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DEVELOPMENT OF PROTECTIVE COATINGS FOR TANTALUM T-222 ALLOY

By

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TABLE OF CONTENTS

Page

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ABSTRACT

A variety of single phase and binary intermetallic compounds were electrophoretically deposited upon tantalum T-222 alloy both with and without intervening barrier layers of tungsten and rhenium. These coatings were tested for long term, one atmosphere cyclic oxidation resistance at 1500°F and 2400°F. Promising systems were examined in more detail by metallography and by electron microprobe analysis.

Of the systems studied to date, $MoSi_2$-30VSi_2 has yielded the best results. Two of eight samples of this coating which were tested survived 600 hours exposure at both 1500°F and 2400°F, including approximately 30 cycles to room temperature without failure, Other binary silicide systems containing either WSi_2 or $MoSi_2$ combined with 3-30%$CrSi_2$ or $TiSi_2$ have performed well at 2400°F, but are subject to pest failure at the lower test temperature.

TABLE OF CONTENTS (Continued)

Page

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

LIST OF ILLUSTRATIONS (Continued)

LIST OF ILLUSTRATIONS (Continued)

1. INTRODUCTION

This is the Final Summary Report on Contract NAS 3-7613, covering the period 28 May 1965 through 31 July 1966. This report has been assigned NASA No. CR 54578. The Project Manager and Research Advisor for this program were R. E. Oldrieve and S. J. Grisaffe, respectively, of the **NASA** Lewis Research Center. Personnel at Vitro contributing to the performance of this program included:

Dr. S. Grand	Program Manager
M. Ortner	Project Leader
S. Klach	Senior Chemist
H. Tamm, D. Adams, T. Sharpe	Research Technicians

The ultimate goal of this program is to develop a coating system for T-222 alloy which will permit its use as a turbine stator vane for advanced jet engines. The objective of the present contract was the development of coatings for T-222 which protect the alloy from interstitial embrittlement, and which provide up to 600 hours protection from cyclic air oxidation over the temperature range 1500°-2500°F. The following combinations of oxidation resistant coatings and diffusion barriers were investigated for this application:

Diffusion Barrier	Surface Coating	Diffusion Barrier	Surface Coating
Tungsten	ZrB_2	Rhenium	$ReSi_2$
Tungsten	$TaAl_3$	Rhenium	ZrB_2
Tungsten	WSi_2	Rhenium	Hf-27Ta
Tungsten	$MoSi_2$	Rhenium	WSi_2
Tungsten	$MoSi_2+VSi_2$, $TiSi_2$ or $CrSi_2$	Rhenium	$MoSi_2+VSi_2$ or $TiSi_2$
Tungsten	WSi_2+VSi_2, $TiSi_2$, or $CrSi_2$		

Many of the silicide systems were also prepared as coatings and tested in the absence of a barrier.

All coatings studied in this program were prepared by electrophoretic deposition and subsequent vacuum or inert atmosphere sintering.
This report has been assigned Vitro Laboratories' internal number VL-2403-15-0.

2. SUMMARY

A variety of electrophoretically deposited, intermetallic compound coating systems and diffusion barrier layers were screened to identify potential coating materials for the protection of tantalum T-222 alloy from cyclic oxidation for periods up to 600 hours at 1500°F and at 2400°F. Based upon the initial screening tests, Hf-27Ta, $TaAl_3$, ZrB_2, and $ReSi_2$ surface coatings, and rhenium barrier layers were eliminated from further study and additional work was performed on single phase and binary metal silicide coatings containing $MoSi_2$ or WSi_2 either alone, or combined with $CrSi_2$, $TiSi_2$, or VSi_2.

In subsequent tests, a few sub-size (1" x 0.5" x 0.030") test coupons coated with the systems WSi_2, $MoSi_2$, $MoSi_2$-3VSi_2, and $MoSi_2$-3$TiSi_2$, when post siliconized and preoxidized prior to oxidation testing, were found to provide protection for up to 600 hours exposure at 1500°F and at 2400°F. The results were erratic, however, and nonreproducible on full size (1" X 2" X 0.060") test specimens. In all four systems edge and corner failures were frequent and most specimens tests at 1500°F were found to be susceptible to pest failure.

In an effort to reduce the frequency of pest failures at 1500°F, binary silicide systems based upon WSi_2 and $MoSi_2$ were investigated in which the concentration of the second phase (VSi_2, $CrSi_2$, $TiSi_2$) was increased to 10-30%. Among the systems tested, $MoSi_2$-30VSi_2 gave the best performance with two specimens surviving 600 hours (including 30 cycles to room temperature) at 1500°F and at 2400°F without failure, three specimens surviving 100-200 hours oxidation at each temperature prior to edge or corner failure, and three specimens surviving 12-100 hours at each temperature before failure. Four specimens from the system WSi_2-30VSi_2 also survived 600 hours exposure at 2400°F without failure, but gave much poorer results at 1500°F.

Electron microprobe analysis was made of selected specimens from most of the silicide coating systems. This technique yielded valuable information regarding the distribution of coating and alloy elements and the depth of diffusion into the substrate, but gave little insight into the reason for the poor reproducibility of the earlier tests.

3. EXPERIMENTAL

3 1 Analysis of Coating And Substrate Materials

In preliminary screening studies of the candidate coating systems, a variety of commercial powders were electrophoretically deposited on 0.05 inch Ta-10W and 0.030 in, **or** 1/16 in. T-222 alloy, The specifications for the purchased powders are listed below, and analyses and properties of the coating materials and. of the tantalum alloy sheet materials are listed in Tables 1 through 4.

Specifications For Coating Materials

Material	Specifications
W	99.9%, 2μ powder
ZrB_2	98.9%, 5-8μ powder
$TaAl_3$	98.5%, -100 mesh powder
WSi_2	99.670, <10μ powder
$MoSi_2$	99.99%, -325 mesh, <0.5% free Si and Mo
VSi_2	99.5%, <10μ, <50 ppm Ca, <0.5% free Si and V
$TiSi_2$	98.8%, <10μ, <0.5% free Si and Ti
Re	99+%, 1-10μ powder
Kf/ 27Ta	98%, single phase <10μ powder
$ReSi_2$	99+%, <10μ powder

TABLE 1

TANTALUM ALLOY T-222 INGOT ANALYSIS

Heat No. 65041-T222

INGOT ANALYSIS

COMPOSITION IN PERCENT

Hf	2.9	2.7	2.7	2.4
W	8.8	8.6	9.0	9.4
Ta	88.3	88.7	88.3	88.2

IMPURITY CONTENT, PPM

Al	<20	<20	<20	<20
C	110	90	110	120
Cb	525	600	590	445
Cd	<5	<5	<5	<5
Co	<10	<10	<10	<10
Cr	<20	<20	<20	<20
Cu	<40	<40	<40	<40
Fe	<40	<40	<40	40
Mg	<20	<20	<20	<20
Mn	<20	<20	<20	<20
Mo	30	40	30	30
N	20	20	25	20
Ni	<20	<20	<20	<20
Pb	<20	<20	<20	<20
Si	<40	<40	<40	<40
Sn	<20	<20	<20	<20
Ti	<50	<50	<50	<50
V	<20	<20	<20	<20
H	3.1			3.2
O	<50			<50

HARDNESS IN BHN

Average	254
Range	248 - 262

PRODUCT CHEMISTRY, PPM

C	180
O	50
N	8
H	2

TENSILE TEST RESULTS AT ROOM TEMPERATURE

Sample	Tensile Strength	Yield Strength (0.2% Offset)	Elongation % in 2"
Long. #1	114,000 psi	102,000 psi	22.5
Long. #2	114,000 psi	101,000 psi	22.5
Trans. #1	117,000 psi	103,000 psi	22.5
Trans. #2	118,000 psi	106,000 psi	21.5

ASTM GRAIN SIZE

7.5

PRODUCT HARDNESS, DPH

Sample	Center	
#1	301	302
#2	309	317

BEND TEST RESULTS AT ROOM TEMPERATURE

Trans. - Acceptable - Samples Bent
Long. - Without Cracking

TABLE 2

SPECTROGRAPHIC ANALYSIS OF BARRIER AND SURFACE COATING MATERIALS

	Tungsten	Rhenium	ungsten Disilicid	olybdenun Disilicide	Vanadium Disilicide	Titanium isilicide	Tantalum luminide	Hafnium-7 Tantalum	Zirconium Diboride
Mn	.001 Max	ND	0.002	0.003	1.01-0.1	0.1 -1.0	0.003	0.01 -0.1	0.001-0.01
Cr	.001-0.0	ND	0.15	0.07	1.05-0.5	3.01-0.1	0.05	0.001 Max	1.01 -0.1
Ni	.001 Max	ND	0.005	0.007	1.5 -5.0	0.05-0.5	0.007	0.5 - 5.0	1.01 -9.1
cu	.001 Max	<0. 001	0.007	ND	1.01-0.1	3.1 -1.0	0.05	0.01 - 0.1	1.001 Max
Fe	.01-0.1	<0. 001	0.20	0.09	1.1 - 1.0	3.1 -1.0	0.15	3.001-0.01	1.01 -0.1
Nb	ND	ND	ND	ND	1.01 Max	ND	0.01	0.01 Max	1.01 Max
CO	.01 Max	ND	0.003	ND	1.01 Max	0.01 Max	ND	0.01 Max	1.01 Max
Al	.01 Max	ND	0.08	0.02	1.1 -1.0	0.1 -1.0	High	0.01-0.1	0.01 Max
Mo	1.001 Max	ND	0.05	High	1.5 -5.0	0.1 -1.0	0.04	0.05-0.5	1.01 -0.1
V	.001 Max	ND	0.001	0.003	High	0.05-0.5	0.001	0.001 Max	0.001 Max
W	High	ND	High	ND	1.1 Max	0.1 Max	ND	0.1 Max	1. 1 Max
Re	ND	High	ND	ND	ND	ND	ND	ND	ND
Ti	1.001 Max	ND	0.005	0.003	1.1 -1.0	High	0.02	0.001 Max	1-10
B	1.001 Max	ND	0.007	ND	1.01-0.1	0.01-0.1	0.07	0.01 -0.1	High
Zr	.001 Max	ND	0.003	ND	1.1 -1.0	0.001-0.0	0.02	0.5 -5.0	High
Si	.005-0.0	<0. 001	High	High	High	High	0.15	0.001-0.1	0.001 Max
Hf	ND	ND	ND	ND	ND	ND	ND	High	ND
Ta	ND	ND	ND	ND	ND	ND	High	High	ND
Mg	ND	<0. 001	0.001	0.005	ND	ND	0.002	ND	ND
Ca	ND	ND	0.005	0.005	ND	ND	ND	ND	ND
Na	ND	ND	0.002	ND	ND	ND	ND	ND	ND
N	—	—	—	—	—	—	—	0.006	—
O	—	—	—	4.13	—	—	1.17	0.2	—

ND - Not Detected

TABLE 3

INGOT ANALYSIS OF 0.030 in. T-222 SHEET

	Composition in Percent	
Metal	Top	Bottom
W	9.0	9.4
Hf	2.7	2.4
Ta	Balance	

T-222 INGOT IMPURITIES IN PPM

Impurity	Top	Bottom
C	110	120
O	<50	<50
N	20	20
H	3.1	3.2
Cb	525	445
Fe	<40	40
Mo	30	30
Ni	<20	<20

TABLE 4

CERTIFIED ANALYSIS OF ANNEALED, 0.050 in. Ta-10W STRIP

(Tungsten Analysis = 9.8%)

Element	ppm	Element	ppm
O	89	Fe	15
N	31	Mo	30
C	17	Nb	<25
Al	<25	Ni	<5
Cr	<5	Ti	<5

3.2 Temperature Measurement Calibration

A multi-tube Globar-heated furnace and a Brew high-vacuum resistance heated furnace were used for sintering and for oxidation testing in this program. The temperature of the Clobar furnace was indicated by a Pt/10Rh-Pt/30Rh thermocouple and the accuracy of the furnace thermocouple was checked periodically against a standard thermocouple of the same type. The standard thermocouple is a certified instrument, whose EMF at eight temperature points between 1450°F and 2900°F was obtained by comparison with a primary standard. A typical calibration curve for indicated furnace temperature (laboratory thermocouple) versus actual furnace temperature (standard thermocouple) is shown in Figure 1.

