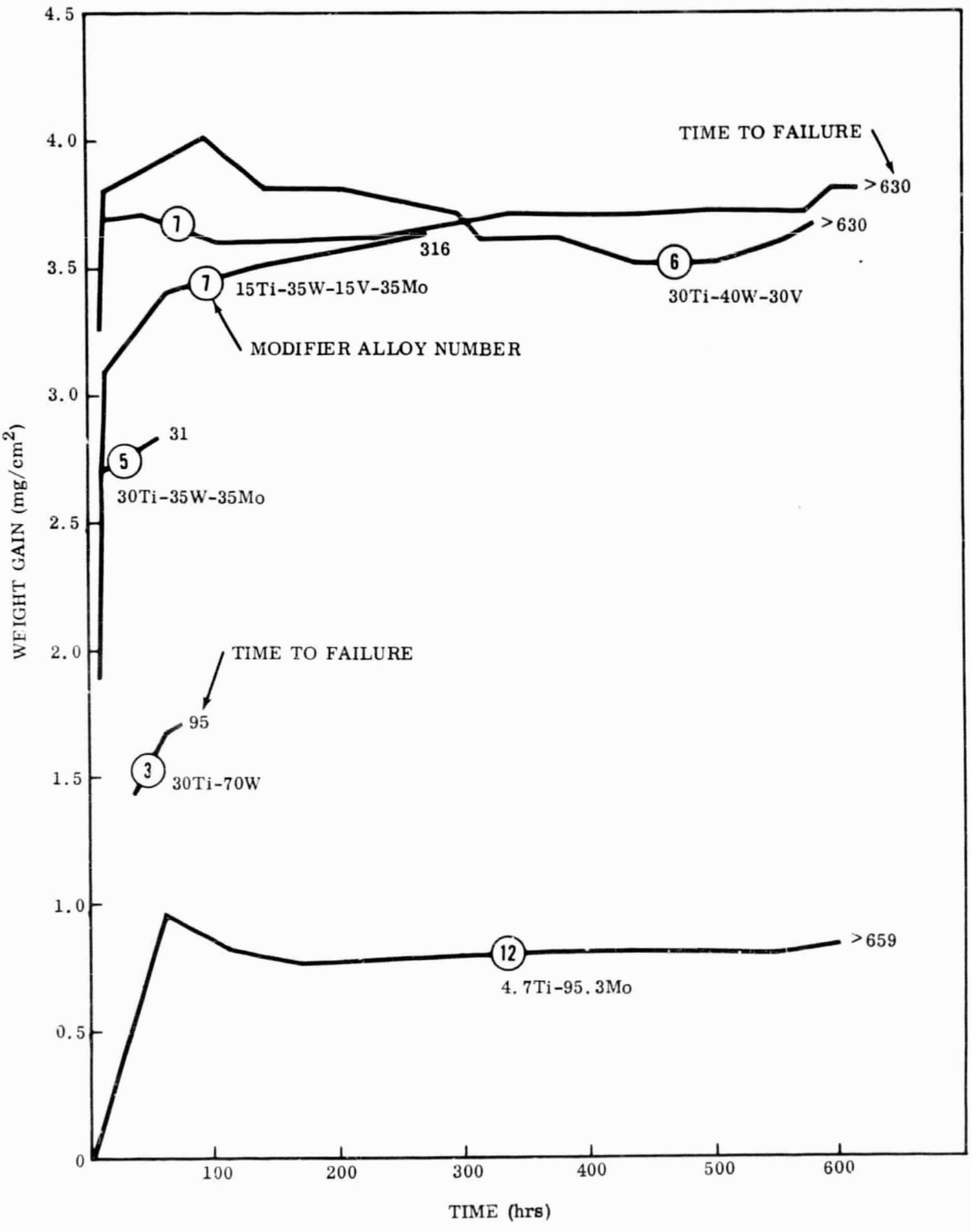


FIGURE 33. WEIGHT GAIN DATA FOR EXTENDED 200-HOUR OXIDATION TESTING OF SLURRY COATED SAMPLES AT 1600 F

specimens which failed early in the test were observed to be virtually coincidental with the weigh-gain curve for the specimen which survived 612 hours.

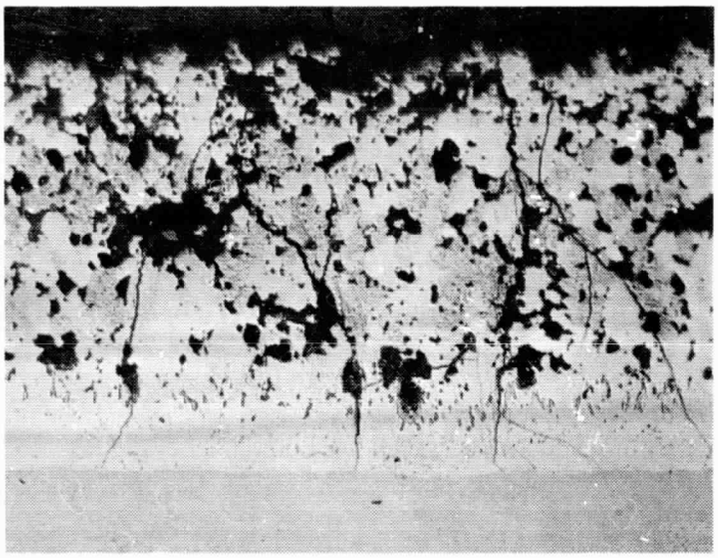
In many cases, oxidation at 1600 F yielded a weight-gain curve showing a rapid initial rise followed by a gradual, small decline preceding a slow, gradual rise. The decline was attributed to volatilization of either MoO_3 or WO_3 during an initial period before the oxide layer had sealed the surface. Similar to oxidation at 2400 F, oxidation at 1600 F was observed to give rise to greater weight gains when higher percentages of titanium, vanadium, or chromium were present.

The microstructure of the TNV-7 and TNV-12 coatings after extended oxidation are shown in Figures 34 and 35. Figure 3 of Appendix D corresponds to the microstructure of TNV-3 and TNV-9 after oxidation at 2400 F.

Much of the character of the as-silicided TNV-7 coating was retained during 600 hours of oxidation at either 1600 or 2400 F. During siliciding, the silicon diffused completely through the coating and into the substrate; during oxidation testing, the silicon continued to diffuse into the substrate, at a greater rate at 2400 F than at 1600 F. Cracks travel clear through the coating to the substrate for oxidation at either 1600 or 2400 F (the photomicrograph and hardness tranverse of the TNV-7 coating, oxidized for 622 hours at 2400 F, was taken in a region between cracks in the coating). A more thorough analysis of the TNV-7, -12, and -13 coatings after oxidation is presented in Paragraphs 3.4.6 following presentation of the 600-hour test results.

The microstructure (Fig. 35) of the TNV-12 coating which survived 612 hours of oxidation at 2400 F is of interest, particularly when compared to the as-silicided microstructure shown in Figure 21. The long exposure at 2400 F resulted in the formation of a light-colored zone of high hardness (2735 KHN) beneath the porous coating (the as-silicided coating has no light-colored zone beneath the porous coating). This light-colored, hard sublayer was shown (by microbe analysis) to result from silicon diffusion and does not have the ability to stop the coating cracks from penetrating to the substrate.

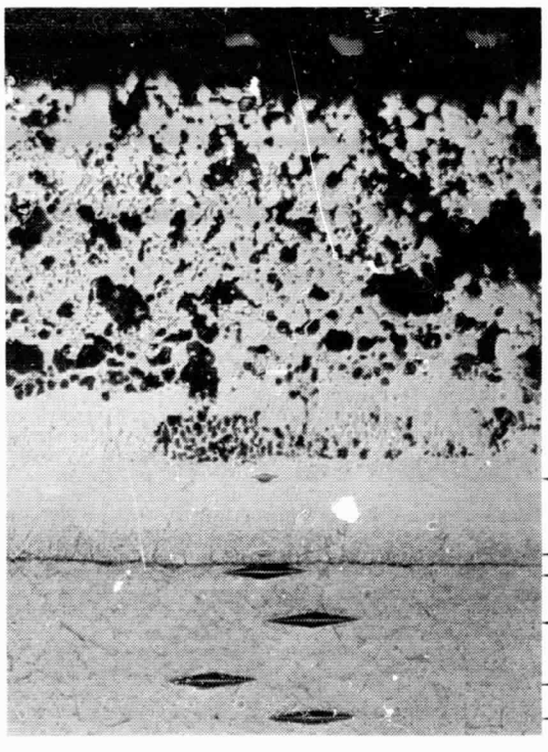
The microstructure (Fig. 35) of the TNV-12 coating oxidized for 659 hours at 1600 F retained much of the character of the as-silicided microstructure. Although part of the light-colored zone within the porous layer was consumed, no hard sublayer developed at 1600 F. The remaining portion of the light-colored zone in the porous layer appears to have retained its crack-stopping ability as suggested by the photomicrograph.



Oxidation Time: 630 Hours

Oxidation Temperature: 1600 F

KHN
(50-gram load)



Experiment Number: T_2-187

Substrate: T222

Coating: TNV-7 (15Ti-35W-15V-35Mo)

Sintered: 15 Hours at 2760 F (55 mg/cm^2 gain)

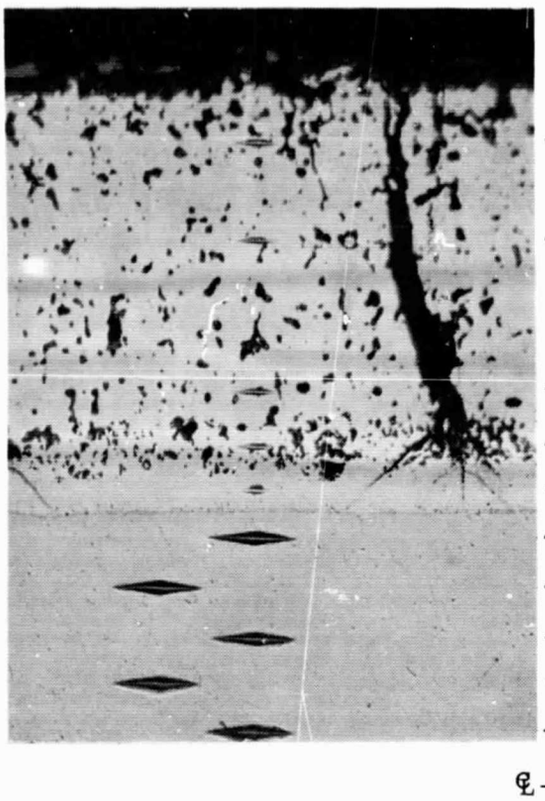
Silicided: 7 Hours at 2150 F (40 mg/cm^2 gain)

Magnification: 40X

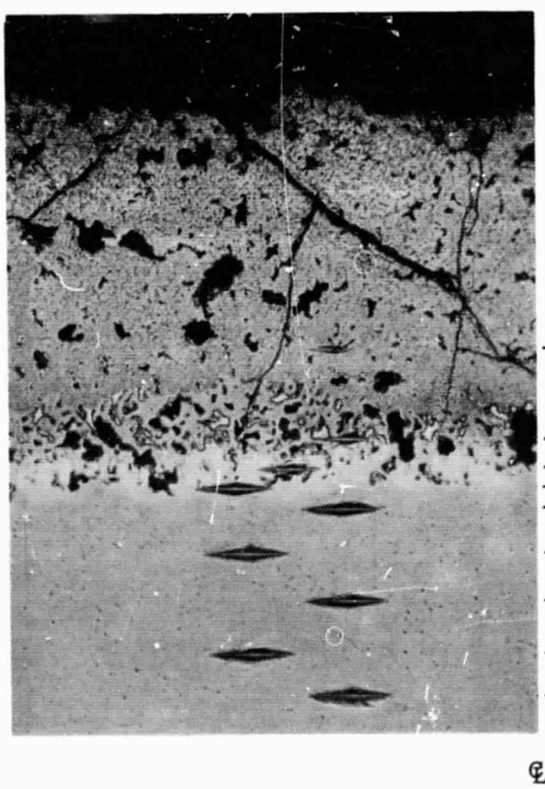
Oxidation Time: 622 Hours

Oxidation Temperature: 2400 F

FIGURE 34. TNV-7 COATING OXIDIZED IN EXTENDED 200-HOUR TEST



Experiment Number: T_2-142
Substrate: T222
Coating: TNV-12
Oxidation Time: 612 hours
Oxidation Temperature: 2400 F
Etchant: 60% Lactic Acid (85% solution)
20% Concentrated HF
20% Concentrated HNO_3
Magnification: 250X



Experiment Number: T_2-144
Substrate: T222
Coating: TNV-12
Oxidation Time: 659 Hours
Oxidation Temperature: 1600 F
Etchant: 60% Lactic Acid (85% solution)
20% Concentrated HF
20% Concentrated HNO_3
Magnification: 250X

FIGURE 35 TNV-12 COATING OXIDIZED IN EXTENDED 200-HOUR TEST

Oxidation of TNV-12 Slurry Coatings of Varied Thickness

Oxidation of the silicided specimens initially provided with 0.003-, 0.006-, and 0.010-inch thick as-sintered modifier layers resulted in failure of all specimens in the first 16-hour cycle at 1600 F. However, the two specimens that were initially provided with a 0.006-inch thick modifier layer failed at 126 hours at 2400 F, the specimens provided with a 0.010-inch thick modifier layer failed at 237 and 252 hours at 2400 F, and the specimens provided with a 0.003-inch thick modifier layer showed one failure at 409 hours and a second specimen having no failure in 607 hours of testing at 2400 F.

These results suggested that a relatively thin slurry coating can be very effective, and that complete penetration of the TNV-12 modifier layer by the silicon is not det.rimental.

Oxidation of Slurry Coatings Applied to Substrates Modified by Pack Cementation

The oxidation resistance of the as-silicided TNV-12 slurry coating applied to T222 substrates previously modified in a TNV-3 pack appeared to be slightly superior to that of the same coating applied to unmodified substrates. Pack modification of the substrate resulted in oxidation lives of 16, 31, and 252 hours at 1600 F rather than typical lives in the range of 16 to 47 hours for the TNV-12 coating involving the use of ethylcellulose as the binder in the spraying vehicle. One specimen pack modified before coating was removed from 2400 F oxidation testing at 332 hours without failure, while a second specimen failed at 568 hours during the slow cooling following electrical power outage; one specimen survived the slow cooling to room temperature, but was observed to fail during the subsequent oxidation cycle.

Oxidation of Coatings Based on Sintering of Slurries of Silicon and Modifier Metal Powder Mixtures

The specimens provided with a 0.005-inch thick TNV-10 silicon coating (TNV-10 plus 80 at% silicon) were oxidized at 1600 and 2400 F. All three of the specimens tested at 2400 F failed before 80 hours had passed, but two specimens did not fail in 605 hours of oxidation at 1600 F (one specimen was removed from testing at 206 hours without failure).

Oxidation Testing of Glass-Impregnated Slurry Coatings

Table XXVI contains the oxidation lives of specimens provided with the TNV-7, TNV-12, TNV-13, and TNV-14 through TNV-17 coatings modified by glass-impregnation. Lives of unimpregnated control specimens prepared concurrently are included in the table. A barium borosilicate glass (Solar Frit No. S-5210) was used in all of these experiments with the exception of Experiments T_2-178 and T_2-189 where the TNV-13 coating was impregnated with either a pyrex frit or a modified barium borosilicate glass frit (XG-201 Frit manufactured by the Ferro Corporation), both of which were observed to be less effective than the S-5210 Frit. The absence of failures in the unimpregnated control specimens provided with the TNV-7 coating precluded a determination of any improvement in the oxidation resistance of the TNV-7 coating as a result of glass impregnation. The results suggested that the relatively poor oxidation resistance of the TNV-12 coating at 1600 F was not improved by glass impregnation. However, the very modest 1600 F oxidation resistance of the TNV-13 coating was dramatically improved from a typical value of 16 hours to either 111 or 347 hours. Although TNV-14 and TNV-17 coatings did not appear to benefit from glass impregnation, the TNV-15 coating did appear to benefit.

TABLE XXVI

EFFECTS OF GLASS IMPREGNATION ON OXIDATION LIVES OF SLURRY COATING

Coating	Experiment Number	Oxidation Lives			
		As-Silicided		Impregnated[a]	
		Hours at 1600 F	Hours at 2400 F	Hours at 1600 F	Hours at 2400 F
TNV-7 (15Ti-35W-15V-35Mo)	T_2-187	2 at >630[b]	>622, >1089[d]	>213[b], 2 at >637	>213[b], 2 at >606
TNV-12 (4.7Ti-95.3Mo)	T_2-195	2 at 16	>332[b], 473	3 at 16	316, >332[b], >568[c]
TNV-13 (5Ti-95W)	T_2-177	2 at 16, 47	---	>237[b], 347, 361	---
	T_2-196	2 at 16	>332[b], >568[c]	3 at 111	>332[b], 362, >568[c]
TNV-13 (Pyrex Frit)	T_2-178	2 at 16, 47	---	127, 2 at 143	---
TNV-13 (XG-201 Frit)	T_2-189	2 at 16	---	2 at 95	---
TNV-14 (2.5Ti-97.5Mo)	T_2-197	2 at 16	2 at >338[c]	2 at 16, 111	283, 2 at >338[c]
TNV-15 (10Ti-90Mo)	T_2-198	2 at 16	2 at >338[c]	2 at 126, 267	2 at >338[c], >354[d]
TNV-16 (5Ti-5V-45W-45Mo)	T_2-199	2 at 16, >636[b]	3 at >338[c]	16, 111, 173	322, 2 at >354[d]
TNV-17 (5Ti-5V-90W)	T_2-200	3 at 16	2 at >338[c]	2 at 16	2 at 16, >338[c]

a. Borium borosilicate glass (Solar Frit No. S-5210) used except as noted.
b. Sample to metallography before failure.
c. Sample failed during furnace power outage.
d. Sample failed in first cycle after power outage.