In calibrating the Brew Vacuum Furnace, Model 1064, the temperature of a specimen positioned at the geometric center of the heat shield was determined by observing the melting points of the pure metals - copper (1981°F), nickel (2647°F), palladium (2826°F), rhodium (3571°F), and hafnium (3902°F). Strips of these metals, 0.001 - 0.002" x 1/8" x 1/2" long, were cut into triangles and the bases bent to provide a support stand. The strips were placed into a dished tungsten pellet which was located on a tungsten support stand.

Each strip was heated to near its melting point and held for approximately 5 minutes to reach equilibrium. The temperature was then raised in approximately 68°F increments and held for 5 minutes after each incremental increase until melting occurred. A duplicate determination was made using smaller incremental increases in temperature between the last two settings of the previous run to further refine the location of the melting point.

The Brew Furnace Temperature Recorder reads percent of maximum power input to the heating element. A chart was prepared in which the percent power input is plotted against the melting points of the foregoing pure metals. This data is shown in Figures 2 and 3.

3.3 Coating Development

3.3.1 General Procedures

The coating development portion of this program consisted of determining optimum processing conditions for various surface and barrier coatings on tantalum-base alloys (Ta-10W and T-222) with and without an intervening tungsten or rhenium barrier layer. **For** the purposes of this report, the coatings investigated are divided into four groups. Coatings discussed under each group are as follows:

Group I	Tungsten and Rhenium Barrier Layers
Group II	WSi_2 and $MoSi_2$ Coatings containing low concentrations (0, 1%, and 3%) of VSi_2 and $TiSi_2$ additives.
Group III	WSi_2 and $MoSi_2$ Coatings containing 30% VSi_2 or $TiSi_2$, and 20% $CrSi_2$ additives.
Group IV	$ReSi_2$, ZrB_2, $TaAl_3$ and Hf-27Ta Coatings

All coatings were electrophoretically applied to the tantalum substrates for 2-5 minutes at 100 Volts DC and approximately 20 ma from a dispersion of 50 grams of solids in a medium of the following composition:

0.81 liters	of 60 wt % isopropanol - 40 wt % nitromethane
1 gram	zein activator
50 mgs	$Co(NO_3)_2 \cdot 6H_2O$ (stabilizer)

Prior to coating, the powders (with the exception of tungsten and rhenium which were used in the as-received condition) were ballmilled for 36 hours under isopropanol in a chromium steel jar, leached with dilute acid, to remove metallic contaminants, washed and dried. The substrates used in this program were sheared from either T-222 or Ta-10W sheet stock and were tumbled for 24 hours in an alumina mill containing water and Burundum cylinders to radius the edges and corners. This treatment yielded specimens with an approximate 60 mil radius on the corners and a 30 mil radius on the edges. All specimens were then sandblasted with 60 grit alumina, washed, and degreased with trichloroethylene. For the preliminary studies, 1 in. X 0.5 in. X 0.030 in. (sub-size) test coupons were used while for the final evaluation studies specimens 2 in. X 1 in. X 0.060 in. (full size) were employed. All of the full size specimens were stress-relieved at 2550°F **for** one hour in a vacuum prior to coating.

3.3.2 Group I - Tungsten and Rhenium Diffusion Barriers

Tungsten and rhenium barrier coatings were electrophoretically deposited upon Ta-10W and T-222 sub-size test panels from dispersions of 20 grams of the metal powder contained in 250 ml isopropanol, 100 ml nitromethane, 0.4 grams of zein, and a trace of electrolyte. The resultant coatings were isostatically densified at a pressure of 20 tsi and fired over a range of conditions as indicated in Table 5 to yield an approximately 0. 5 mil-thick sintered film. Photomicrographs of typical tungsten and rhenium coatings are shown in Figures 4 - 7. Based upon the photomicrographic evidence, a sintering cycle of 3 hours at 3630°F under reduced pressure (0.01 micron) was selected as optimum and all barrier layer coatings used in later phases of the program were prepared by this procedure. After preparation of the barrier coatings by this method, the substrates remained ductile in bend tests, and no subsurface hardening of the substrate could be detected by microhardness measurements. No diffusion of the barrier layers into the substrates could be detected in the unetched specimens by optical microscopy or by electron microprobe analysis.

In order to determine the effect of high temperature (3630°F) sintering on the physical properties of T-222 alloy, a comparative tensile test was performed using a T-222 alloy 1/4-20 stud in the as-manufactured condition and an uncoated specimen after heat treatment at 3630°F for 3 hours at 0. 01μ pressure. The tensile strength of the as-manufactured specimen was 136,000 psi as compared to 112,000 psi for the heat treated stud. The approximately 17 percent reduction in strength after heat-treatment was to be expected due to recrystallization of the alloy(1)*.

3.3.3 Group II - WSi_2 and $MoSi_2$ Coatings - Containinn Low (0, 1, and 3%) Concentrations of VSi_2 and $TiSi_2$

In previous work at Vitro(2), WSi_2 and $MoSi_2$-base coatings were developed for the protection of tantalum-base alloys from oxidation in the temperature range 2700°-3000°F for relatively short periods of time. Based upon this experience the $MoSi_2$ and WSi_2-base systems were chosen for initial studies in this program. The coating systems studied, however, were modified in an attempt to achieve 600 hour performance in the range 1500°-2400°F and to decrease the possibility of pest formation (3, 4) at 1500' -1800°F. The initial system modifications included:

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* Numbers in parenthesis refer to literature sources listed under 'References.

(a) Use of an intervening tungsten or rhenium diffusion barrier to reduce the rate of migration of tantalum to the surface(5).

(b) Additions of low concentrations (1% - 3%) of second phase silicides such as VSi_2 and $TiSi_2$ to reduce the tendency tawards pest formation of the unmodified $MoSi_2$ and WSi_2 coatings.

Preliminary studies, however, indicated that these system modifications were insufficient in providing a substantial improvement in the oxidation life, and further changes were subsequently made in the coating processing conditions. These changes are described in the ensuing paragraphs of this section of the report.

To investigate the sintering behavior of the silicide-base surface coatings over the barrier layer coatings, a series of 0.5 mil tungsten coatings were initially prepared on Ta-10W sub-size coupons as described in Section 3.3.1, electrophoretic coatings of WSi_2, $MoSi_2$, $MoSi_2$-1 VSi_2, $MoSi_2$-3VSi_2, $MoSi_2$-1$TiSi_2$ and $MoSi_2$-3$TiSi_2$ were deposited over the tungsten barrier which were isostatically densified at a pressure of 30 tsi, and sintering experiments were performed over the temperature range 2550°F-2910°F in flowing argon. The results are summarized in Table 6, and photomicrographs of typical sintered coatings are shown in Figures 8 - 13.

In each of the silicide systems the highest density was obtained at 2910°F in argon. After this heat treatment, as shown in Figure 8, it was noted that a hard, thin diffusion zone was formed in the substrate and a porous region appeared adjacent to the diffusion zone. It was believed that the porosity arose due to depletion of silicon from the coating. In another series of experiments, as shown in Figure 9, it was found that the porous region could be repaired and the h'ardness of the diffusion zone increased to a value expected for a mixed silicide. This was achieved by depositing silicon metal over the silicide coating and heat treating for 16 hours at 2370°F and at an argon pressure of about 100 microns.

Typical examples of siliconized $MoSi_2$-VS_2 coatings and $MoSi_2$-$TiSi_2$ coatings over tungsten-coated Ta-10W are shown in Figures 10 - 13. As shown in the figures, there was little change in the hardness of the substrate after the initial heat-treatment, and the coated substrates apparently retained their ductility after the application of the tungsten barrier, surface silicide coating, and post-siliconization.

TABLE 5

SINTERING RESULTS FOR TUNGSTEN BARRIER COATINGS ON Ta-10W AND T-222 SUBSTRATES

			Metallographic Results	
Sintering Temp.(°F)	Sintering Time (hr.)	Sintering Atmosphere	Substrate Hardness Kg/mm^2, 50 gm Load	Remarks
2550	24	Argon	263	Sintered, adherent porous coating no diffusion
2550	40	Argon	423	Sintered, adherent porous coating no diffusion
2550	48	Argon	695	Sintered, adherent porous coating no diffusion
2910	4	Argon	322	Sintered, adherent porous coating no diffusion
2730	7	Vacuum (0.01μ)	274	Sintered, adherent porous coating no diffusion
2910	7	Vacuum (0.01μ)	322	Sintered, adherent porous coating no diffusion
3630	3	Vacuum (0.01μ)	310	Sintered, adherent high density coating no diffusion
3630	7	Vacuum (0.01μ)	322	Sintered, adherent high density coating no diffusion

TABLE 6

SINTERING EXPERIMENTS FOR SURFACE SILICIDE COATINGS ON TUNGSTEN-COATED Ta-10W

(Test Coupons Sintered 2 Hours in Argon at Indicated Temperature)

Coating System	Sintering Temp. (°F)	Substrate Knoop Hardness kg/mm^2-50 gm load	Results*
WSi_2	2550	260	a
WSi_2	2730	280	b
WSi_2	2910	320	c
$MoSi_2$-1%$TiSi_2$	2550	309	a
$MoSi_2$-1%$TiSi_2$	2730	322	b
$MoSi_2$-1%$TiSi_2$	2910	322	c
$MoSi_2$-3%$TiSi_2$	2550	302	a
$MoSi_2$-3%$TiSi_2$	2730	296	b
$MoSi_2$-3%$TiSi_2$	2910	296	c
$MoSi_2$-1%VSi_2	2550	285	a
$MoSi_2$-1%VSi_2	2730	322	b
$MoSi_2$-1%VSi_2	2910	322	c
$MoSi_2$-3%VSi_2	2550	309	a
$MoSi_2$-3%VSi_2	2730	309	b
$MoSi_2$-3%VSi_2	2910	296	c

*Results a, b, and c correspond to coatings that were each well-sintered and adherent to the substrate but which increased in density according to the relationship $a < b < c$.

In further exploratory coupon studies on some of the candidate coating systems, it was also noted that preoxidizing the siliconized surface coating at 2910°F in air at 5 or 15 minutes promoted the formation of a self-healing SiO_2 glassy layer which extended the oxidation life of the silicide coating system as indicated in Tables A-1 through A-5 of Appendix A.

In subsequent oxidation tests conducted on full size preoxidized silicide coated specimens, it was found that early failures occurred in the 1500°F test test series (Section 3.4.1) and it was suspected that insufficient glass (SiO_2) was formed during the 15 minutes preoxidation treatment at 2910°F. In order to test this hypothesis an experiment was designed to correlate preoxidation exposure time with weight gain and with oxidation life at 1500°F for each of the four coating systems. Specimens were prepared according to established procedures and two specimens of each coating system were preoxidized at 2910°F for 5, 15, 25, and 35 minute intervals. Weight gain data are plotted as a function of exposure time in Figure 24 for the four coating systems. It may be seen that the oxidation rate in each case was parabolic.

Photomicrographs showing the microstructure of several coating systems after preoxidation are shown in Figure 14. As indicated in the micrographs, no change in the hardness of the substrate was noted.

The preoxidized specimens were subsequently oxidation tested at 1500°F. Of the 32 specimen tests, 25 failed during the first 2-hour cycle, 6 failed during the second 2-hour cycle, and the remaining specimens failed on the third 2-hour cycle. This data which is summarized in Table 7, together with microscopic examination of the failed specimens, indicates that the extreme difference in thermal expansion between the SiO_2 glass surface coating (0.30×10^{-6} in/in/°F) and the T-222 substrate (3.5×10^{-6} in/in/°F) was probably a prime factor causing premature coating failure rather than the hypothesis of insufficient glass formation. This was evidenced by cracking of the SiO_2 glass coatings during heat-up which apparently exposed the underlying silicide coating to rapid deterioration at 1500°F by the well-known "pest" type of failure. It should be noted that only WSi_2, of the four preoxidized coating systems tested, had previously experienced "pest" failure on the sub-size (1/2" x 1" x 0.030") test specimens used for screening purposes.

TABLE 7

OXIDATION LIFE VS. PREOXIDATION TIME OF SILICIDE COATINGS AT 1500°F

Specimen No.	Coating	Preoxidation Time (min)	Oxidation Life Hours	Oxidation Life Cycles	Region of Failure
WO-393-34-1	WSi_2	5	2	1	edges
WO-393-34-2	WSi_2	5	2	1	edges
WO-393-34-3	WSi_2	15	2	1	edges
WO-393-34-4	WSi_2	15	2	1	edges
WO-393-34-5	WSi_2	25	2	1	edges
WO-393-34-6	WSi_2	25	2	1	edges
WO-393-34-7	WSi_2	35	2	1	edges
WO-393-34-8	WSi_2	35	2	1	edges
WO-393-42-1	$MoSi_2$	5	2	1	edges
WO-393-42-2	$MoSi_2$	5	2	1	edges
WO-393-42-3	$MoSi_2$	15	2	1	edges
WO-393-42-4	$MoSi_2$	15	2	1	edges and surface
WO-393-42-5	$MoSi_2$	25	6	3	edges
WO-393-42-6	$MoSi_2$	25	2	1	edges
WO-393-42-7	$MoSi_2$	35	4	2	edges
WO-393-42-8	$MoSi_2$	35	2	1	edges and surface
WO-393-44-1*	$MoSi_2$-3%VSi_2	5	2	1	edges
WO-393-44-2	$MoSi_2$-3%VSi_2	5	2	1	edges and surface
WO-393-44-3	$MoSi_2$-3%VSi_2	15	2	1	edges and surface
WO-393-44-4	$MoSi_2$-3%VSi_2	15	2	1	edges and surface
WO-393-44-5	$MoSi_2$-3%VSi_2	25	4	2	edges
WO-393-44-6	$MoSi_2$-3%VSi_2	25	4	2	edges and surface
WO-393-44-7	$MoSi_2$-3%VSi_2	35	4	2	edges
WO-393-44-8	$MoSi_2$-3%VSi_2	35	2	1	edges

TABLE 7 (continued)

Specimen No.	Coating	Preoxidation Time (min)	Oxidation Life Hours	Oxidation Life Cycles	Region of Failure
WO-393-46-1*	$MoSi_2$-3%$TiSi_2$	5	2	1	edges and surface
WO-393-46-2	$MoSi_2$-3%$TiSi_2$	5	4	2	edges and surface
WO-393-46-3	$MoSi_2$-3%$TiSi_2$	15	2	1	edges and surface
WO-393-46-4	$MoSi_2$-3%$TiSi_2$	15	2	1	edges and surface
WO-393-46-5	$MoSi_2$-3%$TiSi_2$	25	2	1	edges
WO-393-46-6	$MoSi_2$-3%$TiSi_2$	25	2	1	edges and surface
WO-393-46-7	$MoSi_2$-3%$TiSi_2$	35	2	1	edges and surface
WO-393-46-8	$MoSi_2$-3%$TiSi_2$	35	4	2	edges

“’Series WO-393-44 and WO-393-46 on tungsten barrier

The unmodified WSi_2 coating and several binary $MoSi_2$-base coating systems were also evaluated in early screening tests over a rhenium barrier layer coating. It was found, however, that the siliconization procedure used to densify the surface silicide coating converted the rhenium metal to one or 'more rhenium silicides. A typical example of a siliconized WSi_2/Re coating is shown in Figure 15 where it may be noted that the hardness of the original rhenium layer (493 kg/mm^2 - see Figure 7) has increased to 1138 kg/mm^2. The latter value is in close agreement to the single literature value of 1500 kg/mm^2 reported for $ReSi_2$ (6).

In summation, the following is a concise description of the electrophoretic processing conditions developed and utilized hereafter as a result of the experimental effort performed and reported in this section on the WSi_2 and MoSi, base coating systems containing low concentrations of VSi_2 and $TiSi_2$.

(1) Electrophoretically deposit surface silicide coating according to procedures established in Section 3.3.1.

(2) Isostatically densify coating at 30 tsi

(3) Sinter coatings at 2910°F for 2 hours under argon

(4) Siliconize sintered coating at 2370°F for 16 hours at a reduced pressure of about 100 microns

(5) Preoxidize siliconized coatings at 2910°F for 15 minutes in air

(6) Inspect all specimens for defects prior to testing.

3.3.4 Group III - WSi_2 and MoSi, Coatings - Containing High Concentrations of VSi_2, TiSi, and $CrSi_2$

Because the low concentration modified disilicide coatings exhibited "pest" at 1500°F on full size test specimens, even though they had not on sub-size specimens (see Section 3.4.1), this group of coatings containing high concentrations of VSi_2, TiSi,, and $CrSi_2$ was evaluated only on full size T-222 or W/T-222 test specimens. As will be discussed, the screening test results indicated that pest formation could be reduced by increasing the VSi_2 and $TiSi_2$ contents of $MoSi_2$ and

WSi_2 base systems. **A** study was subsequently undertaken to develop coating compositions with increased modifier content and including systems which incorporate $CrSi_2$ as follows:

a - WSi_2-30%VSi_2

b - WSi_2-30%$TiSi_2$

c - WSi_2-20%$CrSi_2$

d - $MoSi_2$-30%VSi_2

e - $MoSi_2$-30%$TiSi_2$

f - $MoSi_2$-20%$CrSi_2$

The 20 - 30% levels of concentration for the second phase silicide were selected arbitrarily, since time did not permit the study of compositions containing intermediate concentrations between 3 and 30 percent.

Initially, the WSi_2 and $MoSi_2$ coatings containing high concentrations of VSi_2 and $TiSi_2$ were mechanically blended, electrophoretically deposited on full-size T-222 panels, densified at various pressures ranging from 0 tsi to 50 tsi, and sintered at 2910°F for 2 hours under argon. In all cases, the coatings were poorly sintered and bonded to the substrate, presumably due to the preferential deposition of one of the components of the silicide system which resulted in non-uniform shrinkage during the sintering operation. In order to remedy this problem, the materials for each of the above coating combinations were mechanically blended, pelletized at 30 tsi, and homogenized for 2 hours at 2910°F under argon. The sintered or prealloyed pellets were crushed and ground to -100 mesh, ball milled for 36 hours, leached with acid, washed and dried. Dispersions were then prepared from the milled powders according to established procedures. It was originally intended that each of the six binary silicide compositions would be tested both with and without a tungsten barrier coating. An adherence problem was encountered, however, with the $MoSi_2$-30VSi_2 and $MoSi_2$-30$TiSi_2$ coating on T-222 and with the $MoSi_2$-20$CrSi_2$ coating on W/T-222. Since time did not permit resolution of this problem, these systems were eliminated from the preliminary study. The coating procedure used previously was also altered in order to overcome a thermal expansion mismatch problem which arose with the highly modified coating systems. Instead of the usual 30 tsi densification pressure used previously, a lower pressure (20 tsi) was employed. In the $MoSi_2$-20$CrSi_2$ coating system the previously used sintering temperature of 2910°F was reduced to 2730°F. The preoxidation treatment prior to testing was also eliminated for this series of tests in order to eliminate the SiO_2 glass overlay coating and establish the oxidation behavior of the coating material per se.

In the final oxidation tests (Section 3.4.4) of these coating systems, some difficulty was encountered in obtaining the required number of specimens for testing due to poor adherence; particularly with the WSi_2-$30VSi_2$ on W/T-222 and T-222 and $MoSi_2$-$30TiSi_2$ on W/T-222 coating systems. In all cases poor adherence was noted, at edges and corners, presumably due to a thermal expansion mismatch. In the more drastic cases the coating was observed to pull away from the substrate during insertion of the specimens into the hot zone of the furnace. This phenomenon was more pronounced with the specimens containing the tungsten underlayer. In previous work, and on the basis of a few experimental full size samples, lower densification pressures (20 instead of 30 tsi) appeared to remedy the adherence problem. However, this improvement was not maintained when a large group of full size specimens was coated. Approximately 3 out of 4 specimens, when fired, exhibited the adherence defect.