A preliminary analysis of weight gain data for the glass-impregnated specimens compared to the unimpregnated specimens from the same modification and siliciding experiment suggested that impregnation reduced the rate of silicon consumption (the weight gain during oxidation testing was noticeably less for the impregnated specimens). However, when the weight gain observed for the air firing of the impregnated coatings preparatory to oxidation testing (1.2 to 1.4 mg/cm^2) was added to the weight gains observed for oxidation testing, it was seen that the silicon consumption (measured by weight gain) was virtually identical for the impregnated and unimpregnated specimens.

Oxidation Testing of Coatings Involving Activated Sintering

Oxidation testing at 1600 F and 2400 F was performed on the silicided (W-2.5Ti-0.25Ni) coating obtained by low-temperature sintering of the nickel-coated tungsten powder of reduced particle size. All of the three specimens tested at 1600 F failed at 111 hours; however, the first failure at 2400 F occurred at 412 hours, and two specimens with an accumulation of 602 hours showed no signs of failure. Comparison of the results of oxidation of the TNV-11 coating with the silicided (W-2.5Ti-0.25Ni) coating, which is the TNV-11 coating modified by the addition of 0.25 percent nickel, was interesting. All of the TNV-11 coated samples tested at 1600 F failed in the first 16-hour cycle. Oxidation of the TNV-11 coated specimens produced in Experiment T_2-155 resulted in failures at 363, 520, and 561 hours at 2400 F. Thus, it appears that the use of nickel-activated sintering (along with tungsten powder of reduced particle size) provided an improvement in the oxidation resistance of the tungsten-rich TNV-11 coating while allowing the use of greatly reduced sintering time and temperature.

3.4.5 Results of 600-Hour Oxidation Tests

The 600-hour test was intended to provide a statistical feeling for the reliability of the two best coatings, as determined by extended 200-hour oxidation testing. The reproducible outstanding performance of the TNV-7 coating readily suggested that it should be one of the two coatings selected for the 600-hour test. Because the oxidation lives exceeding 600 hours for the TNV-12 coated specimens oxidized at 1600 F were not reproducible, and because the 1600 F oxidation resistance of the TNV-12 coating did not respond to glass impregnation as did the TNV-13 coating, the TNV-13 coating, in the glass-impregnated condition, was selected as the second coating for the 600-hour test. In actuality both the TNV-7 and TNV-13 coatings were glass impregnated;

the TNV-7 coating was impregnated on the basis that glass impregnation had no adverse effect on the oxidation resistance and was originally thought (erroneously) to reduce silicon consumption.

Twenty specimens of each coating were started into testing at each temperature and were removed (without failure) from testing at the rate of one every forty hours.

None of the TNV-7 coated specimens failed at any time during the 600-hour test at either 1600 or 2400 F.

The lives of the TNV-13 coated specimens oxidized at 1600 F were in the range of 40 to 160 hours while the lives at 2400 F were in the range of 380 to 440 hours. The actual distribution of failures at each temperature is shown in Table XXVII. The weight gains experienced by each of the two coatings during oxidation at each of the two temperatures are shown in Figure 36.

A Weibull plot of the oxidation lives of the TNV-13 coated specimens at 1600 and 2400 F is shown in Figure 37. The plot was prepared following the procedure of Wurst and Cherry (Ref. 12). Examination of the plot suggested that the distribution function for failure of the specimens is not particularly well characterized by the Weibull distribution function. The slopes of the median rank curves for oxidation at 1600 and 2400 F were observed to be approximately 2.7 and 10.5, respectively.

TABLE XXVII

RESULTS OF 600-HOUR OXIDATION TEST OF TNV-13 COATED SPECIMENS*

Oxidation Lives at 1600 F (hr)	Oxidation Lives at 2400 F (hr)
3 at 40	3 at 380
1 at 80	4 at 400
5 at 100	1 at 440
6 at 120	
2 at 160	

* Impregnated with Solar Frit No. S-5210 Barium Borosilicate Glass

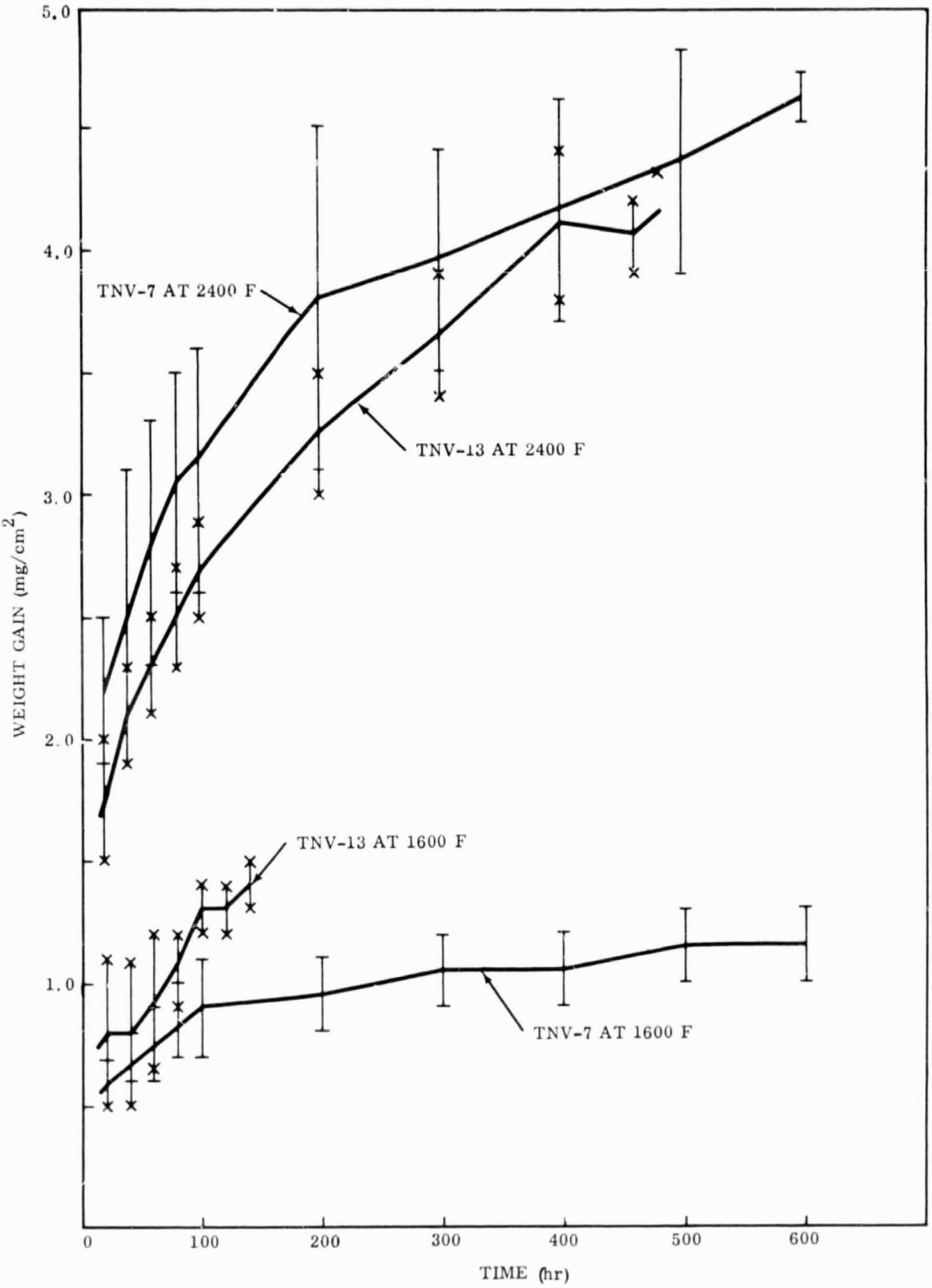


FIGURE 36. WEIGHT GAIN DATA FOR 600-HOUR OXIDATION TESTING OF TNV-7 AND TNV-13 GLASS-IMPREGNATED SLURRY COATINGS

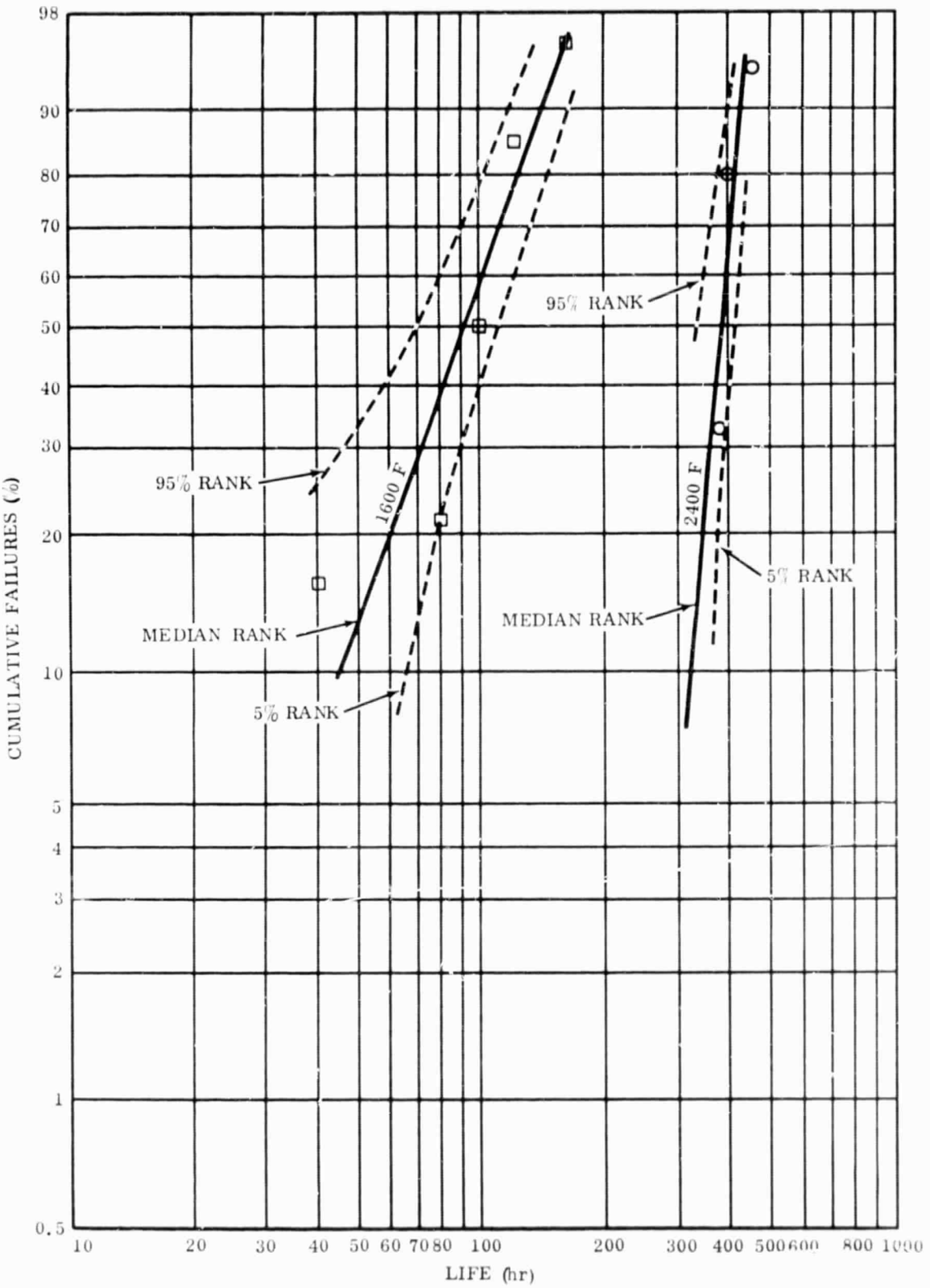


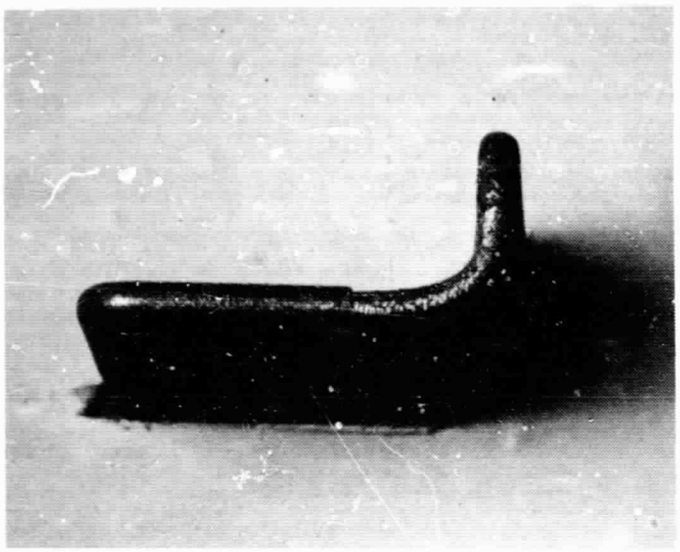
FIGURE 37. WEIBULL PLOT OF 600-HOUR TEST RESULTS FOR TNV-13

3.4.6 Analysis of Specimens

Conventional metallography and Knoop hardness determinations were supplemented by vacuum fusion, X-ray diffraction, electron-microscopic, and electron-microprobe analyses. Because the glass-impregnated TNV-7 and TNV-13 coatings appeared to be the two most promising coatings and because they were selected for the 600-hour oxidation test, these two coatings were subjected to a more extensive analysis than the other coatings. Because of the initial promising results obtained with the unimpregnated TNV-12 coating, it too was analysed, but less extensively.

Samples for vacuum fusion analysis were obtained by blasting and etching the coatings from selected specimens. Unfortunately, the acid etching of the substrates for removal of any visibly detectable coating resulted in removal of substantial quantities of the substrate. Because oxygen and nitrogen diffuse into the substrate from the surface, the highest concentration is closest to the outer surface; removal of the outer layer in an uncontrolled fashion during the acid etching may have rendered the vacuum fusion analytical results almost meaningless. In the case of the TNV-7 coated specimens the oxygen analysis for the as-coated specimen was over twice as great as that for the specimens oxidized for 600 hours at either 1600 or 2400 F. The highest measured concentrations of oxygen and nitrogen were observed in the case of the TNV-12 specimen oxidized 612 hours at 2400 F. The observed oxygen analysis of 850 $\pm$ 45 ppm, and the nitrogen analysis of 180 $\pm$ 75 ppm correspond to an average over the substrate remaining after acid etching. Although of unknown magnitude, the oxygen and nitrogen contamination did not cause a loss of room-temperature ductility of the substrate. Samples provided with either the TNV-7 or TNV-12 coating showed excellent ductility during a simple bend test performed after oxidation in excess of 600 hours at 2400 F. The sample (Fig. 38) was mounted in a bench vise and bent sharply through an angle of 90 degrees without fracturing the substrate. Good room-temperature impact resistance was displayed by each of the two coatings in that neither coating spalled or chipped in the area struck by the hammer when bending the specimens.

A Norelco X-ray diffractometer was used in obtaining X-ray diffraction patterns of the in situ coatings by placing coated specimens directly in the clamp that is normally used to retain the sample holder used with powder specimens.



TNV-12 coated specimen oxidized 612 hours at 2400 F before bending at room temperature

FIGURE 38.

BEND TEST SPECIMEN TYPICAL OF TNV-7 AND TNV-12 COATED SAMPLES; Oxidized in Excess of 600 Hours at 2400 F

A Model 100C Norelco Phillips electron-microscope was used in examing replicas taken from the undisturbed flat surfaces of coated specimens. Attempts at obtaining usable replicas from polished sections proved to be fruitless.

A Model AMR/3 Norelco Phillips electro-microprobe analyzer was employed in making the electron-microprobe studies reported in the paragraphs that follow.

Analysis of TNV-7 Coated Specimens

The microstructure and hardness profile of specimens oxidized for various periods of time at either 1600 or 2400 F are similar to those for the samples in the as-silicided condition or after oxidation for 622 hours at 2400 F (Fig. 20 and 34). No difference between the microstructures of the impregnated and unimpregnated coatings could be detected. The outer layer developed during oxidation of the specimens had a strong tendency to pull out during sample polishing. Figure 39 shows the microstructure of a retained portion of the outer oxide surface on the coating that was oxidized for 400 hours at 2400 F. This outer oxide layer is seen to consist of a white phase, a light grey phase, and a dark grey phase.

The X-ray diffraction patterns of all the TNV-7 coated specimens contained numerous sharp lines, many of which could not be assigned to ASTM powder patterns. No halos suggestive of short-range order were observed. Because all of the X-ray diffraction patterns were obtained for in situ coatings, utilization of the ASTM powder patterns, obtained for presumably randomly oriented crystallites, contributed some

Unetched
Magnification: 750X

FIGURE 39.

OXIDE LAYER ON GLASS-IMPREGNATED TNV-7 COATING OXIDIZED 400 HOURS AT 2400 F

uncertainty to the analysis of the in situ coatings. Orientation effects tend to disturb the relative intensity ratios for the different lines of a given compound and, thus, reduce the effectiveness of establishing compound identity by comparison of the lines of the unknown pattern with those presented in the ASTM card file.

Comparison of the diffraction pattern obtained for the unimpregnated as-silicided TNV-7 coating with ASTM cards 6-0681 and 11-195 indicated the probable presence of $MoSi_2$ and WSi_2, or a possible solid solution of the two. Differentiation between these two compounds was quite difficult when the experimental uncertainty in the measurement of the d-spacings was considered together with the above-mentioned problem in using the relative intensity ratios found on the ASTM cards. More readily detectable than either of these two disilicides was the diffraction pattern of the $(Ti_{0.8}Mo_{0.2})Si_2$ material characterized on ASTM card 7-331. Vanadium disilicide (13-260) also appeared to be present as a separate phase.