In order to improve the mechanical bond between the as-deposited coating and substrate, the tungsten coated T-222 specimens were lightly sandblasted with 90 grit alumina and the as-received T-222 panels were abraded with 60 grit alumina prior to coating with the silicides. Although this technique did not completely eliminate the adherence problem, a sufficient number of specimens of the following coating systems were prepared for evaluation as reported in Section 3.4.3.

WSi_2-$30VSi_1$ - on T-222

WSi_2-$30VSi_2$ - on W/T-222

$MoSi_2$-$30VSi_2$ - on W/T-222

$MoSi_2$-$20CrSi_2$ - on T-222

Photomicrographs of these coating systems are shown in Figure 16.

3.3.5 Group IV - $ReSi_2$, ZrB_2, $TaAl_3$ and Hf-27Ta Coatings

As noted in the Introduction, one of the candidate coating materials to be investigated in this program was rhenium disilicide. A ReSi, powder was therefore purchased with an average particle size of 10 microns, and the material was found to be pyrophoric in air. In view of this result, a second method of preparing a $ReSi_2$ coating was investigated whereby rhenium metal was electrophoretically deposited and processed according to the procedure described in Section 3.3.2, and the metal coating was then siliconized for 16 hours at 2370°F under reduced pressure (< 0.1 torr) to convert the rhenium to rhenium disilicide. The rhenium coating hardness, after sintering, was 493 kg/mm^2 (50 gram load) and, after siliconization, the silicided rhenium layer hardness increased to 1470 kg/mm^2 indicating formation of one or more rhenium silicide intermetallic compounds. After completion of siliconization, the T-222 substrate hardness adjacent to the rhenium silicide layer was 290 kg/mm^2, and the coated coupon could be bent 90" without cracking.

In order to determine the sintering conditions required for densification of ZrB_2 and $TaAl_3$, coatings of these materials were prepared and subjected to several heat treatments. The coatings were applied directly to Ta-10W panels which were used merely as carriers for the coatings or to Ta-10W panels to which a tungsten barrier coating was applied by the method of Section 3.3.2.

The ZrB_2 and $TaAl_3$ coatings were isostatically densified at a pressure of 30 tsi and sintered in argon for periods up to 7 hours at temperatures between 2550" and 2910°F. The ZrB_2 coatings remained soft and unsintered under these conditions, but the TaAl, coating appeared to be well sintered and adherent after 2 hours at 2910°F. A photomicrograph of this coating is shown in Figure 17. The sintering of ZrB_2 was then investigated in the presence of various binders as indicated in Table 8.

TABLE 8
ZIRCONIUM BORIDE SINTERING EXPERIMENTS

Binder	Sintering Temp. (°F)	Time (hrs)	Atmosphere
None	2550, 2730, 2910	2, 7	argon
3% Re	3090	2	argon
3% Ir	3090	2	argon
19% Ir	2910	2	argon
10 mol % $MoSi_2$	2910	2	argon
10 mol % WSi_2	2910	2	argon
3% Re	3630	2	vacuum (0. Olmicron)
10 mol % preoxidized frit formed from 66Si-34B	2550	2	argon
10 mol % Vycor	2910	2	argon
10 mol % (43Cr-57Ti)	2910	2	argon

The rhenium and iridium binders studied in these experiments were selected on the basis of work reported in the literature (7) in which high density was obtained in furnace-sintered ZrB_2-3Re or ZrB_2-3Ir at a temperature of 3630°F. This result could not be confirmed in our experiments and good sintered density was not achieved, The silicide binders were intended to simulate the familiar "Boride-Z" material which is normally hot-pressed at about 4000°F to obtain high density. It is likely that many of these ZrB_2 coating systems might be successfully prepared by isostatic hot-pressing at elevated temperatures; however, such studies were beyond the scope of the present program.

None of the conditions listed in Table 8 yielded dense coatings and this coating system was abandoned in favor of the more promising silicide surface coatings.

Considerable difficulty was encountered in obtaining 10 micron Hf-27Ta powder for coating and sintering experiments. The vendor lost several lots of this material because it was found to be pyrophoric in 10-micron size. **A** non-pyrophoric, -400 mesh, Hf-27Ta prealloyed powder was finally prepared and successfully coated on T-222 coupons, The Hf-27Ta coating was then densified at 30 tsi and sintered for *2* hours at 2910°F in argon to yield an adherent, relatively dense coating which was subsequently oxidation tested.

3.4 Coating Evaluation Studies

3.4.1 Oxidation Screening Tests and Selection of Candidate Coating Systems

In this task the oxidation resistance of the candidate coating systems described in Section 3.3 was evaluated by screening sub-size specimens at 1500°F and at 2400°F for a maximum period of 600 hours with periodic cycling to room temperature. These experiments were performed in order to select optimum systems for more intensive evaluation and to uncover weaknesses in the available coatings which might be eliminated by modification of the coating preparation technique.

The 1500"F tests were conducted in a split-tube, nichrome-wound furnace and the 2400°F tests in a multi-tube Globar-heated furnace. The specimens were set in a square, fused-silica boat for the 1500°F tests and supported on alumina plates (plates cast from type **33-HD** aluminum oxide grain and fired at 1600°C in air) for the 2400°F tests. The over-all coating thickness of each specimen was approximately 2.5 mils.

The raw data for all screening tests is tabulated in Appendix A which contains the laboratory notebook reference for all specimens, the number of cycles to room temperature experienced by each sample during testing, and the type of failure observed (i.e. , edge, corner, or general failure). An example of each type of failure observed on a set of silicide-coated specimens is shown in Figure 18. General failure of a coating system after short time exposure was interpreted as extremely poor coating performance, and systems exhibiting this mode of failure were eliminated from further screening. These systems included $ReSi_2$, $TaAl_3$, Hf-27Ta, and the various silicide systems over a rhenium barrier which were tested at 1500°F. The $TaAl_3$ coatings were apparently too porous to provide adequate protection and, as in the case of the ZrB_2 systems described in Section 3. 3. 5, isostatic hot-pressing of the $TaAl_3$ may be necessary to improve its performance if it is to be used as a protective coating. The Hf-27Ta performed approximately as expected, yielding an adherent oxide film. The coating, however, was extremely pervious to oxygen. **As** confirmed by recent studies at IITRI(8) and Marquardt(9), extremely thick layers or claddings of Hf-27Ta would be required to provide 600-hour protection at 2400°F and further study of this system was therefore not undertaken in this program.

The number of hours to failure at 1500°F and at 2400°F for all coating systems is summarized in Table 9. It will be noted that in the silicide coating systems a variety of post-sintering operations were investigated, including siliconization of the sintered silicide layer (see Section 3. 3. 3), and several types of preoxidation ranging from 15 minutes at 2500°F to 15 minutes at 2910°F. It was found that all samples which received no siliconization or preoxidation (post-treatment condition "a") and all samples which were preoxidized for 5 minutes at 2910°F but which were not siliconized (post-treatment condition "d") failed catastrophically in 2 hours or less at each test temperature. Siliconization was, therefore, .employed as described in Section 3. 3. 3 to heal porosity in the sintered coatings, and preoxidation was performed before the test exposure to promote the formation of a high-temperature, self-healing, thermal shock-resistant glassy layer at the surface of the coatings. With these modifications to the coating preparation procedure, several of the coating systems yielded lifetimes of 600 hours or more at 1500° and 2400°F including up to 30 cycles to room temperature, and remained intact after this exposure. The most consistent protective systems in this group were:

TABLE 9

SUMMARY OF OXIDATION TEST RESULTS FOR COATINGS ON Ta-10W AND T-222 COUPONS

(Life In Hours At Indicated Temperature, °F)

Coating System	Coating(1) Post Treatment	No Barrier 1500°F	No Barrier 2400°F	Tungsten Barrier 1500°F	Tungsten Barrier 2400°F	Rhenium 1500°F	
WSi$_2$	a		-		0	-	
	b		38, 44, 576		16, 36	-	
	c	2(4	) 137, 414, 280, 597(2)		-	2 (6 samp.)	
	d		-		2, 2	-	
MoSi$_2$ 1%VSi$_2$	a		-		2, 2	-	
	b		-		4, 40	-	
MoSi$_2$-3%VSi$_2$	a		-		2, 2	-	
	b		-	→	230-300, 18, 167	-	
	c		434, 157, 137, 597(2)		-	2 (6 samp.)	
	e		153-177		-	-	
	f		153-177		-	-	
MoSi$_2$-1%TiSi$_2$	a		-		2, 2	-	
	b		-		521, 60, 64	-	
MoSi$_2$-3%TiSi$_2$	a		-		2, 2	-	
	b		-	→	541, 38, 167	2 (6 samp.)	
	c	2(4	289, 597(2), 597(2)		-	-	
MoSi$_2$	c		2, 157, 157, 268, 597(2)677		-	2 (6 samp.)	
	e		677(2)		-	-	
	f		677(2)		-	-	
TaAl$_3$	a		-		2, 2	-	
Hf-27Ta	a		<1 (4 samples)		-	<1 (4 samp.)	

NOTES

(1) Code for Post Treatment:

	Siliconized	Preoxidized Time (min)	Preoxidized Temp°F
a	No	-	-
b	Yes	5	2910
c	Yes	15	2910
d	No	5	2910
e	Yes	15	2700
f	Yes	15	2500

(2) These samples were unfailed after indicated test period.

Coating	Post-Treatment	Barrier Layer	Oxidation Life* Hrs. at 1500°F	 Cycles at 1500°F	 Hrs. at 2400°F	Cycles at 2400°F
WSi_2	Si + 15 min. preox. at 2910°F	none	597	20	597	20
$MoSi_2$	Si + 15 min. preox. at 2910°F	none	6, 8, 10	3, 4, 5	597	20
$MoSi_2$-$3VSi_2$	Si + 5 min. preox. at 2910°F	Tungsten	589, 589	25, 25	230-300**	10
$MoSi_2$-$3TiSi_2$	Si + 5 min. preox. at 2910°F	Tungsten	589, 589	25, 25	541**	16

*All samples with 589 hours exposure at 1500°F were intact after the test.

**These are the same samples which previously survived 589 hours exposure at 1500°F.

The four systems tabulated above were chosen for evaluation involving electron microprobe analysis before and after oxidation (see Section 3.4. 5) and cyclic oxidation testing on full size specimens as reported in Section 3.4.2.

Returning to the coupon test data of Table 9, it will be noted that in the systems yielding the best performance in the screening tests (i.e., WSi_2, $MoSi_2$-$3VSi_2$, etc.) several replicate samples evidenced lives less than 600 hours. As inspection of the complete data of Appendix A will indicate, these specimens invariably failed at a corner or at an edge rather than catastrophically. This result indicated that the reliability of the systems might be improved by optimization of one or more steps in the processing cycle, or by process modifications to reduce surface stresses at edges and corners. In an in-house research program performed by Vitro in which the Si/WSi_2 system was used for the protection of tantalum alloys from oxidation at temperatures to 3200°F, it was found that annealing of the tantalum substrates at 2550°F for 1 hour in vacuum before deposition of the initial tungsten silicide coating resulted in improved coating reliability. For this reason all specimens which were coated for subsequent oxidation tests were annealed.

Of the 36 specimens tested which contained silicide surface coatings over a rhenium barrier layer, only five provided more than 100 hours protection at 2400°F and none was protective for more than 2 hours at 1500°F. In the

$ReSi_2$-coated specimens, two of the converted rhenium coatings on T-222 which were tested at 2400°F failed immediately upon insertion into the furnace with considerable evolution of smoke. After cooling, a loose black material (probably rhenium oxide) was present on all surfaces of the specimens. No glass formation was observed after the 2400°F exposure. Two other $ReSi_2$-coated specimens were tested at 1500°F and these also failed rapidly without smoke evolution to form a loose black scale.

The five specimens which survived more than 100 hours exposure at 2400°F consisted of two $MoSi_2$-3VSi_2 surface coatings, two $MoSi_2$-3$TiSi_2$ coatings, and one $MoSi_2$ coating over rhenium and, in previous evaluation of these same surface coatings on tungsten barriers or applied directly to T-222 alloy with no barrier present, six out of seven samples tested yielded lifetimes between 157 and 487 hours at 2400°F. The protection obtained for the two specimens on rhenium barriers was therefore believed to be due to the surface coating and not to the presence of the rhenium barrier. It should also be noted that all surface silicide coatings on the rhenium barrier was either partially or fully converted to a rhenium silicide by this treatment. This may be the reason for the apparent higher reliability of the surface coatings when applied to T-222 alloy over a tungsten barrier or with no barrier as compared to the same coatings on the silicided rhenium barrier. Due to these results, further work on rhenium barrier layers and on $ReSi_2$ surface coatings was discontinued.

3.4.2 Oxidation Tests of Four Silicide Coating Systems at 1500"F and 2400"F

Based upon the initial screening tests described in Section 3.4.1, cyclic oxidation tests were conducted on the WSi_2, $MoSi_2$, $MoSi_2$-3%VSi_2 and $MoSi_2$-3%TiSi coating systems on full size specimens at 1500"F and 2400°F, using processing conditions previously developed. The 1500°F tests were performed in a 5-in. diameter, split-tube, nichrome-wound furnace with a uniformly heated zone of ten inche's. For these tests a four-tier setter was constructed of 1/4-inch quartz plates, and eight specimens of each coating system were placed on each of the four tiers. The specimen arrangement is shown in more detail in Figure 19.

The 2400°F tests were conducted in an 8-tube, Globar-heated furnace. For these tests two-tier, 1/4-inch thick setters were constructed from type 33-HD castable alumina (cast and fired at 2900°F in air). Each setter plate contained two specimens (four specimens per furnace tube), and the temperature variation of the furnace was found to be 2417" ±5 °F over the length and height of the setter plates. The specimen arrangement is shown in more detail in Figure 20.

The test procedure at each temperature was as follows:

(1) Weigh all specimens before and after preoxidation.

(2) Cycle to room temperature, inspect, and weigh every 2 hours during the first 20 hours of exposure.

(3) Cycle to room temperature, inspect, and weigh every 20 hours during the next 180 hours of exposure.

(4) Cycle to room temperature and inspect every 20 hours during the next 400 hours of exposure. Weigh every 100 hours during this period.

The oxidation test data is summarized in Figure 21.

At 1500°F all 16 specimens of the WSi_2 and $MoSi_2$ coating systems failed during the first 2-hour cycle. In the case of the $MoSi_2$-3%$TiSi_2$ coating system, six of the eight specimens tested failed during the second 2-hour cycle and the remaining two specimens failed during the third 2-hour cycle. The eight specimens of the $MoSi_2$-3%VSi_2 coating system, on the other hand, exhibited improved oxidation resistance. Three of the eight specimens yielded oxidation lives of 80 (ten 2-hour cycles and three 20-hour cycles), 120 (ten 2-hour and five 20-hour cycles), and 300 hours (ten 2-hour and thirteen 20-hour cycles), and the latter specimen was intact after 300 hours exposure. The other five specimens failed after time intervals of 6, 14 (3 specimens), and 40 hours. Failure occurred in most cases at the edges of the specimens of all systems tested.

Weight change measurements taken after each cycle of the $MoSi_2$-3%VSi_2 coating system showed no significant change. For example, on the undamaged $MoSi_2$-3%VSi_2 specimen, a weight gain of 0.1 mg/cm^2 was observed after 300 hours.

Cyclic oxidation tests were also conducted at 2400°F and the results of these tests are shown in Figure 21. Although many specimens were still intact, this test was intentionally terminated after a 100 hour exposure time because of a contamination problem which began at the onset of testing. Contamination of the specimens was attributed to 33-HD alumina setters used in this series of tests. Apparently a contaminant present in this batch of alumina setters reacted with the outer silica layer of the coating forming a lower melting glass which attacked the silicide coating and caused premature failures. In some cases reaction was not severe and some of the specimens ($MoSi_2$-3%VSi_2 and $MoSi_2$-3%$TiSi_2$) survived 100 hours without failing. It should also be noted that in previous work this type of setter had proved satisfactory. Interposing a thoria pellet between the cast alumina and the specimen reduced but did not eliminate the contamination effect. Substitution of silica plates as the setter material finally resolved the problem. The surface condition of silicide coated specimens after being exposed for 2 hours at 2400°F on the 3 setter materials is shown in Figure 22.

The 2400°F test was then repeated using silica as the setter material. In previous tests one side of the test specimen was in intimate contact with the setter material resulting in underexposure to the atmosphere for this side of the specimen. All future tests were conducted with the specimen raised off the setter plate by means of two 1/4" x 1/4" platelets placed at each end of the test specimen, thus assuring approximately the same exposure conditions for both sides of the sample. A summary of the results of the second test is shown in Figure 23.

For each system tested the oxidation behavior was comparable to the previous series of tests that utilized the contaminated **33-HD** alumina setters. Of the 32 specimens tested (8 for each coating system), only three from the $MoSi_2$-3%VSi_2 coating system were still intact after 240 hours exposure (ten 2-hour cycles and eleven 20-hour cycles). Examination of the failed specimens showed that oxidation occurred primarily at localized edges or corners. Two of the three specimens exhibited surface failure after 260 hours of exposure (ten 2-hour cycles plus twelve 20-hour cycles) and the third specimen failed at a corner after 360 hours (ten 2-hour cycles plus seventeen 20-hour cycles).

To overcome this problem, an approach was pursued to improve the performance of these coating systmes at a lower timperature. Since screening tests indicated that a 3%VSi_2 or $TiSi_2$ addition to $MoSi_2$ did improve the oxidation life at low temperatures, and the'literature (10) indicated that both TiSi, and VSi_2 exhibit excellent oxidation behavior at 1500°F and 2400°F, coatings containing higher concentrations of VSi_2, TiSi,, and CrSi, were investigated.

3.4.3 Screening Tests of WSi_2 and $MoSi_2$ Base Coatings Containing High Concentrations of VSi_2, TiSi,, and CrSi,

In this study the following mixed silicides were chosen to evaluate the effect of additives on pest formation:

$MoSi_2$-30%VSi_2
$MoSi_2$-30%$TiSi_2$
$MoSi_2$-20%$CrSi_2$
WSi_2 - 30%VSi_2
WSi_2 - 30%$TiSi_2$
WSi_2 - 20%$CrSi_2$
WSi_2 - 10%$CrSi_2$

The procedure chosen for evaluating these systems was as follows:

(a) Mechanically blend the mixed compositions

(b) Press the composite powders at 30 tsi into pellet form

(c) Sinter pellets at 2910°F for 2 hours under argon

(d) Fracture pellets

(e) Test half of the pellets at 1500°F overnight (approx. 18 hours)

(f) Examine pellets microscopically at 28X for evidence of oxide growth

The results of these tests are presented in Table 10.

TABLE 10

RESULTS OF OXIDATION TESTS OF VARIOUS MIXED SILICIDE PELLETS AT 1500°F

Specimen No.	Exposure Time At 1500°F (Hrs)	Results
$MoSi_2$-$30VSi_2$	18	No indication of pest
$MoSi_2$-$30TiSi_2$	18	No indication of pest
$MoSi_2$-$20CrSi_2$	18	No indication of pest
WSi_2-$10CrSi_2$	18	Slight formation of pest on fractured surface
WSi_2-$20CrSi_2$	18	No indication of pest
WSi_2-$30VSi_2$	18	Formation of pest at some sites on fractured surface
WSi_2-$30TiSi_2$	18	No indication of pest

Of the compositions tested only the WSi_2-$10CrSi_2$ and the WSi_2-$30VSi_2$ showed slight oxide formation. This may have resulted from incomplete interaction of the two components during the alloying cycle. The mixed silicide systems that showed no evidence of pest formation together with the WSi_2-$30VSi_2$ were subsequently tested for oxidation resistance at 1500°F and 2400°F as coatings on full-size T-222 and W/T-222 coupons. The WSi_2-$30VSi_2$ system was included in this series of tests because it was felt that the additional 2-hour sintering cycle at 2910°F would result in further interaction of the WSi_2 and VSi_2 and thus inhibit pest formation. The coating systems tested were as follows:

a.	WSi_2 - 30% VSi_2	on	W/T-222
b.	WSi_2 - 30% VSi_2	on	T-222
c.	WSi_2 - 30% $TiSi_2$	on	W/T-222
d.	WSi_2 - 30% $TiSi_2$	on	T-222
e.	WSi_2 - 20% $CrSi_2$	on	W/T-222
f.	WSi_2 - 20% $CrSi_2$	on	T-222
g.	$MoSi_2$ - 30% VSi_2	on	W/T-222
h.	$MoSi_2$ - 30% $TiSi_2$	on	W/T-222
i.	$MoSi_2$ - 20% $CrSi_2$	on	T-222

The coatings were prepared as described in Section 3.3.4. The results of the oxidation tests are shown in Figure 25. Of the systems tested (two specimens from each system at 1500" and 2400°F) the WSi_2-30$TiSi_2$ and WSi_2-20$CrSi_2$ coatings on both T-222 and W/T-222 exhibited pest formation at 1500°F which resulted in catastrophic failure of the coating which is contrary to what was observed in the pellet studies. This discrepancy of results could be attributed to the improper preparation (blending, alloying, etc.) of these materials for coating.