After 600 hours of oxidation at 1600 F, the impregnated TNV-7 coating still showed the compounds found in the as-silicided coating together with a possibile occurance of the impure silica phase having the distorted quartz structure characterized on card 12-708. In addition, the three strongest lines for rutile TiO_2 (4-0551) were barely detectable. Oxidation for either 40 or 600 hours at 2400 F resulted in the formation of readily detected rutile with the (110) plane preferentially oriented parallel to the surface. The diffraction pattern of the specimen oxidized for 600 hours at 2400 F

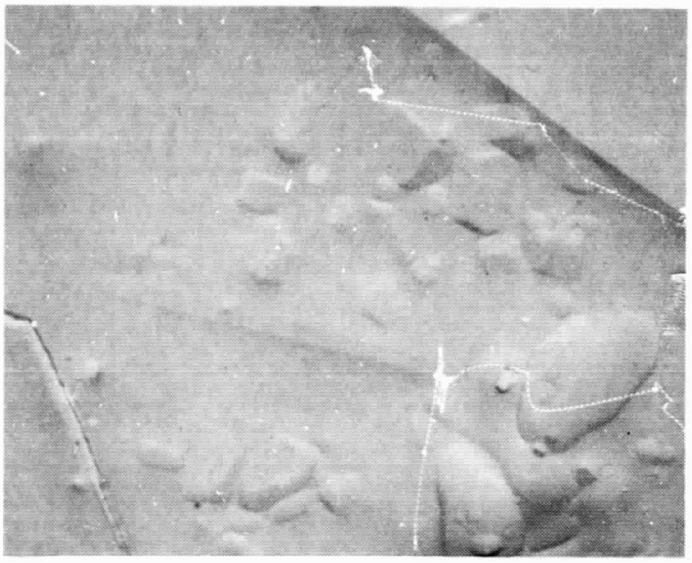
suggested the possible presence of the beta-cristobalite and low-tridymite forms of silica (cards 4-0359 and 3-0227, respectively).

With all of the oxidized specimens, the disilicide compounds were observed; however, the detectability diminished with increasing extent of oxidation. Neither Ta_2O_5 nor M_5Si_3 type compounds were detected.

Electron micrographs of the undisturbed flat surfaces of the TNV-7 coated specimens are shown in Figure 40. The surface of the as-silicided TNV-7 specimen was rough (porous) enough to necessitate use of the tape technique of replication. Prolonged oxidation at 2400 F resulted in a glassy appearance to the unaided eye, and yielded the relatively smooth surfaces shown in Figure 40. Figures 40F and 40G suggest the presence of small clusters of dendritic oxide in the surface of a glassy layer. Cracks, healed in varying degrees, can be seen in Figure 40C, 40D, and 40H.

The microprobe traces for molybdenum, titanium, silicon, vanadium, tungsten, and tantalum together with photomicrographs showing the location of the traverses are shown in Figures 41 through 45. The distances the different elements have diffused across the presintered coating-substrate interface are tabulated in Table XXVIII; molybdenum and tungsten did not appear to have diffused to any perceptible distance, even after 1,000 hours at 2400 F. Examination of the table suggests that after the initial sintering of the modifier alloy, titanium and vanadium did not diffuse to any appreciable extent, while both silicon and tantalum were diffusing across the coating-substrate interface throughout oxidation at 2400 F.

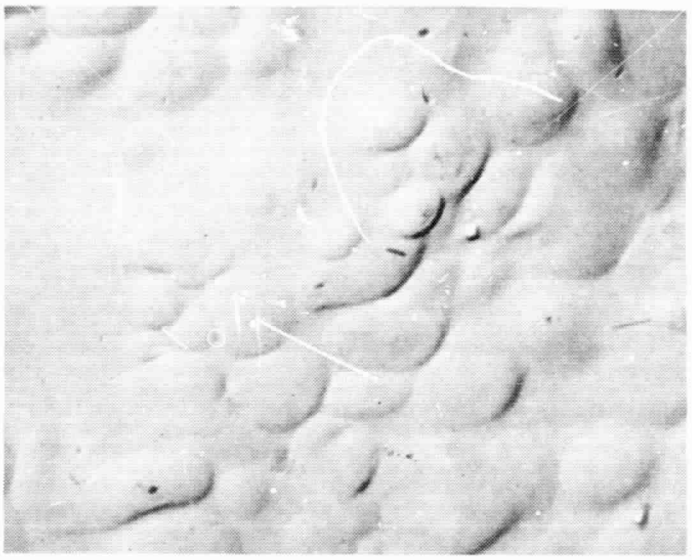
An experimental uncertainty of approximately ± 0.5 mil inch in the determination of the diffusion distances from the microprobe traces was suggested by comparison of the results for titanium and vanadium for the specimens oxidized for various periods of time at 1600 or 2400 F. This uncertainty resulted from variation of coating thicknesses with location on a single specimen and variation from specimen to specimen. It appeared that both titanium and vanadium diffused a distance of 1.0 to 1.5 mils into the substrate during the initial coating of the specimens. During the siliciding operation (7 hours at 2150 F) silicon diffused across the coating-substrate interface a distance of about 1.5 mils (the same distance the titanium and vanadium diffused during sintering for 15 hours at 2760 F). During oxidation testing at 2400 F diffusion of the silicon continued to a depth of approximately 2.5 mils in 1080 hours. During this

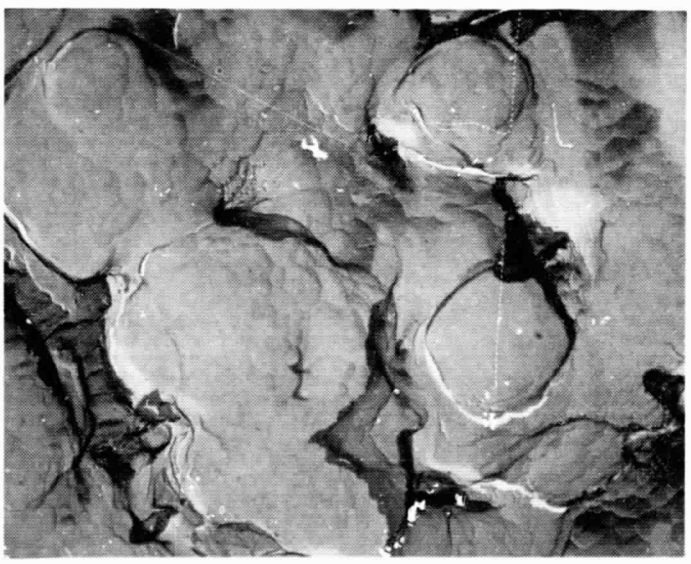


A. As Silicided

Magnification: 4000X

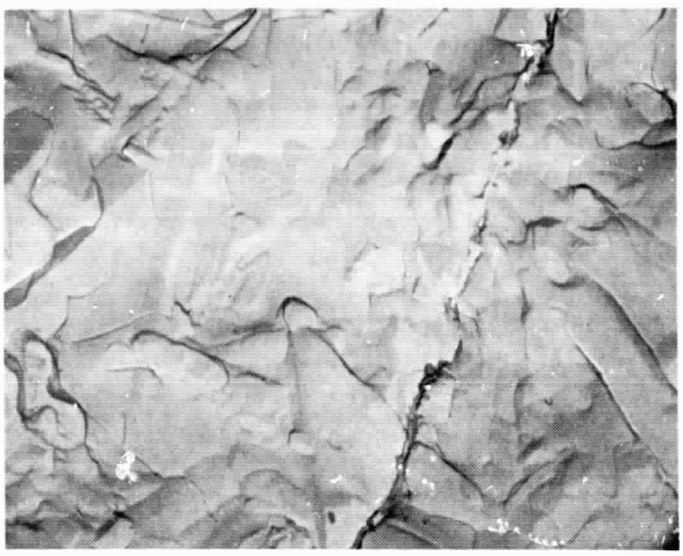
B. As Glassed





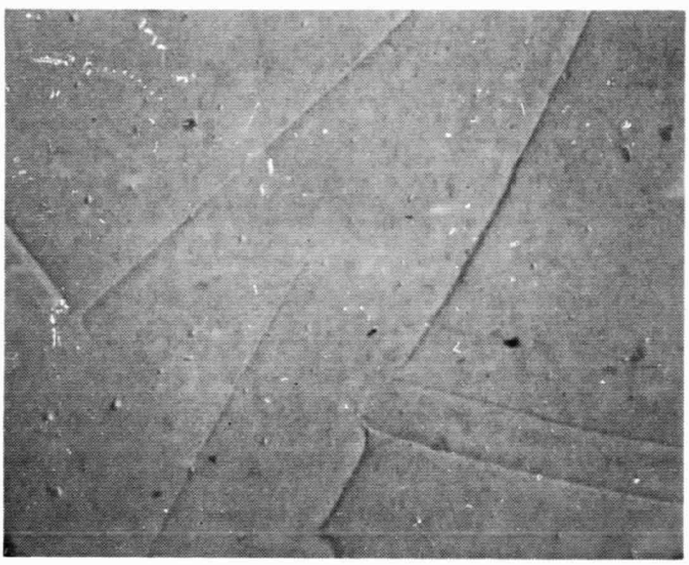
C. 40 Hours at 1600 F

FIGURE 40. ELECTRON MICROGRAPHS OF TNV-7 COATING (Sheet 1 of 3)

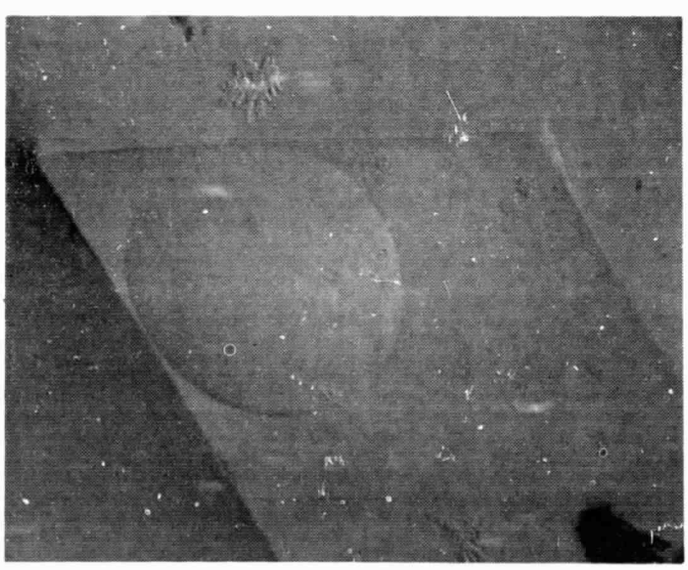


D. 600 Hours at 1600 F

Magnification: 4000X

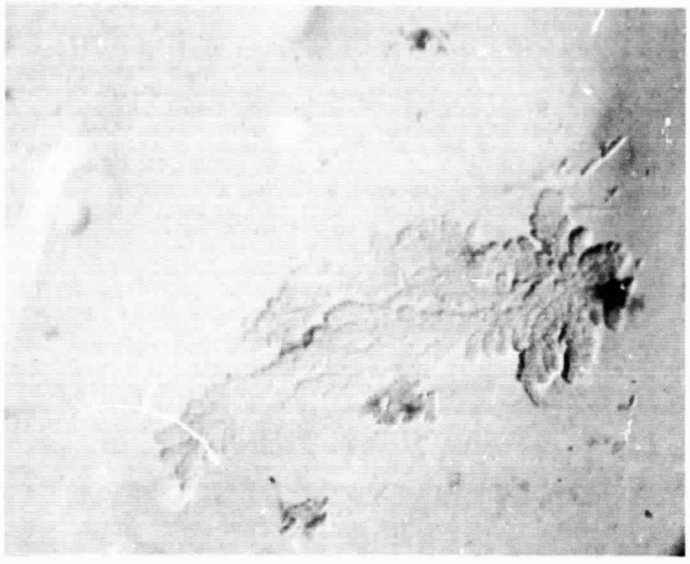


E. 40 Hours at 2400 F



F. 600 Hours at 2400 F

FIGURE 40. ELECTRON MICROGRAPHS OF TNV-7 COATING (Sheet 2 of 3)



G. 1080 Hours at 2400 F

Magnification: 4000X

H. 1080 Hours at 2400 F

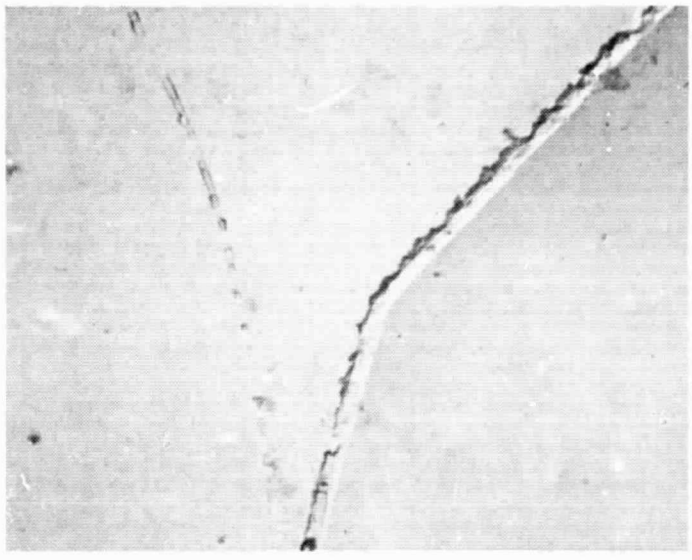


FIGURE 40. ELECTRON MICROGRAPHS OF TNV-7 COATING (Sheet 3 of 3)

same period tantalum was observed to have diffused into the coating a distance on the order of 3 to 6 mils, while oxidation for 600 hours at 1600 F corresponded to a diffusion distance of about 1.5 mils.

There appeared to be no correlation between the peaks and valleys on the traces for the different elements for specimens oxidized 200 hours or less at either temperature. Generally, for prolonged oxidation at either temperature, there was a tendency for association of peaks in both the molybdenum and tungsten curves with peaks in the silicon curve, and also with valleys in the titanium and vanadium curves.

TABLE XXVIII

APPROXIMATE DISTANCES OF DIFFUSION ACROSS ORIGINAL COATING-SUBSTRATE INTERFACE

Oxidation Time (hr)	Diffusion Distances (mil)							
	1600 F				2400 F			
	Si	Ti	V	Ta	Si	Ti	V	Ta
TNV-7								
0 (As-Coated)	1.5	1.5	1.5	0.8	1.5	1.5	1.5	0.8
200	1.0	2.0	1.75	1.3	1.4	1.3	1.4	1.8
600	1.0	1.0	1.0	1.5	2.0	0.5	0	2.5
1,080	-	-	-	-	2.6	1.5	0.5	3.5 to 5.5

Oxidation Time (hr)	Diffusion Distances (mil)					
	1600 F			2400 F		
	Si	Ti	Ta	Si	Ti	Ta
TNV-13						
0 (As-Coated)	0	0.5	0.6	0	0.5	0.6
40	0	0.5	-	-	-	-
120	0	0.5	0.6	-	-	-
200	-	-	-	0.4	1.2	1.0
480	-	-	-	0.5	0.8	1.0

There was also a tendency for association of peaks in both the titanium and vanadium curves with valleys in the silicon, tungsten, and molybdenum curves; however, exceptions were noted. These observations were enigmatic in that peaks in the titanium and vanadium curves would have been expected to be associated with peaks in the silicon curve on the basis that titanium and vanadium have lower atomic weights than tungsten and molybdenum and, thus, the corresponding disilicides for titanium and vanadium contain higher weight percentages of silicon, and, in general, would be expected to have less X-ray absorption tendencies.