Catastrophic failure was also noted for the WSi_2-30$TiSi_2$ coating on W/T-222 and the WSi_2-20$CrSi_2$ coating on T-222 at the 2400°F test temperature, The remaining systems appeared promising since failures were noted only at edges, corners, and patches due to coating defects, and the remainder of the surfaces of the test specimens were unaffected.

On the basis of these results, the following four systems were chosen for a final series of cyclic oxidation tests as described in the next section.

a. WSi_2 - 30VSi_2 on W/T-222
b. WSi_2 - 30VSi_2 on T-222
c. $MoSi_2$ - 30VSi_2 on W/T-222
d. $MoSi_2$ - 20$CrSi_2$ on T-222

3.4.4 Final Cyclic Oxidation Tests of Four Silicide Coating Systems Containing High Concentrations of VSi_2 and $CrSi_2$

The four coating systems selected for final oxidation testing were as follows:

WSi_2 - 30VSi_2 on W/T-222
WSi_2 - 30VSi_2 on T-222
$MoSi_2$ - 30VSi_2 on W/T-222
MoSi, - 20$CrSi_2$ on T-222

At both test temperatures the full-size specimens were cycled every two hours for the first 10 cycles and thereafter cycled every 20 hours with the exception of weekends when all specimens were continuously exposed at constant temperature. **A** summary of the oxidation test results obtained are shown in Figures 26 and 27. Weight gain data versus exposure times for the various specimens are also plotted in Figures 28 - 33 inclusive. The oxidation rates in most cases are plotted as averages of several specimens since the slopes of the curves for the inclusive specimens were approximately the same, Failure time of the specimens is also indicated on the graphs.

At the 1500°F test temperature, the $MoSi_2$-30VSi_2 and $MoSi_2$-20$CrSi_2$ coating systems on W/T-222 and T-222 respectively showed a substantial improve7 ment in oxidation resistance over previously tested silicide systems on full size specimens. All of the specimens of both systems survived ten 2-hour cycles and one 20-hour cycle. After this time interval, specimens of both systems began failing, particularly at edges and corners. Two specimens of the $MoSi_2$-30VSi_2 coating system together with one specimen of the $MoSi_2$-20$CrSi_2$ system survived 600 hours of cyclic testing. In the case of the WSi_2-base coating system, the pest problem reappeared, resulting in premature failure of the majority of specimens at the onset of testing,

The oxidation test results obtained at 2400°F were comparable to the previously tested WSi_2 and $MoSi_2$ base coating systems containing the low **(3%)** VSi_2 additive. **A** few specimens from each system with the exception of the $MoSi_2$-20$CrSi_2$ survived the 600 hour test. The longest oxidation life obtained for the $MoSi_2$-20$CrSi_2$ coating was 40 hours. Failure at this temperature occurred predominantly at edges and corners.

Evaluation of the oxidation rate data of Figures 28 to 33 showed that the specimen gained weight (SiO_2 formation) rapidly during the first few hours (4-10 hours) of testing and gained weight at a much slower rate thereafter. In some instances a sudden decrease in specimen weight was noted which was probably due to a combination of volatization of MoO_3 or to loss of material through spalling resulting from the thermal cycling. Examination of the specimens indicated that most of this weight loss was due to spalling. No appreciable weight change was noted for specimens which survived the 600 hour test at 2400°F after the first 100 hours of exposure, while at 1500°F the specimen weights (for those specimens surviving 600 hours) remained constant after the first 20 hours of exposure indicating complete protection of the coating system by the SiO_2 base outer layer.

3.4. 5 Electron Microprobe Analysis of Silicide Coating

Electron microprobe analysis was performed by E. F. Fullam, Inc. during this program to determine the distribution of coating and substrate constituents before and after oxidation testing in an effort to understand the cause of failure of the silicide coating systems. The following specimens were analyzed.

Item	Sample No.	Description
a	WO-393-17-3	WSi_2 on full size T-222 panel before oxidation testing
b	WO-393-21-1	MoSi, on full size T-222 panel before oxidation testing
c	WO-393-25-2	$MoSi_2$-$3VSi_2$ on full size W/T-222 panel before oxidation testing
d	WO-393-29-7	$MoSi_2$-$3TiSi_2$ on full size W/T-222 panel before oxidation testing
e	WO-393-44-3	$MoSi_2$-$3VSi_2$/W-T-222 (full size specimen) tested at 1500°F which failed after the first 2-hour cycle
f	WO-379-100-14	$MoSi_2$-$3VSi_2$/W-Ta-10W (sub-size specimen) tested at 1500°F and still intact after 589 hours of exposure
g	WO-403-12-21	$MoSi_2$-$3TiSi_2$/W-Ta10W (sub-size specimen) tested at 1500°F for 589 hours and then at 2400°F for 541 hours with failure occurring at a corner
h	WO-393-36-13	$MoSi_2$/T-222 (full size specimen) tested at 2400°F which failed after the tenth 2-hour cycle
i	WO-379-73-6	$MoSi_2$/T-222 (sub-size specimen) tested at 2400°F and still intact after 677 hours of exposure
j	WO-403-6-46	WSi_2/T-222 (sub-size specimen) tested at 2400°F and still intact after 597 hours of exposure

The specimens were submitted in coupon form, and small sections were taken from items a-j, mounted in epoxy resin, ground with silicon carbide discs, and polished with diamond abrasives. The polished specimens were then coated with an evaporated carbon film to dissipate the charge of the electron beam. With the exception of Item b, a representative area was selected for analysis from each side of each sample, and a hardness indentation was made in the substrate for reference. On Item b, however the two areas analyzed were selected on the same side of the specimen.

The electron microprobe was adjusted to an accelerating potential of 30 kv and a beam of current of approximately 0.08 microamperes. The elements Ta and W were analyzed with lithium fluoride crystal and scintillation counter, Hf, Si, Mo, and Ti were analyzed with an ADP crystal and flow proportional counter, and V was analyzed with a lithium fluoride crystal and flow proportional counter, and V was analyzed with a lithium fluoride crystal and flow proportional counter. The specimens were traversed under the electron beam at a linear rate of 20 microns per minute in a direction perpendicular to the analyzing crystal. The same track was used for each element, beginning at the reference mark, approximately 100 microns beneath the unaffected substrate and continuing beyond the indicated surface of the coating. The element concentrations in the coating and diffusion zone were obtained from the counting rate by comparison with the rate obtained for pure samples in the case of Ti, V, Si, and Mo; and by comparison with the counting rate observed for the substrate in the case of Ta, W, and Hf. The substrate chemistry was assumed to be 88Ta-9.6W-2.4Hf for the T-222 substrate and 90Ta-10W for the Ta-10W substrate. Background intensity was obtained by setting the goniometer one degree off the peak for each element, and the background was subtracted from the recorded intensities to obtain the net counting rate. No corrections were made for self-absorption or for absorption of radiation originating from one element by another. The concentration values are, therefore, qualitative with an estimated accuracy of ±30%.

Photomicrographs of the two areas analyzed on samples a-j are shown in Figures 34, 36, 38, 40, 42, 44, 46, 48, 50, and 52 inclusive and the charts of element concentration versus position in the samples are shown in Figures 35, 37, 39, 41, 43, 45, 47, 49 and 51 inclusive. In the graphs of the analytical traces, elements such as Hf, V and Ti which were present in low concentrations were not plotted. The concentration profiles which are plotted are smoothed averages of the analytical traces obtained from the electron microprobe recorder. A copy of the original traces for sample WO-393-25-2A is shown in Figures 54-66 inclusive for comparison. In the original traces, it may be seen that the hafnium concentration is highly irregular in the substrate, indicating discrete particles enriched in hafnium which are probably HfC. It may also be noted that the silicon concentration is highly variable in the coating as might be expected since one of the steps of preparing the coating involves diffusion of silicon into the sintered $MoSi_2$-$3VSi_2$ layer. The stepwise decrease in silicon concentration through the diffusion zone (typically, the region between 40-80 microns beneath the coating surface) is typical of most of the samples and is attributed to the formation of two or more stable $M_x Si_y$ phases.

Examining the photomicrographs of the nonoxidized specimens, particularly Figure 34 which are typical of the nonoxidized specimens, at least four coating phases are clearly delineated, as well as the reference indentation and a contamination line due to the electron beam. The surface WSi_2 coating is the light region at the left of the photos. Thislayer is 30-40 microns in thickness and corresponds to the W and Si plateau shown in the concentration profile of Figure 35. The original substrate surface, prior to siliconization begins at the right edge of the central grey area of the coating proper as shown in both photomicrographs of Figure 34. In this diffusion region, approximately 35 microns thick, the tantalum concentration gradually increases and the W and Si concentration decreases until a stable Ta-Si and W-Si phase is established and results in the broad light grey zone as indicated in the photomicrograph. The innermost diffusion zone to the right of the light grey zone and approximately 15 microns thick is a region of increasing Ta and decreasing Si concentration until the unaffected substrate is reached at a depth of approximately 90 microns. Beneath this point the Ta and W concentrations remain constant at the alloy composition and no silicon is present. The over-all coating therefore consists of approximately 40 microns of WSi_2 plus 40-50 microns of a complex multiphase diffusion zone which consists of the 3 discreet regions described above containing several silicides of Ta, W and perhaps Hf which were formed during siliconization. The scattered bright areas of Figure 34 are artifacts due to evaporated carbon which remained on the mounted specimen.

Scattered porosity is evident in many of the photomicrographs both within the surface coating layer and the area adjacent to the diffusion zone. This type of porosity was also noted in specimens prior to siliconization as shown in Figure 8.

The coating thickness is the same within 0.5 mil on both sides of each specimen, however, the concentration profiles reveal some differences in diffusion rate on opposite sides of the specimens. Compare, for example, the Ta, Mo, and W curves on Figure 41 for the two surfaces of the $MoSi_2$-$3TiSi_2$ coating on W/T-222. It is not known whether these differences are real and due to compositional variations and/or temperature differences, or whether they arise from inaccurate location of the outer edge of the coating on opposite sides of the sample. It is interesting to note, however, that samples WO-393-21-1A and E (which were analyzed on the same side of the coated specimen) show almost identical traces for Ta, Mo, and W (Figure 37).

In examining the photomicrographs of the oxidized specimens (items e-j) a striking similarity to the nonoxidized specimens is evident. Referring to Figure 42 which is typical, the $MoSi_2$ coating is the light porous region which extends approximately 45 microns from the surface into the coating proper. The coating at this point becomes denser and corresponds to the original substrate surface. Diffusion occurred in this region during the siliconization process which resulted in the formation of a multiphase system of Ta, Mo, W and Hf silicides. The grey area approximately 10 microns thick and adjacent to the unaffected substrate consists of silicides of the corresponding metals comprising the T-222 alloy composition. **A** major difference noted among the oxidized specimens was the diffusion rate of the various elements within the coating. This, however, would be expected since each specimen was exposed at the elevated temperatures (1500°F **or** 2400°F) for various time intervals. In some instances a difference was noted in the concentration profile of W and Mo at the coating surface on opposite sides of the specimen. For example, in specimen No's. WO-393-36-13, WO-393-44-3, and WO WO-403-6-46 and shown in respective Figures 42, 46, and 52, the Mo and W extend to the surface on one side of the coating while these element concentrations on the other side fall off gradually or abruptly at approximately 20 microns from the coating surface. This abnormality in the concentration profile of specimen No. WO-393-44-3 can be explained by the existence of a different phase at the coating surface as is evident in Figure 46. This is probably due to the fact that this side of the specimen contained a thicker SiO_2 layer as a result of its position in the tube furnace during the preoxidation treatment.

In the case of the microprobes on specimens WO-393-31-13 (Figure 43) and WO-403-6-46 (Figure 53), the concentration difference could be attributed to the inaccurate location of the coating surface, since the coating thickness of the recorded traces for these specimens do not correspond to the coating thickness of the actual coating as shown in the photomicrographs of Figures 42 and 52. In examining the photomicrographs of specimen No's. WO-379-73-6, WO-403-12-21, and WO-403-6-46 (Figures 44, 50 and 52 respectively) it appears that the oxidation products (outer silica base layer) penetrated the silicide coating through defects and attacked the multiphase silicides of the diffusion zone.

The SiO_2 penetration is more pronounced at sites of coating defects which extend into the inner diffusion zone. This deep penetration resulted in a further migration of the inner diffusion zone into the tantalum substrate as indicated in the photomicrographs. Corrosive attack of SiO_2 upon the silicide of tantalum was **also** observed by other investigators[11].

4. CONCLUSIONS

4.1 Coating Development

(a) The coatings listed below were successfully applied to tantalum substrates by establishing coating processing conditions fully described in Section 3.3.

1. Tungsten and rhenium barrier diffusion coating
2. WSi_2 and $MoSi_2$ base coating containing low (0 - 3%) concentrations of VSi_2 and TiSi,
3. WSi_2 and MoSi, base coatings containing high (10% - 30%) concentrations of VSi_2, TiSi, and CrSi,
4. $ReSi_2$, $TaAl_3$ and Hf-27Ta coating

(b) The unmodified and modified ZrB_2 coating systems investigated during this program indicates the need of higher sintering temperatures and/or hot pressing techniques to achieve the desired coating characteristics. Since such studies were beyond the scope of this program, the ZrB_2 coating system was not considered a candidate coating for tantalum alloys.

4.2 Coating Evaluation

(a) Binary silicide coating systems based upon WSi_2 and MoSi, containing 10% - 30% additions of VSi_2, $TiSi_2$ or $CrSi_2$ have indicated the potential of providing 600 hours oxidation protection at 1500°F and 2400°F to T-222 alloy under cyclic exposure conditions.

(b) The extremely poor coating performance at 1500°F of the $ReSi_2$, $TaAl_3$, and Hf-27Ta coating systems precludes their use as possible coatings for protecting tantalum base alloy at these temperatures.

(c) One of the objectives of this program was to prevent interstitial embrittlement of the T-222 substrate. To achieve this objective, a tungsten or rhenium coating interposed between the T-222 substrate and the surface coating to act as a diffusion barrier was investigated and was found to be ineffective. The processing conditions established for the surface coating during the program converted the barrier layer to the corresponding silicides which in turn provided a diffusion path for the coating and substrate constituents.

(d) Due to the "pest" phenomenon, the unmodified WSi_2 and $MoSi_2$ coating systems showed no promise for protecting tantalum at temperatures of 1500°F.

(e) The siliconization and preoxidation steps in the coating process extended the oxidation lives of the silicide base coating systems, however a thermal expansion mismatch between the preoxidation products (SiO_2) and the silicide coated T-222 substrates posed a serious problem'whereby the SiO_2 (glassy outer layer) would crack under cyclic conditions and not self-heal in time to protect the underlying silicide coating from pest formation. This phenomenon reduced the value of preoxidizing the siliconized specimen prior to testing.

(f) The problem of item (e) was remedied to some degree by modifying the WSi_2 and $MoSi_2$ base coatings with additions of VSi_2, $TiSi_2$ and $CrSi_2$. High concentrations (30%) of the above additives inhibited pest formation and thus extended the oxidation lives of the silicide coating systems, particulary the $MoSi_2$ base systems. **A** number of specimens of this system survived the 600 hour test at 1500°F and 2400°F. Several specimens of the various systems tested failed prematurely at localized edges and corners, probably due to high stress buildup at these areas. This problem has yet to be resolved.

(g) The electron microprobe analytical technique was found useful in yielding information regarding the distribution of coating and alloy constituents and depth of diffusion into the substrate but gave little insight into the cause of the poor reliability problem associated with the candidate coating systems.

5. RECOMMENDATIONS

The results of this program have shown the potential use of highly modified silicide base coatings for protecting tantalum alloy from oxidation at 1500°F and 2400°F. However, the reliability of these systems is marginal and additional work is required to determine:

(1) Optimum concentration of the second phase silicide

(2) Effect of prealloying conditions on the pest resistance of the binary silicide systems at 1500°F

(3) Optimum thickness and processing conditions for the protective systems to reduce the frequency of edge, corner and defect failures

(4) The use of barrier coatings such as molybdenum and controlled siliconization so as to prevent diffusion of substrate atoms into the coating

(5) Impact resistance of the coating formulations after their processing is optimized.

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APPENDIX A

OXIDATION TEST DATA

(GROUP II SUB-SIZE TEST SPECIMENS)

TABLE A-1

OXIDATION TEST RESULTS OF SURFACE COATINGS ON W/Ta-10W AT 1500°F UNDER CYCLIC AND STATIC CONDITIONS

Specimen* No.	Coating System	Post(1) Treatment	No. of(2) Cycles	Oxidation Life at 1500°F(hrs)	Type of Failure
379-76-1	WSi_2	a	1	2	General
379-76-2	WSi_2	b	1	2	General
379-76-3	WSi_2	b	1	2	General
379-80-4	WSi_2	c	1	2	General
379-80-5	WSi_2	c	3	20	General
379-84-6(3)	WSi_2	c	3	20	General
379-84-7(3)	WSi_2	c	3	20	General
379-88-8	$MoSi_2$-1%VSi_2	a	1	2	General
379-88-9	$MoSi_2$-1%VSi_2	a	1	2	General
379-92-10	$MoSi_2$-1%VSi_2	c	5	24	Edge
379-92-11	$MoSi_2$-1%VSi_2	c	1	2	Edge
379-96-12	$MoSi_2$-3%VSi_2	a	1	2	General
379-96-13	$MoSi_2$-3%VSi_2	a	1	2	General
379-100-14	$MoSi_2$-3%VSi_2	c	25(4)	589	Still good
379-100-15	$MoSi_2$-3%VSi_2	c	25(4)	589	Still good
379-104-16	$MoSi_2$-1%$TiSi_2$	a	1	2	General
379-104-17	$MoSi_2$-1%$TiSi_2$	a	1	2	General
379-108-18	$MoSi_2$-1%$TiSi_2$	c	25(4)	589	Still Good
379-108-19	$MoSi_2$-1%$TiSi_2$	c	25(4)	589	Still Good
379-112-20	$MoSi_2$-3%$TiSi_2$	a	1	2	General
379-112-21	$MoSi_2$-3%$TiSi_2$	a	1	2	General
379-116-22	$MoSi_2$-3%$TiSi_2$	c	25(4)	589	Still good
379-116-23	$MoSi_2$-3%$TiSi_2$	c	25(4)	589	Still good
379-120-24	$TaAl_3$	a	1	2	General
379-120-25	$TaAl_3$	a	1	2	General

(1) Post-Treatment
a = no post-treatment
b = sintered specimen preoxidized in air at 2910°F for 5 minutes.
c = sintered specimens siliconized at 2370°F for 16 hours under reduced pressure (<0.1 mm) and then preoxidized in air at 2910°F for five minutes.

(2) Specimens were cycled at 2 hour intervals during the working day and tested continuously overnight and during weekends.

(3) Specimens did not contain a tungsten barrier coating.

(4) Specimens were cycled for the first 16 cycles according to (2) and the remaining cycles were at 20 hour intervals.

*Typical Entry 379-104-16 = West Orange Laboratory Notebook No. 379, p. 104, sample No. 16.

TABLE A-2

OXIDATION TEST RESULTS OF SURFACE COATINGS ON W/Ta-10W AT 2400°F UNDER CYCLIC AND STATIC CONDITIONS

Specimen No.	Coating System	Post(1) Treatment	No. of(2) Cycles	Oxidation Life at 2400°F (hrs)	Type of Failure
379-78-1	WSi_2	a	0	0	General
379-78-2	WSi_2	b	1	2	General
379-78-3	WSi_2	b	1	2	General
379-82-4	WSi_2	c	1	2	General
379-82-5	WSi_2	c	4	22	Edge
379-86-6(3)	WSi_2	c	15(4)	576	Still intact
379-86-7(3)	WSi_2	c	5	38	Corner
379-86-8(3)	WSi_2	c	8	44	Corner
379-90-9	$MoSi_2$-1%VSi_2	a	1	2	General
379-90-10	$MoSi_2$-1%VSi_2	a	1	2	General
379-94-11	$MoSi_2$-1%VSi_2	c	2	4	General
379-94-12	$MoSi_2$-1%VSi_2	c	6	40	General
379-98-13	$MoSi_2$-3%VSi_2	a	1	2	Edge
379-98-14	$MoSi_2$-3%VSi_2	a	1	2	Edge
379-102-15	$MoSi_2$-3%VSi_2	c	14	167	Edge & corner
379-102-16	$MoSi_2$-3%VSi_2	c	2	18	Corner
379-106-17	$MoSi_2$-1%$TiSi_2$	a	1	2	Edge
379-106-18	$MoSi_2$-1%$TiSi_2$	a	1	2	Edge
379-110-19	$MoSi_2$-1%$TiSi_2$	c	9	60	Edge
379-110-20	$MoSi_2$-1%$TiSi_2$	c	11	64	Edge
379-114-21	$MoSi_2$-3%$TiSi_2$	a	1	2	Edge
379-114-22	$MoSi_2$-3%$TiSi_2$	a	1	2	Edge & corner
379-118-23	$MoSi_2$-3%$TiSi_2$	c	14	167	Edge & corner
379-118-24	$MoSi_2$-3%$TiSi_2$	c	5	38	Corner
379-122-25	$TaAl_3$	a	1	2	General
379-122-26	$TaAl_3$	a	1	2	General

(1) Post-Treatment
a = no post-treatment
b = sintered specimen preoxidized in air at 2910°F for 5 minutes
c = sintered specimens siliconized at 2370°F for 16 hours under reduced pressure (<0.1 mm) and then preoxidized in air at 2910°F for 5 minutes

(2) Specimens were cycled at 2 hour intervals during the working day and tested continuously overnight and during weekends

(3) Specimens did not contain a tungsten barrier coating.