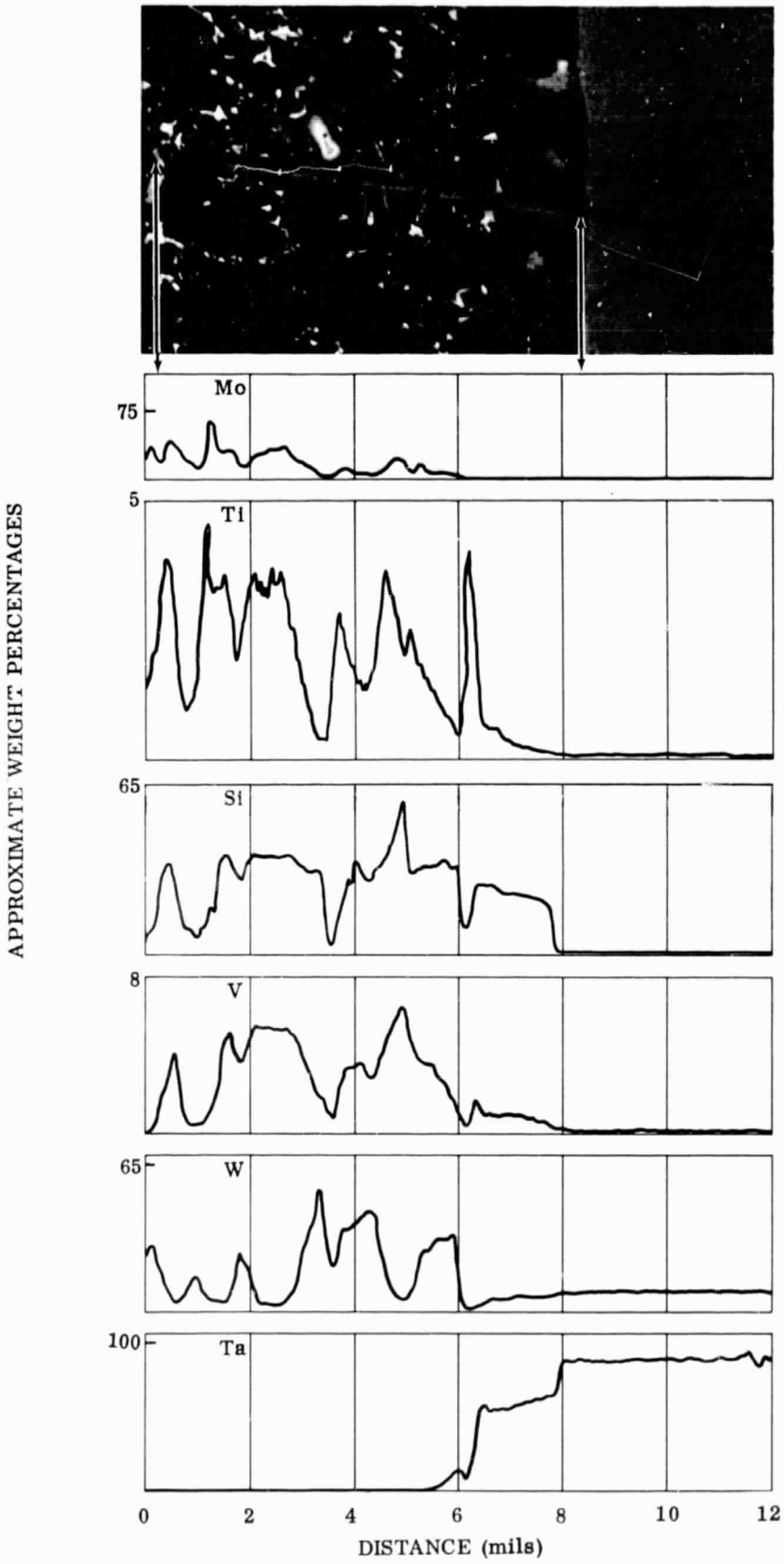


FIGURE 41. ELECTRON MICROPROBE TRAVERSE OF AS-GLASSED TNV-7 COATING

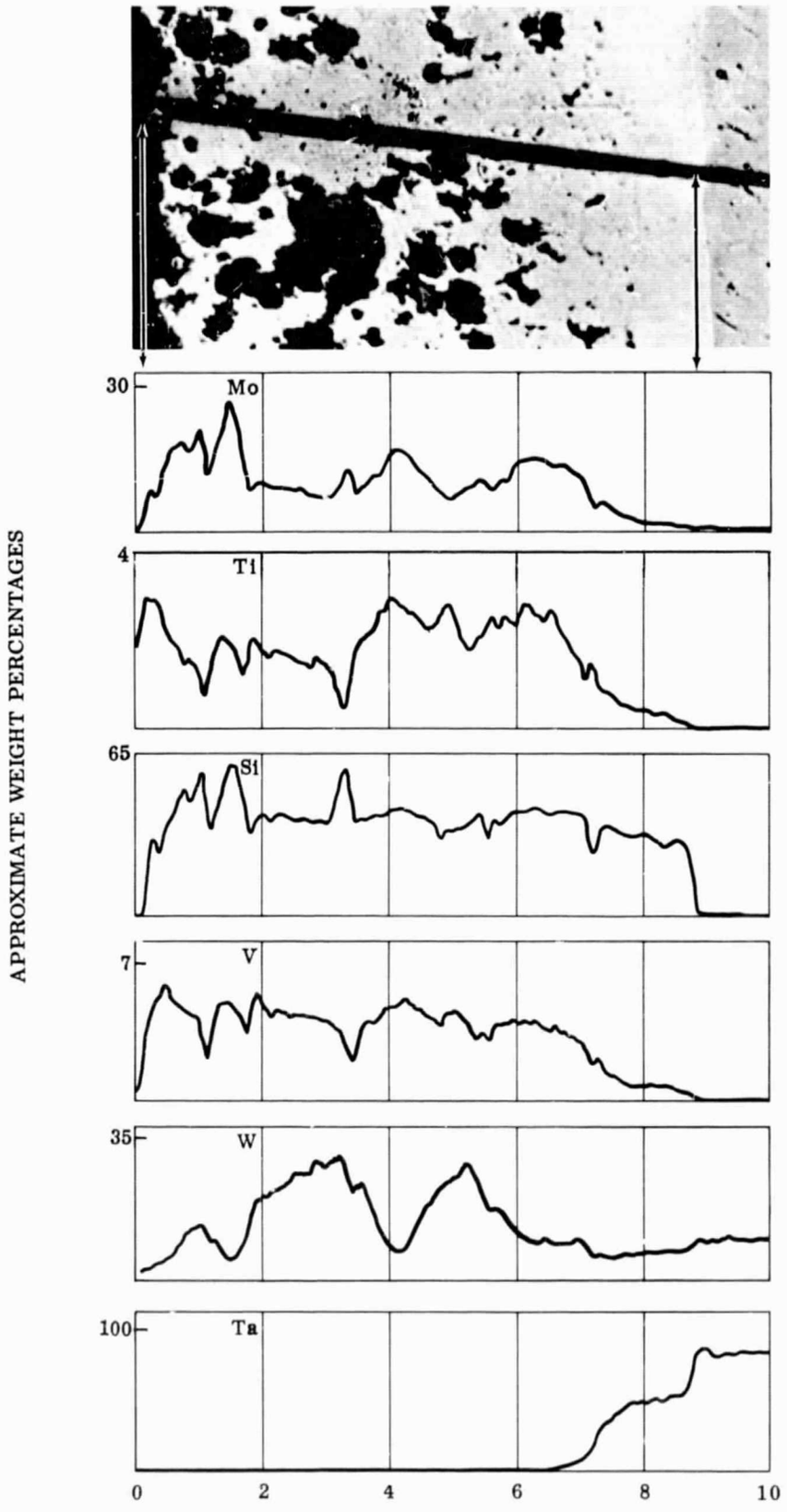


FIGURE 42. ELECTRON MICROPROBE TRAVERSE OF TNV-7 COATING OXIDIZED 600 HOURS AT 1600 F

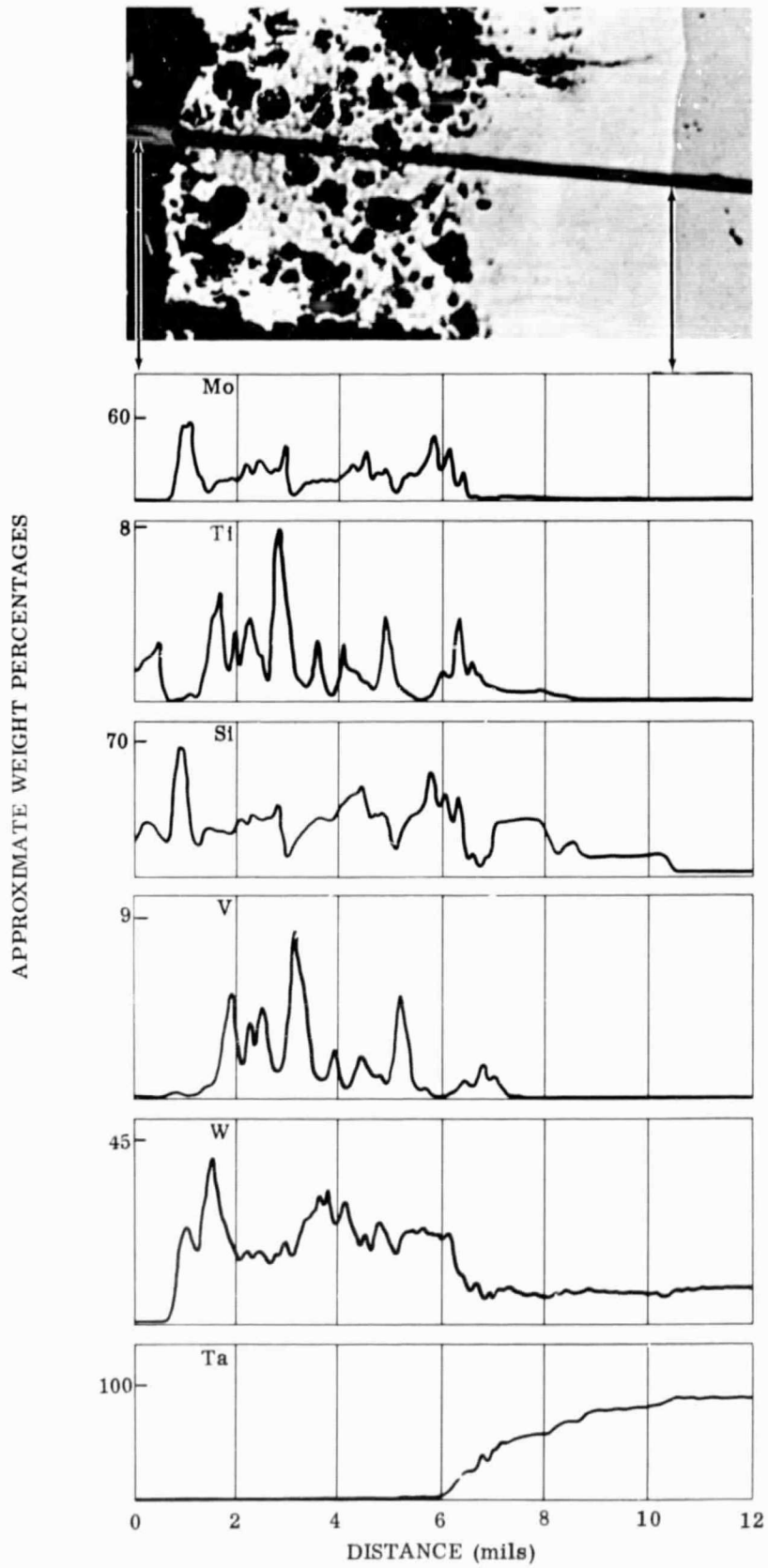


FIGURE 43. ELECTRON MICROPROBE TRAVERSE OF TNV-7 COATING OXIDIZED 600 HOURS AT 2400 F (Sheet 1 of 2)

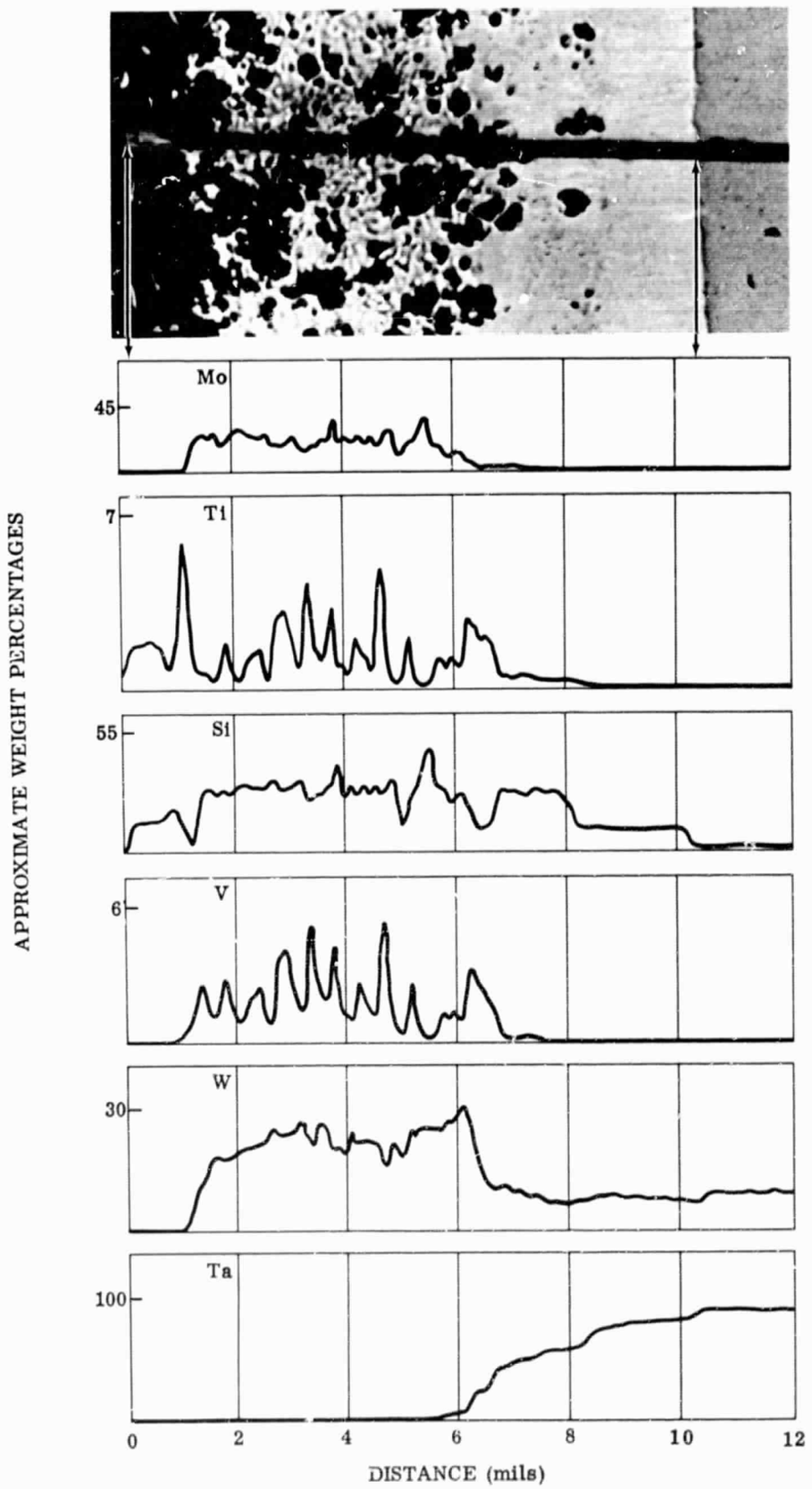


FIGURE 43. ELECTRON MICROPROBE TRAVERSE OF TNV-7 COATING OXIDIZED 600 HOURS AT 2400 F (Sheet 2 of 2)

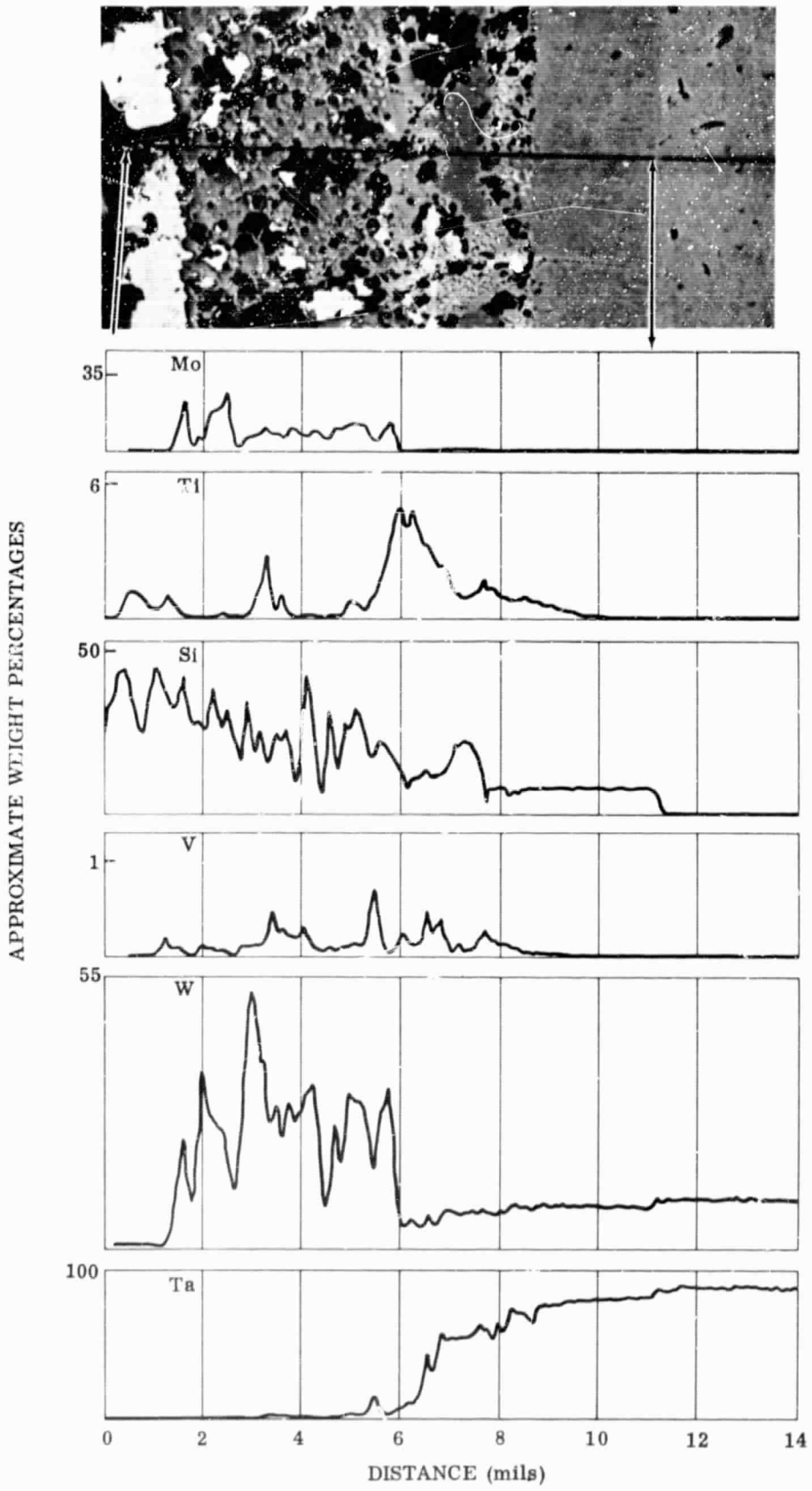
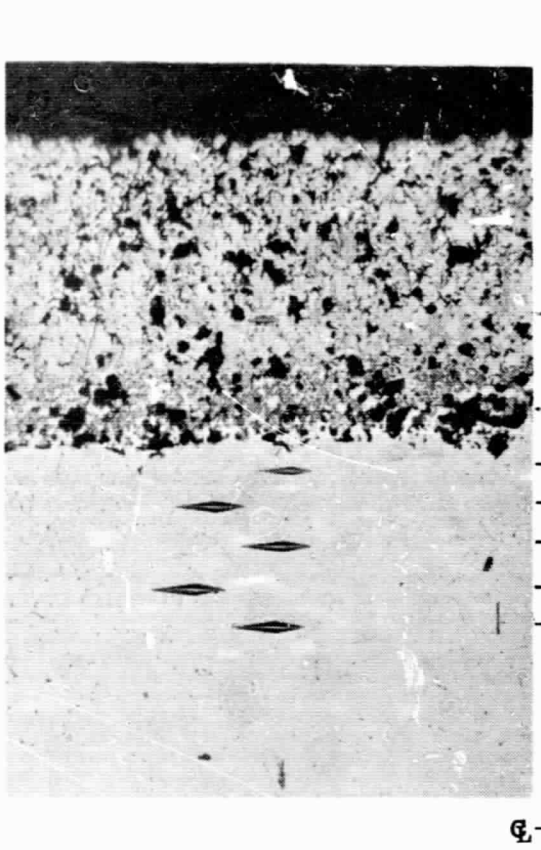
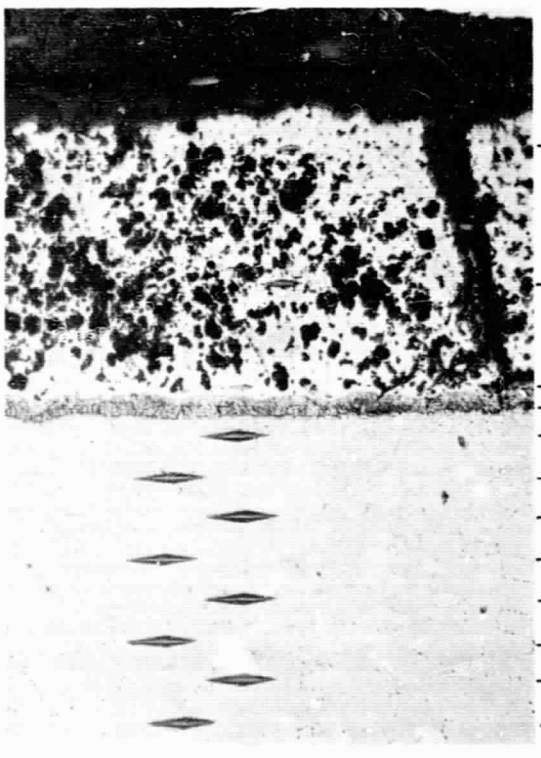


FIGURE 44. ELECTRON MICROPROBE TRAVERSE OF TNV-7 COATING OXIDIZED 1080 HOURS AT 2400 F



Experiment Number: T_2-201
Substrate: T222
Coating: TNV-13 (Glass impregnated) (5Ti-95W)
Oxidation Time: 120 Hours
Oxidation Temperature: 2400 F
Etchant: 60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification: 200X



Experiment Number: T_2-201
Substrate: T222
Coating: TNV-13 (Glass impregnated) (5Ti-95W)
Oxidation Time: 480 Hours
Oxidation Temperature: 1600 F
Etchant: 60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification: 200X

FIGURE 45. GLASS-IMPREGNATED TNV-13 COATING; Subjected to 600-Hour Test

The shapes of the curves representing diffusion of titanium, vanadium, and silicon into the substrate were interesting. While titanium and vanadium displayed curves showing a gradual, smooth decrease in concentration with distance, the curves for silicon are quite different, particularly for prolonged oxidation at 2400 F; a plateau of relatively constant silicon concentration was followed by an abrupt drop to virtually zero silicon concentration. The plateaus in the silicon curves were attributed to the formation of the silicide compounds. Uncorrected intensity ratios were plotted directly as approximate weight percent in Figures 41 through 44; however, the use of disilicide microprobe standards should make the silicon analysis reasonably accurate. The disilicide standards were obtained by converting the outer layer of unalloyed tungsten, unalloyed molybdenum, and unmodified T222 alloy to the corresponding disilicides by the conventional high-pressure pack siliciding technique; these outer layers were taken to be the corresponding disilicides (Ref. 13). The silicon content in the hard sublayer within the substrate of the as-glassed TNV-7 specimens was observed to vary between approximately 28 and 20 percent, and between 35 and 27 percent for the specimen oxidized 600 hours at 1600 F. These values suggest that this hard layer in the substrate corresponded to a mixture of the disilicides of tungsten, tantalum, titanium, and vanadium (23.4, 23.7, 54.0, and 52.4 weight percent silicon, respectively), with the major constituent specie being $TaSi_2$. The level of the silicon plateau in the specimen oxidized 600 hours at 2400 F corresponded to between 10 and 11 weight percent silicon, while the silicon plateau in the specimen oxidized for 1080 hours at 2400 F corresponded to approximately 8 weight percent. It appeared that the prolonged oxidation with the attendant diffusion of silicon into the substrate resulted in the formation of a mixture of W_5Si_3, Ta_5Si_3, Ti_5Si_3, and V_5Si_3 in varying proportions (8.4, 8.5, 26.0 and 24.8 weight percent silicon, respectively) in agreement with the findings of Bracco, Lublin and Sama (Ref. 13).

The traces for electron-microprobe traverses in two different locations on the same TNV-7 coated specimen oxidized for 600 hours at 1600 F are shown in Figure 43. Comparison of the traces for a given element on the two traverses indicated that the shape of the traces varies with location on the specimen surface and suggested that the coating was unhomogeneous.

Examination of the microprobe analyses of the oxide layer formed on the specimens oxidized for either 600 or 1080 hours at 2400 F revealed that this oxide layer contained titanium and silicon, but no molybdenum, tungsten, vanadium, or

tantalum. A microprobe traverse (made parallel to the surface of the specimen) of the oxide layer formed on the TNV-7 coated specimen oxidized for 400 hours at 2400 F suggested that the white phase in the oxide layer shown in Figure 39 corresponded to the rutile TiO_2 detected by X-ray diffraction. The uncorrected intensity ratio for the titanium in the white phase was observed to be approximately 55 weight percent, and is, thus, in agreement with the 60 weight percent titanium content of TiO_2. The light-grey phase in the oxide was observed to contain approximately 4 to 6 percent titanium while the dark-grey phase appeared to contain no titanium. The silicon content of the white phase was observed to be virtually zero, while the light-grey phase contained approximately 10 percent silicon and the dark-grey phase contained approximately 25 weight percent silicon. Stoichiometric SiO_2 contains 46.8 weight percent silicon. In the absence of known compounds in the SiO_2-TiO_2 system (Ref. 14), it would appear that the light-grey phase would correspond to a titania-silica glass. The dark colored titanium-free phase might be a slightly impure, partially devitrified silica glass if the analysis for silicon was assumed to be low as a result of direct conversion of intensity ratios to weight percentages.

Analysis of TNV-12 Coated Specimens

The metallographic analyses of the as-silicided and oxidized TNV-12 coating (Fig. 20 and 33) were supplemented by limited X-ray diffraction and a qualitative electron microprobe analysis.

An X-ray diffraction analysis of the TNV-12 coated specimen oxidized for 659 hours at 1600 F suggested that alpha-cristobalite SiO_2 (ASTM card 11-695), was the principal phase present. Molybdenum disilicide (6-0681) was also readily detected as a major phase which, together with the cristobalite, was observed to be randomly oriented. The most readily detected phase in the TNV-12 coating oxidized 612 hours at 2400 F corresponded to rutile TiO_2 with the (110) plane preferentially oriented parallel to the surface. Randomly oriented alpha-cristobalite was also readily detected as a major phase, while only the most intense lines of the underlying $MoSi_2$ were detected.

A qualitative electron-microprobe analysis of the as-silicided TNV-12 coating revealed no perceptible interdiffusion of the molybdenum and tantalum during coating application. The soft porous inner layer of the as-silicided coating contained virtually no silicon. The hard layer formed within the substrate during 612 hours of

oxidation at 2400 F resulted from silicon diffusion. This prolonged oxidation resulted in diffusion of tantalum into the porous coating a distance of about 1.2 mils, which was about the distance observed with the TNV-7 coating.

Analysis of TNV-13 Coated Specimens

Selected TNV-13 coated specimens which were glass impregnated and oxidized for various periods of time were subjected to metallographic, X-ray diffraction, electron-microscopic, and electron-microprobe analyses.

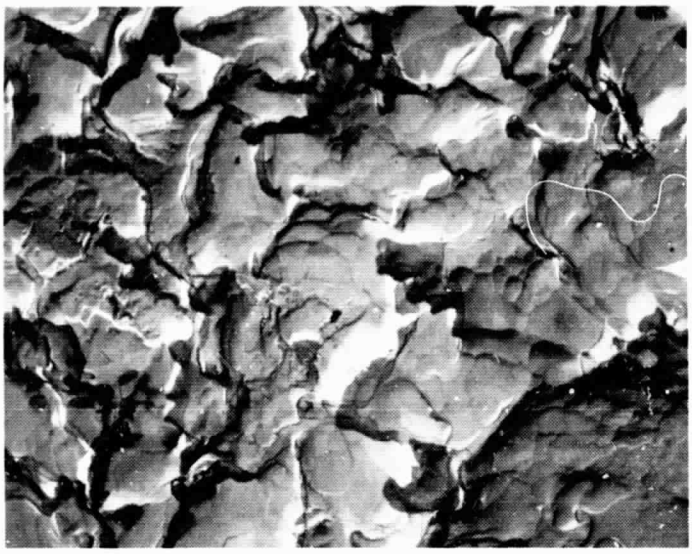
The hardness profile of Figure 45 suggests that silicon did not reach the substrate in 120 hours at 1600 F, but did reach the substrate during 480 hours at 2400 F.

The X-ray diffraction results suggested that all of the specimens contained WSi_2 (ASTM card 11-195). In addition, oxidation for 120 hours at 1600 F may possibly have produced alpha-quartz SiO_2 (5-0490).

The electron micrographs of Figure 46 suggest that crystals were growing in the glassy surface of the coating at 1600 F as early as 40 hours, while the coating exposed to 2400 F oxidation was relatively smooth.

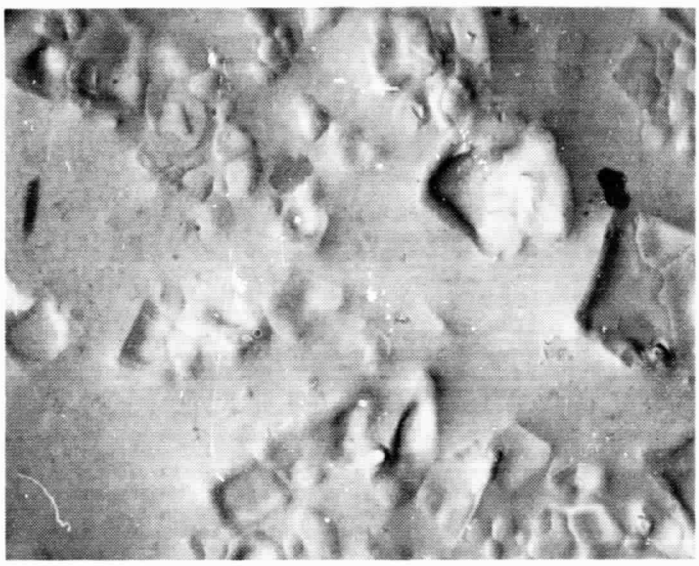
Microprobe traverses for tungsten, titanium, silicon, and tantalum were performed on the coating in the as-glassed condition and after 40 and 120 hours of oxidation at 1600 F, and 200 and 480 hours of oxidation at 2400 F. Generally, there was no correlation between the peaks and valleys in the curves for the different elements, but in the case of the specimen oxidized for 480 hours at 2400 F, there were many cases where the tungsten peaks coincided with titanium peaks and valleys in the silicon curve. The traces for the specimen oxidized for 480 hours and 2400 F, as well as the as-glassed specimen, are shown in Figures 47 and 48.

The distances that the different elements diffused across the initial presintered coating-substrate interface are shown in Table XXVIII with those for the TNV-7 coating. Examination of the table suggested that after the initial sintering operation, the titanium and tungsten remained relatively immobile as silicon diffused into the substrate. Comparison of the results for the TNV-7 and TNV-13 coatings suggested that the rate of diffusion of tantalum into the TNV-13 coating was a bit slower than into the TNV-7 coating.

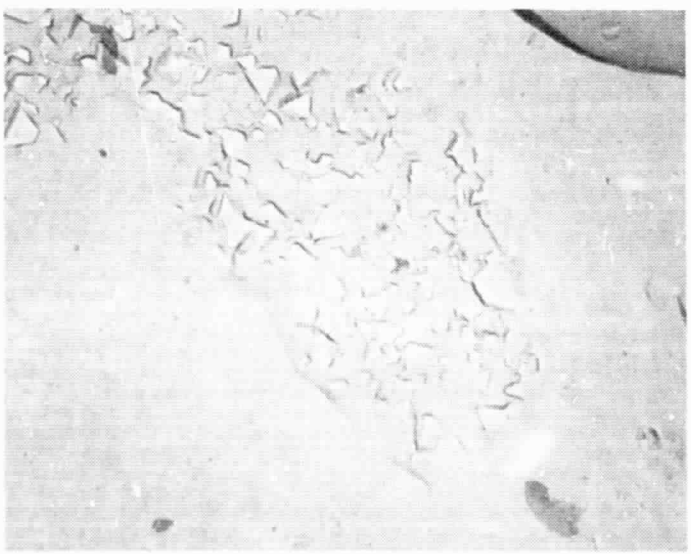


A. As Silicided

Magnification: 4000X

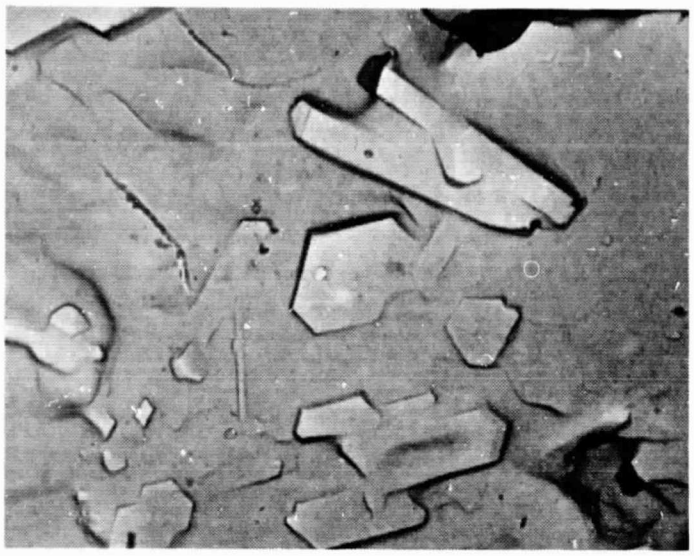


B. As Glassed



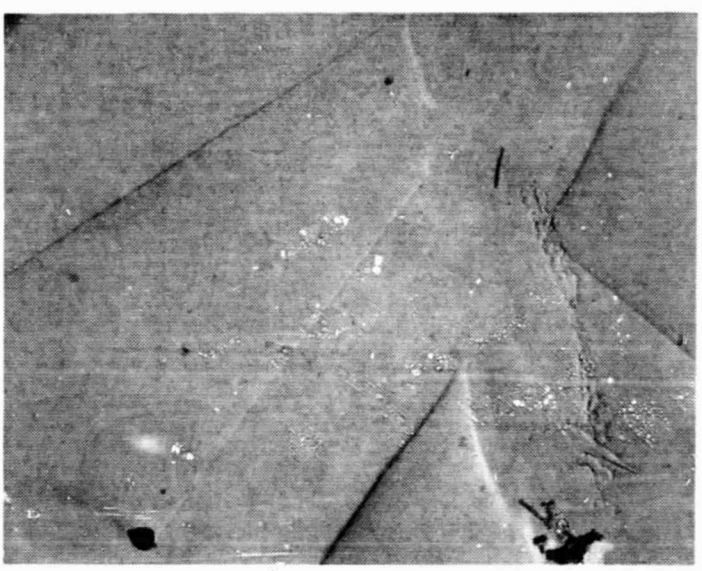
C. 40 Hours at 1600 F

FIGURE 46. ELECTRON MICROGRAPHS OF THE TNV-13 COATING (Sheet 1 of 2)

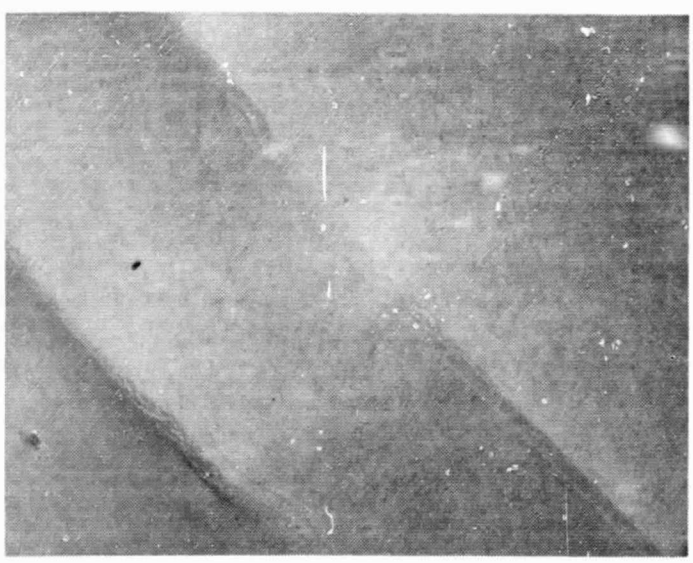


D. 120 Hours at 1600 F

Magnification: 4000X



E. 40 Hours at 2400 F



F. 480 Hours at 2400 F

FIGURE 46. ELECTRON MICROGRAPHS OF THE TNV-13 COATING (Sheet 2 of 2)

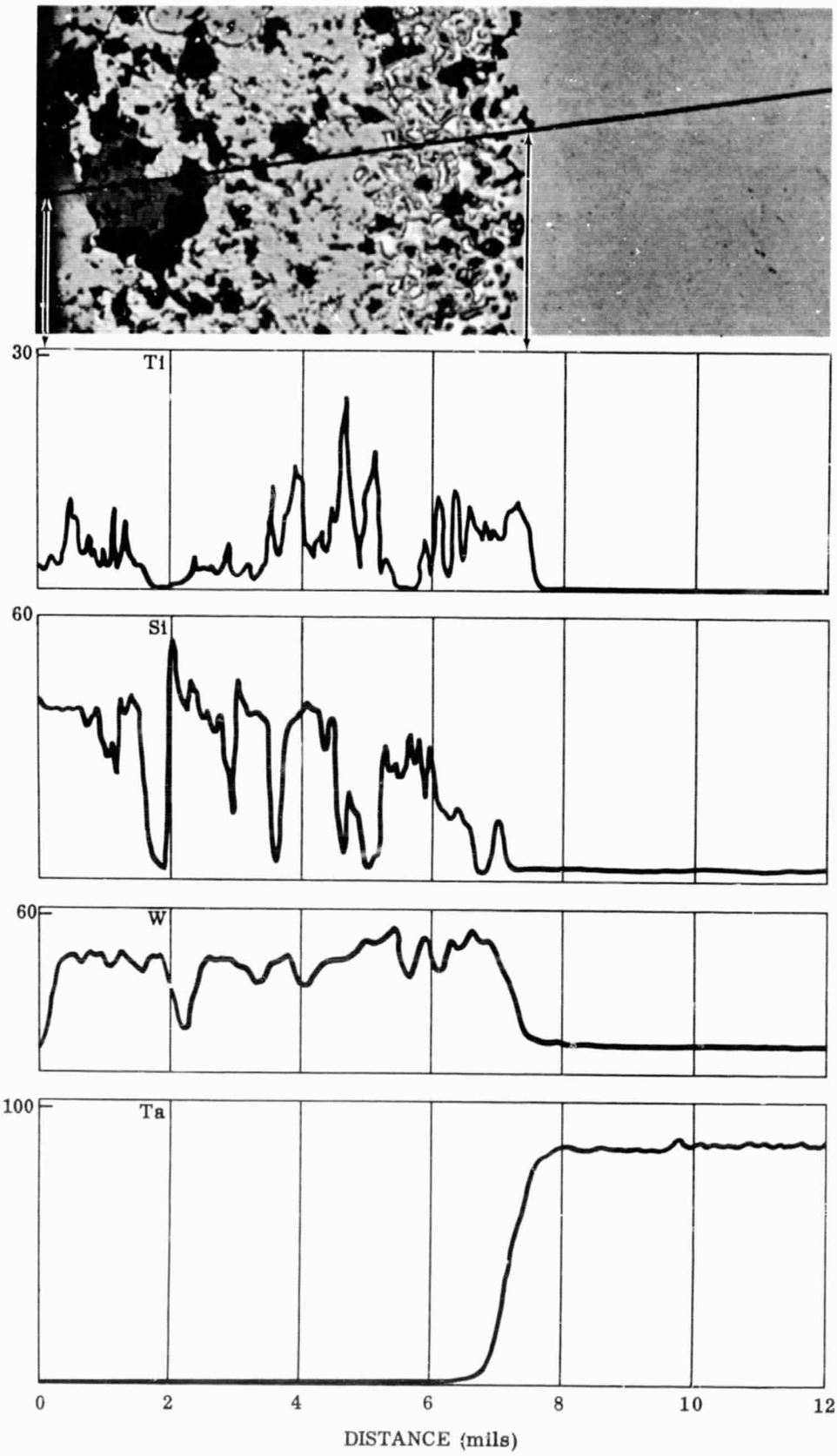


FIGURE 47. ELECTRON MICROPROBE TRAVERSE OF AS-GLASSED TNV-13 COATING

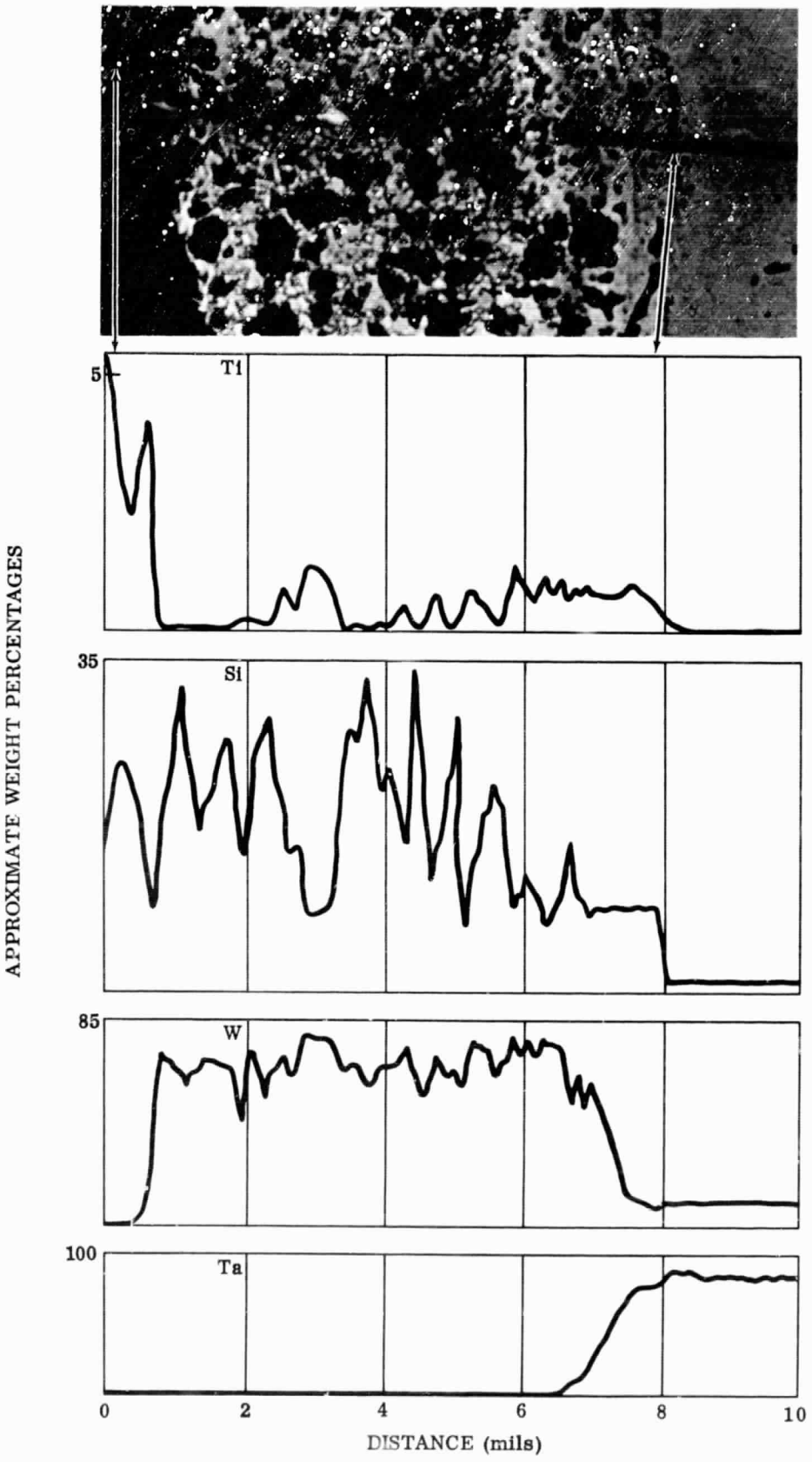


FIGURE 48. ELECTRON MICROPROBE TRAVERSE OF TNV-13 COATING OXIDIZED 480 HOURS AT 2400 F

3.4.7 Application of Slurry Coatings to Columbium-Base Alloys

In a separate research program (Ref. 15), the slurry coatings developed for the T222 tantalum-base alloy were applied to the Cb752 and D43 columbium-base alloys (Cb-10W-2.5Zr and Cb-10W-1Zr-0.1C, respectively). Oxidation testing in static air at 1600 and 2400 F and in the flame of a propane-oxygen rocket motor at a 2400 F specimen temperature demonstrated excellent oxidation resistance for the coatings on the columbium-base alloys.

The D43 alloy with the glass-impregnated TNV-12 coating, survived 1000 cycles in a propane-oxygen high-velocity flame. One cycle corresponded to 30 seconds in the flame, with 10 to 12 seconds required to reach steady state conditions, followed by 60 seconds in a room-temperature air blast. The same coating protected the Cb752 alloy for 223 to 255 hours of testing (one-hour cycles) in static air at 2400 F, and for more than 552 hours at 1600 F where 24-hour cycles were employed.

A difference in the cycling procedure for the tests in static air precluded a direct comparison of the results for the coatings on columbium-base with those on tantalum-base alloys. The columbium-base alloys have a better thermal expansion match with the silicides than do the tantalum-base alloys and, thus, might be expected to be a little more readily protected.

4

DISCUSSION OF RESULTS

4.1 COATINGS BASED ON MODIFICATION ALLOYING BY PACK CEMENTATION TECHNIQUES

The experimental results of the single-cycle high-pressure pack cementation experiments indicated that this technique was not capable of obtaining the desired modification alloying. At temperatures where the mass transfer rates were sufficient to deposit material on the substrate at a practical rate, the same mass transfer produced excessive sintering of the pack particles to the surfaces of the specimens. Either removal of the pack particles from the surface (frequently accompanied by removal of a small portion of the modifier alloy layer) or leaving a portion of the attached pack particle on the surface resulted in coating defects which shortened oxidation lives. Although the multiple cycling technique in which the specimens were removed from the pack after each cycle tended to minimize the sintering of the pack particles, their removal resulted in coating defects which were frequently visible to the unaided eye, and undoubtedly gave rise to the high incidence of failures on the flat surfaces rather than at the edges where the slurry coated specimens normally failed.

Although vacuum pack cementation allowed the use of higher deposition temperatures than the 2300 F maximum obtainable in the Inconel retorts and also allowed modification in a cleaner environment, the adherence of pack particles to the specimens was still manifest as a problem and appeared to render vacuum pack cementation no more effective than high-pressure pack cementation. The inability to transfer tungsten (and presumably molybdenum) from the pack alloys to the specimens (as reported in the technical literature) was confirmed by the X-ray fluorescence analysis reported in Paragraph 3.3.1. The inability to introduce these two elements into the modifier layers constituted a serious shortcoming of the pack process but was not a problem with the slurry-coating process.

4.2 COATINGS BASED ON MODIFICATION ALLOYING BY SLURRY COATING TECHNIQUES

The better coatings applied by slurry techniques displayed much greater oxidation resistance than the better coatings applied by pack cementation techniques by a factor of approximately four or more.

There was observed to be no correlation between the microstructure of the as-silicided slurry coatings with oxidation resistance. Some of the most porous coatings having a low degree of continuity displayed greater oxidation resistance than other coatings with a more dense structure. Elimination of porosity was definitely not a requisite for good oxidation resistance and, indeed, may be undesirable to the extent that the pores appeared to allow the accumulation of relatively large quantities of silicon without disruptive effects. The resultant slurry coatings were thicker than those obtainable by the pack cementation process and, thus, appeared to have greater potential in providing long-term oxidation protection.

Maintenance of an unsilicided modifier alloy zone beneath the silicide coating did not appear to be a requisite for obtaining the desired oxidation resistance. This realization was based on a review of the microprobe analysis of the TNV-7 coating oxidized for 600 or 1080 hours at 2400 F. The microprobe results indicate that silicon diffused into the T222 substrate to a significantly greater depth than had either the titanium or the vanadium. Thus, cracks which were observed to penetrate completely through the coating, including this silicon diffused layer, penetrated to virgin T222 substrate. It appears then that the excellent oxidation resistance of the TNV-7 coating is a result of its ability to generate oxides that heal (seal) the cracks formed by thermal expansion mismatch. When a specimen is oxidized at a temperature significantly below the temperature at which the siliciding is performed, the coating cracks will not be closed by thermal expansion and, thus, self-healing becomes critical. In the absence of an appreciable self-healing ability at temperatures less than the siliciding temperature, provision of an unsilicided modified alloy layer appeared to be helpful in that the TNV-12 coating applied to substrates previously modified in the TNV-3 pack was observed to be more oxidation resistant than the same coating applied to an unmodified substrate.

Complete penetration of the sintered modifier layer during pack siliciding did not appear to be undesirable. Although silicon did not completely penetrate the normal TNV-12 coating showing appreciable oxidation resistance (particularly at 2400 F),

complete penetration of the 0.003-inch thick TNV-12 modifier layer did not preclude good oxidation resistance. In the case of the TNV-13 coating (Fig. 22), some areas within a single specimen, particularly at the edges, experienced complete silicon penetration, while other areas, on the flat faces, did not show complete silicon penetration; these specimens were observed to do quite well in oxidation testing. Thus, although siliciding completely through the tungsten-rich and molybdenum-rich modifier layer seemed desirable in view of the expected poor oxidation resistance of the unsilicided alloys, complete siliciding of the porous sintered modifier layer did not appear to be a requisite for, or a deterrent to, good oxidation resistance.

There appeared to be a reasonable amount of latitude in the thickness of the coating; this was suggested by the observed unintentional variation of the coating thickness at the edge of specimens as well as the study in which the thickness of the TNV-12 coating was varied intentionally.

Although adherence of small quantities of the Dyna-Quartz to the oxidation samples tended to diminish somewhat the usefulness of the plots of weight change data, some observations were noted. Although the plots of the weight gain during oxidation at 2400 F tend to have a general parabolic shape in many cases and, thus, suggest reasonably well behaved diffusion controlled oxidation, numerous steps or discontinuities in the weight gain plots were observed which suggested a cracking and healing process. Without exception, the microstructure of the coatings investigated in this program was observed to contain numerous cracks, undoubtedly arising from the significant difference in the thermal expansivities of the respective silicides compared to the thermal expansion of the T222 alloy. Thermal expansion matching thus appeared to be less important than the chemical nature of the silicides in determining the cyclic oxidation resistance. Oxide composition (and structure) as well as rates of formation as a function of temperature appeared to be critical factors in the crack-healing process.

Conversion of 20 milligrams of silicon/square centimeter to silica would yield a weight gain of 22.8 milligrams/square centimeter. Thus, only a fraction of the silicon was consumed by oxidation as it was introduced into the coatings to the extent of 14 to 48 milligrams/square centimeter. In the case of the TNV-7 and TNV-12 coated specimens oxidized for 600 hours at 2400 F, approximately 12 percent of the silicon was oxidized, and in the case of the TNV-7 coated specimen oxidized for 1080 hours only about 15 percent was consumed. Generally speaking, silicon consumption by oxidation was lower with the molybdenum-rich and tungsten-rich coatings in

comparison with the other compositions containing greater quantities of titanium, vanadium, or chromium. Calculation of silicon consumption by attributing the weight gain to conversion of silicon to silica involves the assumption that no appreciable loss of volatile oxides took place; however, this assumption seemed quite reasonable in view of the absence of tungsten or molybdenum in the outer oxide traversed by the beam of the electron microprobe analyzer. More important than weight loss by volatilization was the undetermined weight gain accompanying formation of the TiO_2 in the case of the TNV-7 coating. Thus, the above-mentioned calculated values for silicon consumption by oxidation are higher than the actual case for the TNV-7 coating.

The approximate silicon consumption of 15 percent for the TNV-7 coated specimen oxidized for 1080 hours at 2400 F was very interesting and suggested that this particular coating has the potential for providing 3000 hours of protection; however, diffusion of silicon into the substrate should be considered because loss of silicon by this mode appeared to be more important than consumption by oxidation for long periods of time. During the pack siliciding operation, silicon diffused through the TNV-7 modifier layer and into the substrate to produce what appears to be an approximately 0.001-inch thick, single-phase layer of $TaSi_2$ containing 9 mole percent WSi_2 and a smaller quantity of $HfSi_2$. During subsequent oxidation, silicon diffused further into the substrate. However, in the absence of the silicon pack that normally kept the silicon activity high enough to maintain the disilicides, diffusion of silicon across the interface between the virgin substrate and its corresponding disilicide phase produced subsilicides (on both sides of the interface). This was considered to be undesirable because the subsilicides normally have lower oxidation resistance. Diffusion of silicon would convert a 1.0-mil thick $TaSi_2$ layer in contact with tantalum metal to a 1.95-mil thick Ta_5Si_3 layer (calculated using molar volumes of 25.9 cc/mole $TaSi_2$ and 75.7 cc/mole Ta_5Si_3). Thus, there would be no need for silicon to diffuse from the silicided porous TNV-7 modifier layer into the substrate until the fully dense 0.001-inch thick disilicide sublayer had become converted to a nearly 0.002-inch thick M_5Si_3-type sublayer. Examination of the microprobe results indicated that about 600 hours at 2400 F were required for completion of this conversion. Thus, diffusional deterioration of the silicided porous modifier layer at 2400 F does not begin until approximately 600 hours have passed (realization of this condition suggested the desirability of siliciding completely through the sintered modifier layer during pack siliciding to form a relatively thick disilicide layer in the substrate).

The diffusional deterioration of the silicided modifier layer is a slow process in and of itself. Although a number of studies (Ref. 16) have been made of diffusion of silicon from refractory metal disilicides into their respective parent metals, there appeared to be a void of information regarding the diffusion of silicon from the disilicide of one metal (or an alloy) into another metal (or a second alloy). The latter condition corresponds to the situation with the coatings of interest. Thus, calculating the rates of loss of silicon from the silicided modifier layers using available diffusion data is impracticable.

Diffusion of tantalum out into the coating may prove to be more serious than diffusion of silicon into the substrate as oxidation times reach the 2000- to 3000-hour range. Perhaps a diffusion barrier will be needed to inhibit the diffusion of tantalum. In this regard the microprobe studies revealed that tantalum appeared to diffuse into the molybdenum-rich TNV-12 and tungsten-rich TNV-13 coatings more slowly than it did into the more extensively alloyed TNV-7 coating. This observation was not surprising when the melting points of the corresponding coating disilicides (in their respective proportions) were considered (WSi_2-3930 F, $MoSi_2$-3685 F, VSi_2-3020 F and $TiSi_2$-2660 to 2805 F; Refs. 17 and 18). Application of a tungsten-rich layer (either TNV-13 or activated-sintered tungsten) adjacent to the substrate prior to application of a layer of the TNV-7 modifier alloy (or its optimized successor) and subsequent siliconization might yield an ideal coating. The diffusion resistance of WSi_2 would be expected to be slightly greater than the structurally similar $MoSi_2$ on the basis of the higher melting point of the former.

Although the failures of the glass-impregnated TNV-13 coated specimens during the 600-hour test did not follow the Weibull distribution function, the reliability of the TNV-13 coating, particularly at 2400 F, was quite good. The complete absence of failure of the TNV-7 coated specimens during the 600-hour test (in addition to the second set of specimens oxidized in the extended 200-hour test) suggested that the reliability of the TNV-7 coating at both 1600 and 2400 F is quite dramatic when compared to the previously developed silicide coatings.

The improvement in the 1600 F oxidation resistance of the TNV-13 coating by glass impregnation was sizable. It appeared that the added glass combines with the products of oxidation of the coating silicides to seal the thermal expansion cracks in the coating, which would tend to be open at temperatures below the 2150 F siliciding

temperature. The quantities of glass produced during the air-firing operation that preceded normal oxidation testing of the glass-impregnated coatings amounted to a weight gain of about 1.2 mg/cm^2 and was thus on the order of the small quantity of glass frit introduced into the coating.

The limited investigation of the use of activated sintering in the slurry coating process revealed that the sintering time and temperature for application of slurry coatings can be drastically reduced from 15 hours at 2760 F to something on the order of 2 hours at 1925 F. The reduction would be conducive to the coating of large numbers of parts with a minimized opportunity for deterioration of the mechanical properties of the refractory metal substrate; this would be particularly important in the case of coating columbium-base alloys. The application of the TNV-11 coating, of slightly greater oxidation resistance by sintering 2.5 hours at 1925 F preparatory to pack siliciding, was probably facilitated more by the use of tungsten particles having an average size of less than one micron (available commercially relatively inexpensively) than it was by the nickel coating of the tungsten powders. However, both of these factors appeared to contribute.

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SUMMARY AND CONCLUSIONS

A group of silicide coatings developed for the T222 tantalum-base alloy provided over 600 hours of protection against oxidation at 1600 and 2400 F during cyclic exposure in air. These coatings were applied in two steps. A modifier alloy was applied by slurry techniques and was sintered in vacuum prior to siliciding by pack cementation in argon. The application of the modifier alloys by slurry techniques was observed to yield more oxidation-resistant coatings than were obtainable by pack cementation modification (followed by pack siliciding). In addition, the slurry-coating process allowed the application of tungsten-rich and molybdenum-rich modifier alloys that could not be applied by pack cementation. The compositions of the modifier alloys applied by slurry techniques and the maximum oxidation lives observed for the resultant silicided coatings are shown in Table XXIX.

TABLE XXIX

COMPOSITION OF MODIFIER ALLOYS APPLIED BY SLURRY TECHNIQUES AND OXIDATION LIVES OF RESULTANT SILICIDE COATINGS

Modifier Alloy Designation	Composition (wt %)					Maximum Oxidation Lives after Siliciding	
	Ti	W	V	Mo	Cr	Hours at 1600 F	Hours at 2400 F
TNV-1	90	10	--	--	--	As-Silicided Coating Spalled	
TNV-2	60	40	--	--	--	31	332
TNV-3	30	70	--	--	--	111	>627
TNV-4	60	--	--	40	--	16	31
TNV-5	30	35	--	35	--	31	>206
TNV-6	30	40	30	--	--	>653	>206
TNV-7	15	35	15	35	--	>630	>1064
TNV-8	30	35	--	--	35	16	95
TNV-9	30	--	--	35	35	16	>610
TNV-10	30	--	30	--	40	16	16
TNV-11	2.5	97.5	--	--	--	16	561
TNV-12	4.7	--	--	95.3	--	>659	947
TNV-13	5	95	--	--	--	47	>615
TNV-14	2.5	--	--	97.5	--	16	>338
TNV-15	10	--	--	90	--	16	>338
TNV-16	5	45	5	45	--	>636	>338
TNV-17	5	90	5	--	--	16	>338

The experimental results prompted the following observations and conclusions:

- Application of the TNV-1 through TNV-10 modifier alloys by either high-pressure pack or vacuum pack cementation was characterized by slow deposition rates, inability to transfer tungsten (and presumably molybdenum) to the specimen surfaces, and sintering of the pack particles to the specimen surfaces.
- In general, titanium and vanadium were observed to be beneficial components in the tungsten-base and molybdenum-base modifier alloys applied by slurry techniques, while the addition of chromium was not helpful.
- After siliciding, the TNV-7 (15Ti-35W-15V-35Mo) modifier alloy exhibited the best performance and was the only coating to reproducibly provide 600 hours of protection at both 1600 and 2400 F. In each of the second and third of three experiments involving oxidation of three to five specimens at each temperature, no failures were observed in 600 hours of testing at either temperature. One sample survived 1064 hours of oxidation at 2400 F; failure occurred in the cycle following the slow cooling of the oxidation furnace as a result of an electrical power outage.
- Good oxidation resistance was obtainable without close control of the uniformity of coating thickness and microstructure. Diffusion of silicon completely through the modifier layer and into the substrate during pack siliciding did not appear to diminish oxidation resistance; on the contrary, it appeared to be desirable by way of inhibiting loss of silicon by diffusion into the substrate during long-term oxidation
- Thermal expansion matching of coating and substrate was observed to be less important than the chemical nature of the silicides in determining the cyclic oxidation resistance. Oxide composition (and structure) as well as rates of formation as a function of temperature appeared to be critical factors in the crack healing process.
- Oxidation in excess of 600 hours at 2400 F did not destroy the ductility (measured by a simple bend test) of substrates protected by the silicided TNV-12 (4.7Ti-95.3Mo) or TNV-7 (15Ti-35W-15V-35Mo) modifier alloys.
- The impregnation of the silicided coatings with a finely milled barium borosilicate glass frit was observed to be helpful in providing improvement in the modest oxidation resistance of the tungsten-righ TNV-13 (5Ti-95W) coating at 1600 F.
- The slurry coatings developed for the T222 tantalum-base alloy were also observed to be protective to the Cb752 and D43 columbium-base alloys.
- Use of nickel-coated fine tungsten powders allowed a sizable reduction in both the sintering time and temperature for the tungsten-rich TNV-11 (2.5Ti-97.5W) modifier alloy and also improved the oxidation resistance of the resultant silicide coating.

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RECOMMENDATIONS

Although the silicided TNV-7 slurry coating has demonstrated excellent oxidation resistance and good reliability, additional work is needed to optimize the coating for the protection of the T222 tantalum alloy and the columbium-base alloys; modifications of these coatings might also be protective to molybdenum- and tungsten-base alloys. In view of the need for optimization, the following recommendations are made:

- The chemical composition of the TNV-7 modifier alloy might be optimized by variation of the relative proportions of titanium, tungsten, vanadium, and molybdenum and by the addition of elements such as iron and boron to further modify the composition of the crack-healing oxides.
- The method of application of the modifier alloy might be optimized by investigation of the effects of using prealloyed powder (rather than a mixture of elemental powders), varying the particle size, and employing nickel- or palladium-activated sintering. It would be desirable to develop the dipping application of slurry coatings as a means of coating hardware that cannot be coated by the conventional spray process.
- Useful information would be expected to result from extending the evaluation of the coatings by way of increasing oxidation time and temperature, exposing oxidizing samples to thermal-cycling between moderate and elevated temperatures (e.g., between 1600 and 2400 F), and impact damaging specimens prior to and during oxidation. The effects of coating application and subsequent oxidation upon the mechanical properties of the substrate should be determined.

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R65F-311

SOLAR DIVISION OF INTERNATIONAL HARVESTER COMPANY

May 4, 1965

RESEARCH MATERIAL SPECIFICATION

SHEET, PLATE, AND STRIP: T-222 (Ta-9.6W-2.4Hf-0.01C) ALLOY

1. SCOPE

1.1. Scope. This specification covers T-222 (Ta-9.6W-2.4Hf-0.01C) alloy in sheet, plate and strip form intended for high temperature structural applications.

2. APPLICABLE DOCUMENTS

2.1. Government Documents. None

2.2. Non-Government Documents

ASTM Designation E8-57T (26 December 1957)	Method of Tension Testing of Metallic Materials
ASTM Designation E29-58T (1958)	Recommended Practices for Designating Significant Places in Specified Limiting Values
ASTM Designation E112-61 (1961)	Estimating the Average Grain Size of Metals
AMS 2242A (1 December 1950)	Tolerances, Corrosion and Heat Resistant Sheet, Strip and Plate
MAB-176-M (6 September 1961)	Evaluation Test Methods for Refractory Metal Sheet Materials

3. REQUIREMENTS

3.1. Acknowledgments. The vendor shall mention this specification in all quotations and all purchase order acknowledgments.

3.2. Manufacture. Material covered by this specification shall be made from ingots which have been double vacuum melted by the electron beam and/or consumable electrode arc melting processes. Breakdown operations shall be performed with conventional extrusion, forging and rolling equipment normally found in primary ferrous and nonferrous plants.

3.3. Processing. The starting stock size, processing temperatures, percentages of reduction, in-process annealing temperatures and times shall be selected by the vendor to achieve the grain size range specified in paragraph 3.6 and mechanical properties specified in paragraph 3.7. The amount of total reduction from the turned

ingot to the final product shall exceed 75%. The amount of final reduction for each mill product, imparted just prior to the final vacuum heat treatment and the total reduction since the previous recrystallization anneal, shall be reported in the certificate of compliance.

3.4. Condition

3.4.1. General. The finished product shall be supplied in the recrystallized condition throughout the cross-sectional area to the grain size range specified in paragraph 3.6.

3.4.2. Heat Treatment. All annealing shall be carried out in a vacuum of less than 1×10^{-5} torr. The conditions of final annealing shall be reported in the certificate of compliance.

3.4.3. Contamination. All items are to be free of contamination or internal oxidation. After final heat treatment, the material shall be examined metallographically for evidence of possible contamination caused by unsatisfactory heat treating atmospheres or processing conditions. A microhardness traverse shall show a hardness increase not greater than 50 VHN from the center to the surface of a cross sectional sample of the final product. At the discretion of the purchaser, samples taken to include at least one surface of the final product, and not exceeding 0.050-inch thick, may be chemically analyzed by the purchaser for oxygen, nitrogen, hydrogen and carbon. The analyses shall not exceed the limits set forth in paragraph 3.5.3. Any indication of contamination shall be cause for rejection of all material represented by that sample. The material shall be acceptable if the contaminated layer is completely eliminated before shipment by a machining operation within the specified dimensions and tolerances.

3.5. Chemical Composition

3.5.1. Ingot/Billet Composition. The chemical composition of ingots and billets for conversion to finished products shall conform to Table I (page 3). A minimum of four analyses shall be obtained as follows: ingot top-center, mid-radius and edge, and ingot bottom-center; all analyses must conform to ranges stated in Table I.

3.5.2. Final Product Composition. The manufacturer's ingot analyses shall be considered the chemical analysis for products supplied under this specification (Table I) except carbon, oxygen, nitrogen and hydrogen content which shall be determined in the finished product.

3.5.3. Check Analysis. Finished product analysis shall not exceed the following limits or variations:

Element	Check Analysis Limits, Max., ppm	Permissible Variations in Check Analysis, ppm
Carbon	80 min; 175 max.	± 10
Oxygen	150	+ 20
Nitrogen	75	+ 10
Hydrogen	10	+ 2

TABLE I

CHEMICAL COMPOSITION

T-222 (Ta-9.6W-2.4Hf-0.01C) ALLOY

Element	Minimum Content ppm	Maximum Content ppm
Carbon	80	175
Nitrogen	-	50
Oxygen	-	100
Hydrogen	-	10
Columbium	-	1000
Molybdenum	-	200
Nickel	-	50
Cobalt	-	50
Iron	-	50
Vanadium	-	20
Tungsten	8.5 $^{w}/_{o}$	10.5 $^{w}/_{o}$
Hafnium	2.2 $^{w}/_{o}$	2.8 $^{w}/_{o}$
Tantalum	Remainder	-

3.6. Grain Size. The grain size of the final products shall conform to the following limits:

Product Thickness, Inches	Minimum Allowable ASTM Grain Size No.	Allowable Spread in ASTM Grain Size Nos. in Any One Item	% R_x Minimum
0.010 to 0.060	6	2	100
0.060 to 0.125	4	2	100
0.125 to 0.187	4	2	100
0.187 to 0.500	3	3	95
0.500 to 1.0	3	3	95
Greater than 1.0	3	3	90

3.7. Mechanical Properties. The final product shall satisfy the following mechanical property requirements:

3.7.1. Room Temperature Tensile Properties. Representative samples of the material in final form shall be capable of the following property limits at room temperature (65° - 85°F).

Ultimate Tensile Strength, ksi		0.2% Yield Strength, ksi		Elong., % in 4D
Minimum	Maximum	Minimum	Maximum	Minimum
105	125	100	120	20

3.7.2 Bend Ductility. Representative samples of the materials in final form shall withstand the following bend test at room temperature without failure when tested according to procedures described in the most recent revision of the Materials Advisory Board report MAB-176M, "Evaluation Test Methods for Refractory Metal Sheet Materials." The samples shall be sectioned with the long axis of the bend specimens perpendicular to the final rolling direction.

3.7.2.1. Sheet 0.060 inch in thickness and under shall be bent over a 1T radius through 105° at a ram speed of 1 inch per minute and subsequently flattened for a total bend of 180°.

3.7.2.2. Sheet over 0.060 inch to 0.187 inch in thickness shall be bent over a 1T radius through 105° at a ram speed of 1 inch per minute.

3.8. Tolerances

3.8.1. Plate

3.8.1.1. Definition. Plate includes material 6 inches wide or over and 0.187 inch or more in thickness.

3.8.1.2. Dimensions. Plate dimensions shall conform to the following tolerances:

Thickness	Width	Length
± 0.025 inch or ± 5%, whichever is less	± 0.125 inch	± 0.125 inch

3.8.1.3. Flatness. Flatness tolerance on plate shall conform to AMS 2242A, "Tolerances, Corrosion and Heat Resistant Sheet, Strip and Plate."

3.8.2. Sheet

3.8.2.1. Definition. Sheet includes material 6 inches wide or over and up to 0.187 inch in thickness.

3.8.2.2 Dimensions. Sheet dimensions shall conform to those presented in Table III

3.8.2.3. Flatness. See paragraph 3.8.3.3.

3.8.3. Strip.

3.8.3.1. Definition. Strip includes material 6 inches wide or less and up to 0.187 inch in thickness.

3.8.3.2. Dimensions. Strip dimensions shall conform to those presented in Table II.

3.8.3.3. Flatness. Total deviation from flatness of sheet and strip shall not exceed 6% as determined by the formula:

$$\frac{H}{L} \times 100 = \% \text{ Flatness Deviation}$$

where

H = maximum distance from a flat reference surface

and

L = minimum distance from this point to the point of contact with the reference surface.

The actual values shall be reported. In determining flatness, the sheet shall not be subject to external pressure at any point but shall lie freely on a flat surface during measurement. Oilcanning will be reported. An estimate of the extent (area, height, etc.,) of these defects shall be made.

3.9. Reports. The manufacturer shall supply at least three copies of a report showing non-proprietary manufacturing methods, processing conditions, and test procedures and results for each lot of material in the shipment. The report shall also include the number of the specification and the purchase order or contract number.

4. MAXIMUM ALLOWABLE DISCONTINUITIES

4.1. General. The finished product shall be visibly free from oxide or scale of any nature, grease, oil, residual lubricants, and other extraneous materials. Cracks, laps, seams, gouges, and fins shall be unacceptable.

4.2. Porosity and Inclusions. Indications of internal porosity and non-metallic inclusions greater than 0.020 inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Those indications in the range 0.010 inch to 0.020 inch or 2% of the thickness, whichever is smaller, shall be a minimum of 0.500 inch apart; those indications less than 0.010 inch shall be a minimum of 0.12 inch apart.

TABLE II

DIMENSIONAL TOLERANCES FOR SHEET AND STRIP

Material Thickness, Inch	Width, Inches	Thickness Tolerances, Inch
0.010-0.019	to 24	± 0.001
0.020-0.039	to 24	± 0.0015
0.040-0.059	to 24	± 0.002
0.060-0.089	to 24	± 0.003
0.090-0.0129	to 24	± 0.004
0.130-0.159	to 24	± 0.005
0.160-0.187	to 24	± 0.010

Material Thickness, Inch	Width Tolerances, Inch
0.010-0.059	+ .031, -0
0.060-0.125	+ 0.046, -0
0.126-0.187	+ 0.125, -0

Material Thickness, Inch	Length Tolerances, Inch
0.010-0.059	+ 0.046, -0
0.060-0.125	+ 0.062, -0
0.126-0.187	+ 0.125, -0

4.3. Surface Rework. All surface pores, gouges and other defects deeper than 0.005 inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Surface imperfections may be faired smooth to remove any notch effect provided dimensional tolerances are still maintained.

5. QUALITY ASSURANCE PROVISIONS

5.1. Vendor Responsibility. The manufacturer shall make all tests and inspections of the material covered by this specification before shipment, unless otherwise specified. All test and inspection results shall be furnished to the purchaser.

5.2. Customer Review. The purchaser or his representative may witness the testing and inspection of the material. The manufacturer shall give the purchaser

ample notice of the time and place of designated tests. If the purchaser's representative is not present at this time and a new date is not set, the requirement for purchaser's inspection at the place of testing is waived. When the purchaser's representative is present at the appointed time and place, the manufacturer shall afford him, without charge, all reasonable facilities to assure that the material is being furnished in accordance with this specification. This inspection shall not interfere unnecessarily with production operations.

5.3. Sample Selection.

Care shall be exercised to insure that the samples selected for testing and chemical analyses are representative of the material and uncontaminated by the sampling procedure. Samples for the determination of mechanical properties shall be sellected so as to consume a minimum amount of material, i.e., specimens may be taken transverse to the final working direction from plate and sheet and from strip if of sufficient width. If there is any question about the sampling technique or the analysis, the methods for sampling and analysis shall be those agreed to by the buyer and seller. The location of test samples shall be reported in the certificate of compliance.

5.4. Test Methods

5.4.1. Chemical Analysis. Chemical analyses shall be conducted by mutually acceptable procedures, such as the vacuum fusion methods for gases, the combustion method for carbon, and the spectrochemical methods for metallic elements.

5.4.2. Tensile Test. The tension test shall be conducted in accordance with ASTM Designation E8-57T, "Methods of Tension Testing of Metallic Materials." Yield strength shall be determined by the offset (0.2%) method. The tensile properties shall be determined using a strain rate of 0.005 inch per inch per minute up to 0.6% offset and then 0.050 inch, plus or minus 0.020 inch, per inch per minute to fracture.

5.4.3. Grain Size. Grain size determinations shall be made according to ASTM Specification E112-61, "Estimating the Average Grain Size of Metals."

5.5. Number of Tests Required. Representative test specimens from the finished product representing each ingot and each lot of material shall be taken to determine conformity to this specification. The minimum frequency of these tests shall be:

Finished Product Chemistry - one per lot per ingot

Tensile Test - two per lot per ingot

Bend Test - two per lot per ingot

Grain Size - two per lot per ingot

Microhardness Traverse - one per lot per ingot

5.6. Retest and Rework

5.6.1. Surface Contamination. Any sample or specimen exhibiting obvious surface contamination or improper preparation which disqualifies it as a truly representative sample shall be replaced with a new sample.

5.6.2. Rework. If inspection and test results of a lot do not conform to the requirements of this specification, the lot may be reworked at the option of the manufacturer. The lot shall be acceptable if all test results, after reworking, conform to this specification.

6. PREPARATION FOR DELIVERY

6.1. Identification. Each bundle, box, or carton shall be legibly and conspicuously marked or tagged with the number of this specification, purchase order or contract number, type, ingot number, lot number, nominal size, and the gross, net, and tare weights. When each bundle, box or carton consists of components from more than one ingot number or lot number, each component shall be identified individually.

6.2. Packing. Each individual item shall be wrapped in heavy gauge polyethylene film or other similar material and packed in a manner assuring safe delivery when properly transported by any common carrier.

7. DEFINITIONS

7.1. Lot. A lot shall include all material of the same size, shape, condition and finish from one heat of material and which has received the same processing, has been annealed in the same vacuum annealing charge and has been processed simultaneously in all operations in which temperatures may reach 500°F or above. When process temperatures and environments are closely controlled or when closely adjacent sizes receive similar processing, lots may be combined for chemical, tensile and stress-rupture tests only, provided prior written approval has been obtained from the Solar Division of International Harvester Company.

7.2. Check Analysis. An analysis may be requested by the purchaser of the metal after it has been processed into finished mill forms, to verify the composition within a heat or lot. Check analysis tolerances do not broaden the specified heat analysis requirements but rather cover variations between laboratories in the measurements of the chemical content.

7.3. Significance of Numerical Limits. For determining compliance with the specified limits for requirements of the properties listed below, and observed value or a calculated value shall be rounded off using the rounding-off method in ASTM Designation E29-58T, "Recommended Practices for Designating Significant Places in Specified Limiting Values."

Test	Rounded-Off Unit for Observed or Calculated Value
Chemical composition and dimensional tolerances (when expressed decimally)	Nearest unit in the last right-hand place of figures of the specified limit
Tensile strength	Nearest 100 psi
Elongation	Nearest 1%

APPENDIX B

PROCEDURES FOR HYDRIDING TITANIUM AND VANADIUM

PROCEDURE USED IN HYDRIDING TITANIUM AND TITANIUM ALLOYS

The arc-melted titanium alloy buttons or the titanium sponge (-20 +50 mesh) were placed in an unlined Type-321 stainless steel or Inconel retort which was subsequently sealed by fusion welding. Following pressurizing the retort to 5 psig with argon, the welds were soap-bubble leak checked. The retort and the titanium-filled gettering unit were vacuum-argon cycle purged a minimum of six times. While filled with argon, the gettering unit was heated from 1600 to 1650 F, at which point the entire system was evacuated and back filled with hydrogen. The retort was then vacuum-hydrogen cycle purged three times at room temperature before the hydrogen pressure in the retort was adjusted to five psig preparatory to placing the retort in a furnace preheated to 1250 F. The retort was left in the furnace for one hour; however, the hydriding was completed in 20 to 30 minutes, as indicated by the flow meter in the hydrogen supply line. The hydrogen pressure was maintained at five psig while the retort was removed from the furnace and allowed to cool to room temperature.

PROCEDURE USED IN HYDRIDING VANADIUM

Vanadium granules were pickled in nitric acid and then rinsed in distilled water and methanol. After vacuum drying at room temperature, the vanadium was placed in the inner box of a double-wall columbium alloy box (the 0.25-inch wide space between the boxes was filled with titanium sponge in an effort to provide some gettering protection). The double wall box was then sealed in an Inconel retort. After pressurization and soap-bubble leak checking the retort, vacuum-hydrogen cycle purging was conducted. In earlier experiments titanium-gettered hydrogen was used while in later experiments hydrogen obtained from palladium-alloy purifier was used. With the hydrogen pressure at approximately five psig, the retort was placed in a furnace preheated to 1700 F for a period of 1.5 hours. After about ten minutes, the pressure in the retort dropped well below atmospheric pressure as a result of the hydrogen consumption by the titanium (in the absence of titanium in the retort, insertion into the furnace should be preceded by partial evacuation because the slow rate of hydrogen pickup by vanadium might otherwise allow the retort pressure to become excessive during heatup). After the retort had been in the furnace approximately 1.5 hours at

1700 F the temperature of the furnace was dropped to 1100 F for a one-hour period prior to removing the retort from the furnace with the hydrogen pressure still maintained at five psig.

In one vanadium hydriding experiment the columbium box was not embrittled by the hydrogen while in a second experiment the anticipated severe embrittlement was observed (lining the Inconel retort with pieces of molybdenum or tungsten sheets in place of the columbium box would undoubtedly prove to be more satisfactory).

APPENDIX C

SLURRY PREPARATION PROCEDURE

A description of the process used in preparing the slurries based on a vehicle containing an ethyl cellulose binder is given in the following paragraphs.

Thirty grams of ethyl cellulose[1] was dissolved in a mixture of 200 cc of secondary butyl alcohol and 800 cc of zylene. One thousand cc of Stoddard solvent (a petroleum distillate having a boiling point range of 312 to 390 F) was added to this solution to obtain the desired vehicle, which was designated E4.

Between 180 and 220 cc of the vehicle and the appropriate quantity of powdered elemental metals needed to give a fluids-to-solids true volume ratio of 2.5 were added to a 1-quart low-silica ball mill[2] that was slightly more than half filled with balls.

After the ball mill had been allowed to tumble for a period of 20 to 24 hours, the slip was transferred to a preweighed graduated cylinder to allow determination of the specific gravity (by weighing the observed volume of slip) prior to spray application.

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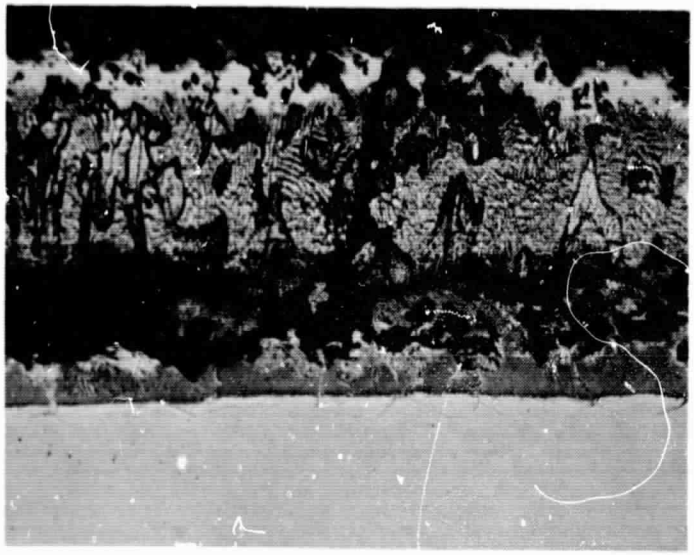
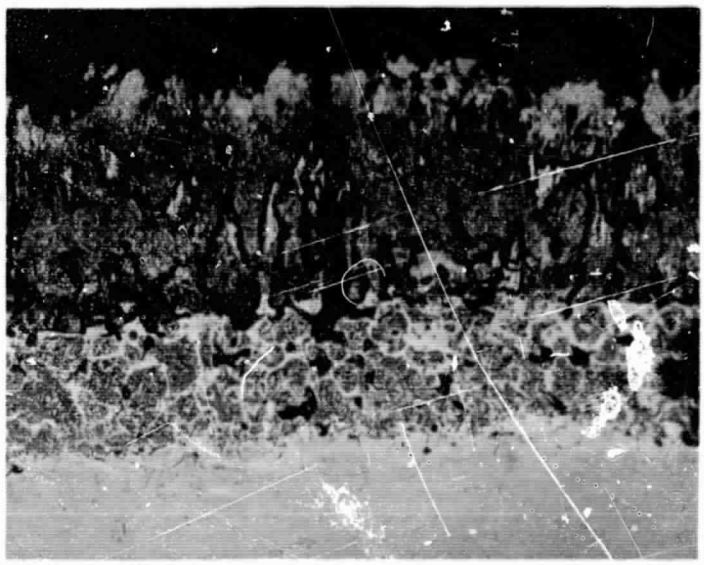
1. N-200 grade ethyl cellulose was supplied by the Polymers Department, Hercules Powder Company, Wilmington, Delaware.
2. Burundum-fortified ball mills and balls were supplied by the U.S. Stoneware Company, Akron, Ohio.

APPENDIX D

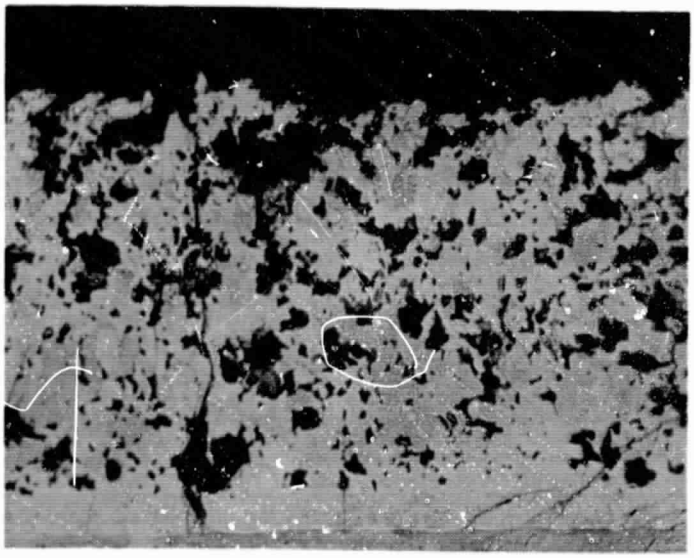
ADDITIONAL METALLOGRAPHY



Experiment Number:	T_2-158
Coating:	TNV-2 (60Ti-40W)
Sintered:	15 Hours at 2435 F
Silicided:	7.5 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

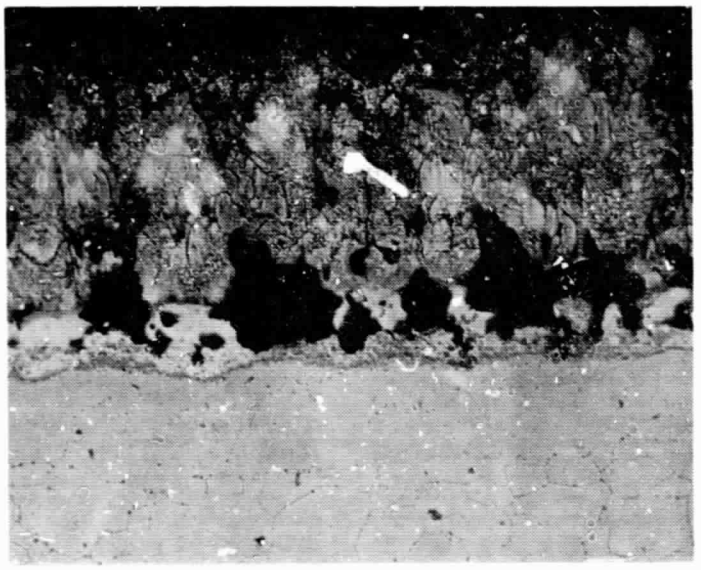


Experiment Number:	T_2-172
Coating:	TNV-4 (60Ti-40Mo)
Sintered:	15 Hours at 2760 F
Silicided:	7 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

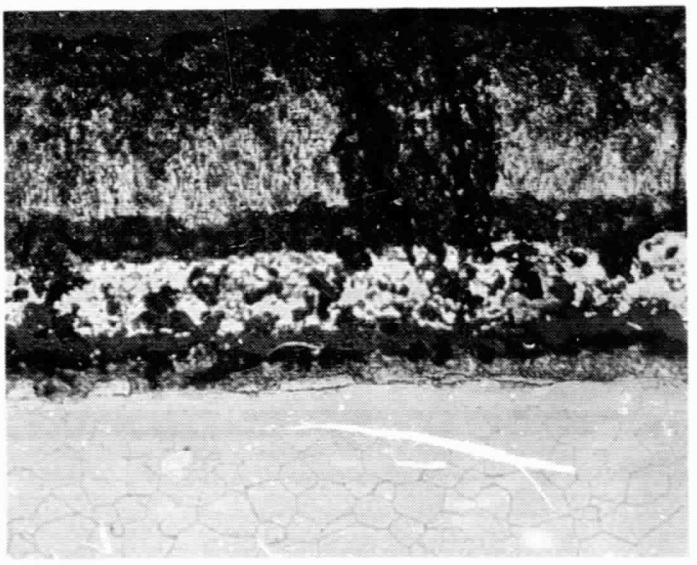


Experiment Number:	T_2-173
Coating:	TNV-5 (30Ti-35W-35Mo)
Sintered:	15 Hours at 2760 F
Silicided:	7 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

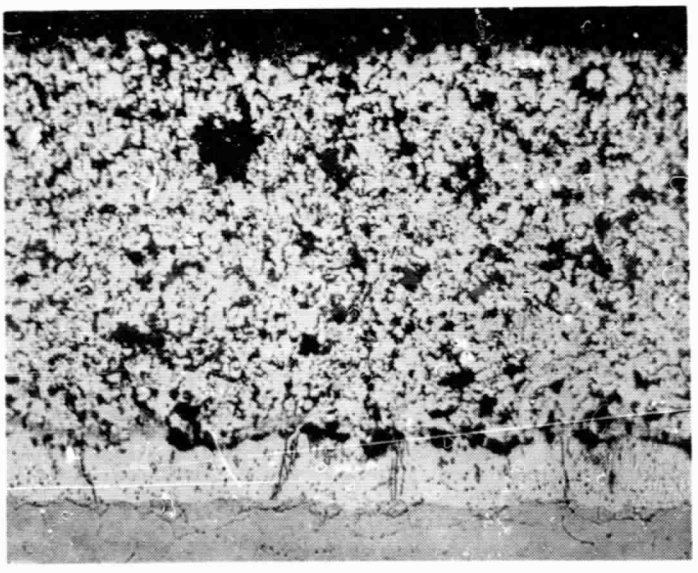
FIGURE D-1. AS-SILICIDED MICROSTRUCTURE OF TNV-2, -4, AND -5 COATINGS



Experiment Number:	179
Coating:	TNV-8 (30Ti-35W-35Cr)
Sintered:	0.5 Hour at 2610 F
Silicided:	7 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

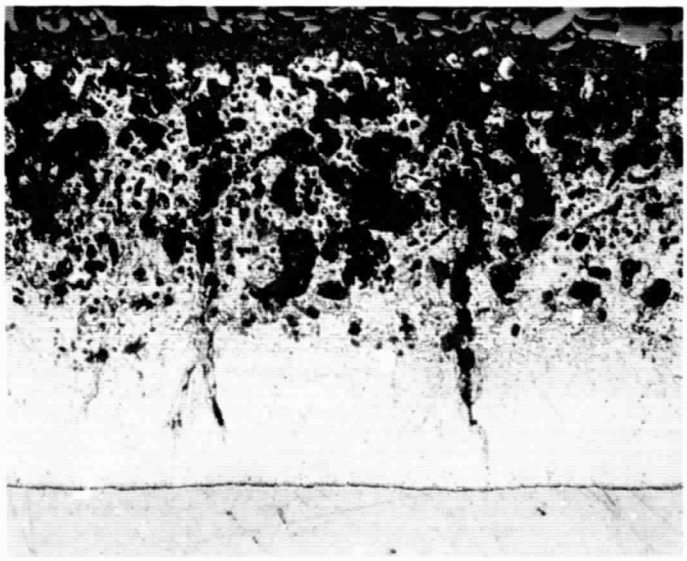


Experiment Number:	181
Coating:	TNV-10 (30Ti-30V-40Cr)
Sintered:	0.5 Hour at 2610 F
Silicided:	7 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

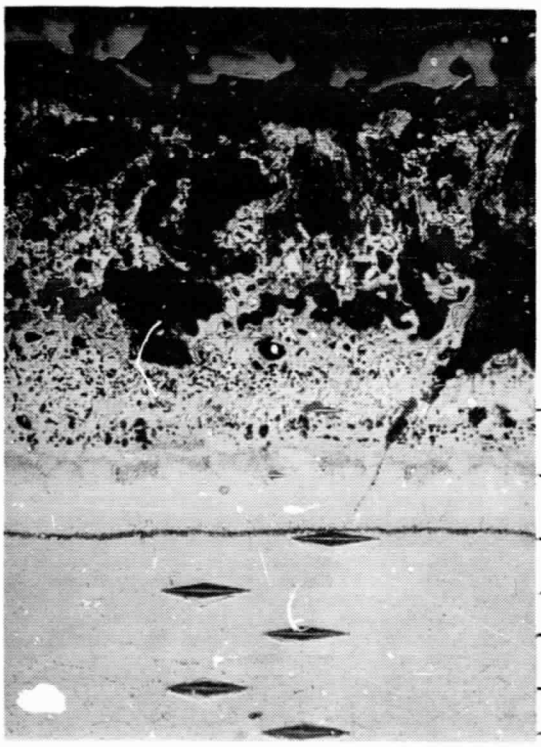


Experiment Number:	T_2-155
Coating:	TNV-11 (2.5Ti-97.5W)
Sintered:	15 Hours at 2760 F
Silicided:	7 Hours at 2150 F
Etchant:	2% HF 3% HNO_3 95% H_2
Magnification:	250X

FIGURE D-2. AS-SILICIDED MICROSTRUCTURE OF TNV-8, -10, AND -11 COATINGS



Experiment Number:	T_2-180
Substrate:	T222
Coating:	TNV-9 (30Ti-35Mo-35Cr)
Oxidation Time:	252 Hours
Oxidation Temperature:	2400 F
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated NF 20% Concentrated HNO_3
Magnification:	250X



Experiment Number:	T_2-143
Substrate:	T222
Coating:	TNV-3
Oxidation Time:	611 hours
Oxidation Temperature:	2400 F
Etchant:	60% Lactic Acid (85% solution) 20% Concentrated HF 20% Concentrated HNO_3
Magnification:	250X

FIGURE D-3. TNV-3 AND TNV-9 SLURRY COATINGS OXIDIZED IN EXTENDED 200 HOUR TEST