(4) Cycling began after 96 hours of static testing; at which time the specimen was cycled to room temperature every 20 hours.

TABLE A-3

OXIDATION TEST RESULTS OF SURFACE COATINGS ON T-222 AT 1500°C UNDER CYCLIC AND STATIC CONDITIONS’’

Specimen No.	Coating System	No. of Cycles	Oxidation Life at 1500°F(hrs)	Type of Failure
403-5-29	WSi_2	20	597	Still good
403-5-44	WSi_2	1	0-2	General
403-5-45	WSi_2	8	44-46	General
403-5-49	WSi_2	1	0-2	General
403-5-50	WSi_2	2	2-4	Edge
403-5-51	WSi_2	1	0-2	Edge
403-21-1	$MoSi_2$	4	6-8	Edge
403-21-2	$MoSi_2$	3	4-6	Edge
403-21-3	$MoSi_2$	5	8-10	Edge
403-17-1	$MoSi_2$-3%VSi_2	5	8-10	Edge
403-17-2	$MoSi_2$-3%VSi_2	5	8-10	Edge
403-17-3	$MoSi_2$-3%VSi_2	5	8-10	Edge
403-11-1	$MoSi_2$-3%$TiSi_2$	3	4-6	Edge
403-11-2	$MoSi_2$-3%$TiSi_2$	3	4-6	Edge
403-11-3	$MoSi_2$-3%$TiSi_2$	3	4-6	Edge & corner
403-11-7	$MoSi_2$-3%$TiSi_2$	19	242-314	Edge
403-11-8	$MoSi_2$-3%$TiSi_2$	17	591	Still good
403-11-9	$MoSi_2$-3%$TiSi_2$	9	31-48	Edge
403-31-1(1)	Hf-27Ta	0	<1	Completely oxidized
403-31-2	Hf-27Ta	0	<1	Completely oxidized
403-31-3	Hf-27Ta	0	<1	Completely oxidized
403-31-4	Hf-27Ta	0	<1	Completely oxidized
403-31-5	Hf-27Ta	0	<1	Completely oxidized

(1) Preoxidized for 2 minutes at 2910°F.

* All specimens except Hf-27Ta series siliconized and preoxidized for fifteen minutes at 2910°F before test exposure.

TABLE A-4

OXIDATION TEST RESULTS OF SURFACE COATINGS ON T-222 AT 2400°F UNDER CYCLIC AND STATIC CONDITIONS*

Specimen No.	Coating System	No. of Cycles	Oxidation Life at 2400"F (hrs)	Type of Failure
403-6-46	WSi_2	20	597	Still good
403-6-47	WSi_2	18	259-280	Edge
403-6-48	WSi_2	13	117-137	General
403-21-4	$MoSi_2$	17	200-268	General
403-21-5	$MoSi_2$	1	0-2	Corner
403-21-8	$MoSi_2$	20	597	Still Good
403-35-3	$MoSi_2$	14	137-157	Edge
403-35-4	$MoSi_2$	14	137-157	Edge
403-17-4	$MoSi_2$-3%VSi_2	14	137-157	Edge
403-17-5	$MoSi_2$-3%VSi_2	13	117-137	General
403-17-6	$MoSi_2$-3%VSi_2	20	597	Still good
403-11-4	$MoSi_2$-3%$TiSi_2$	18	268-289	Edge
403-11-5	$MoSi_2$-3%$TiSi_2$	20	597	Still good
403-11-6	$MoSi_2$-3%$TiSi_2$	20	597	Still good
403-31-6	Hf-27Ta	0	<1	Completely oxidized
403-31-7	Hf-27Ta	0	<1	Completely oxidized
403-31-9	Hf-27Ta	0	<1	Completely oxidized
403-31-8	Hf-27Ta	0	<1	Completely Oxidized

*All specimens except Hf-27Ta series siliconized and preoxidized fifteen minutes at 2910°F before test exposure.

TABLE A-5

OXIDATION TEST RESULTS OF SILICIDE COATINGS ON Ta-10W OR T-222 AT 2400°F

Specimen No.	Coating System	Post(4) Treatment	No. of(1) Cycles	Oxidation(2) Life at 2400°F (hrs)	Type of Failure
379-73-1	$MoSi_2$-3%VSi_2	e	12	153-177	Completely oxidized
379-73-2	$MoSi_2$-3%VSi_2	f	12	153-177	Edge
379-73-3	$MoSi_2$-3%VSi_2	c	23	434	Corner
379-73-4	$MoSi_2$	c	30	677	Still good
379-73-5	$MoSi_2$	e	30	677	Still good
379-73-6	$MoSi_2$	f	30	677	Still good
379-73-7	WSi_2	c	22	414	Corner
403-12-13(3)	$MoSi_2$-3%VSi_2	b	10	232-304	Completely oxidized
403-12-17A(3)	$MoSi_2$-1%$TiSi_2$	b	16	521	Edge
403-12-21(3)	$MoSi_2$-3%$TiSi_2$	b	16	541	Edge

(1) Specimens of the WO-379 series (silicide coated T-222 specimens) were cycled ten times at 2 hour intervals during the working day, and cycled thereafter at approximately 17 hour intervals. Specimens of the WO-403 series (silicide coated W/Ta-10W specimens) cycled at approximately 17 hour intervals. Testing was continuous overnight and during weekends.

(2) Where range is given specimen failed during night or weekend.

(3) These are the specimens that previously survived 589 hours at 1500°F.

(4) See Table 9 in main report for coding.

TABLE A-6

OXIDATION TEST RESULTS OF SURFACE COATINGS ON Re/T-222 AT 1500°F UNDER CYCLIC AND STATIC, CONDITIONS*

Specimen No.	Coating System	No. of Cycles	Oxidation Life at 1500°F(hrs).	Type of Failure
403-9-1	WSi_2	1	0-2	General
403-9-2	WSi_2	1	0-2	General
403-9-3	WSi_2	1	0-2	General
403-9-9	WSi_2	1	0-2	General
403-9-10	WSi_2	1	0-2	General
403-23-1	$MoSi_2$	1	0-2	General
403-23-2	$MoSi_2$	1	0-2	General
403-23-3	$MoSi_2$	1	0-2	General
403-23-6	$MoSi_2$	1	0-2	General
403-35-5	$MoSi_2$	1	0-2	General
403-35-6	$MoSi_2$	1	0-2	General
403-19-1	$MoSi_2$-3%VSi_2	1	0-2	General
403-19-2	$MoSi_2$-3%VSi_2	1	0-2	General
403-19-3	$MoSi_2$-3%VSi_2	1	0-2	General
403-19-7	$MoSi_2$-3%VSi_2	1	0-2	General
403-19-8	$MoSi_2$-3%VSi_2	1	0-2	General
403-19-9	$MoSi_2$-3%VSi_2	1	0-2	General
403-15-1	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-15-2	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-15-3	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-15-8	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-15-9	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-15-10	$MoSi_2$-3%$TiSi_2$	1	0-2	General
403-33-1	Hf-27Ta	0	<1	Completely oxidized
403-33-2	Hf-27Ta	0	<1	Completely oxidized
403-33-3	Hf-27Ta	0	<1	Completely oxidized
403-33-4	Hf-27Ta	0	<1	Completely oxidized

*All specimens except Hf-27Ta series siliconized and preoxidized for fifteen minutes at 2910°F before test exposure.

TABLE A-7

OXIDATION TESTS RESULTS OF SURFACE COATINGS ON Re/Ta-10W AT 2400°F UNDER CYCLIC AND STATIC CONDITIONS*

Specimen No.	Coating System	No. of Cycles	Oxidation Life at 2400°F (hrs)	Type of Failure
403-9-4	WSi_2	1	0-2	Edge
403-9-5	WSi_2	2	2-4	Edge & Corner
403-9-6	WSi_2	1	0-2	Edge
403-9-7	WSi_2	3	4-6	Edge & Corner
403-9-8	WSi_2	1	0-2	General
403-23-5	$MoSi_2$	13	117-137	General
403-19-4	$MoSi_2$-3%VSi_2	12	52-117	General
403-19-5	$MoSi_2$-3%VSi_2	13	117-137	General
403-14-6	$MoSi_2$-3%VSi_2	13	117-137	General
403-15-4	$MoSi_2$-3%$TiSi_2$	13	117-137	Corner
403-15-5	$MoSi_2$-3%$TiSi_2$	13	117-137	General
403-15-6	$MoSi_2$-3%$TiSi_2$	1	0-2	Edge
403-15-7	$MoSi_2$-3%$TiSi_2$	15	175-198	General
403-33-7	Hf-27Ta	0	<1	Completely oxidized
403-33-8	Hf-27Ta	0	<1	Completely oxidized
403-33-9	Hf-27Ta	0	<1	Completely oxidized
403-33-10	Hf-27Ta	0	<1	Completely oxidized

*All specimens except Hf-27Ta series siliconized and preoxidized fifteen minutes at 2910°F before test exposure.

APPENDIX B

ILLUSTRATIONS

PROCESSING CONDITIONS FOR SILICIDE COATED SPECIMENS(1) SHOWN IN FIGURES 34-52,

Sample No.	Figure No.	Coating	Substrate	Size Of Specimen	Preoxidizing Temp.(‘F)	Preoxidizing Time (Min.)
WO-393-17-3(2)	34	WSi_2	T-222	Full Size	2910	15
WO-393-21-1(2)	36	$MoSi_2$	T-222	Full Size	2910	15
WO-393-25-2(2)	38	$MoSi_2$-$3VSi_2$	WIT-222	Full Size	2910	15
WO-393-29-7(2)	40	$MoSi_2$-$3TiSi_2$	WIT-222	Full Size	2910	15
WO-393-36-13(3)	42	$MoSi_2$	T-222	Full Size	2910	15
WO-379-73-6(3)	44	$MoSi_2$	T-222	Sub-Size	2500	15
WO-393-44-3(3)	46	$MoSi_2$-$3VSi_2$	WIT-222	Full Size	2910	15
WO-379-100-14(3)	48	$MoSi_2$-$3VSi_2$	W/Ta-10W	Sub-Size	2910	5
WO-403-12-21(3)	50	$MoSi_2$-$3TiSi_2$	W/Ta-10W	Sub-Size	2910	5
WO-403-6-46(3)	52	WSi_2	T-222	Sub-Size	2910	15

(1) All specimens prior to preoxidation were isostatically densified at 30 tsi, sintered at 2910°F for 2 hours under argon and siliconized for 16 hours at 2370°F under reduced pressures (approximately 100 microns).

(2) Pre-tested specimens

(3) Post-tested specimens

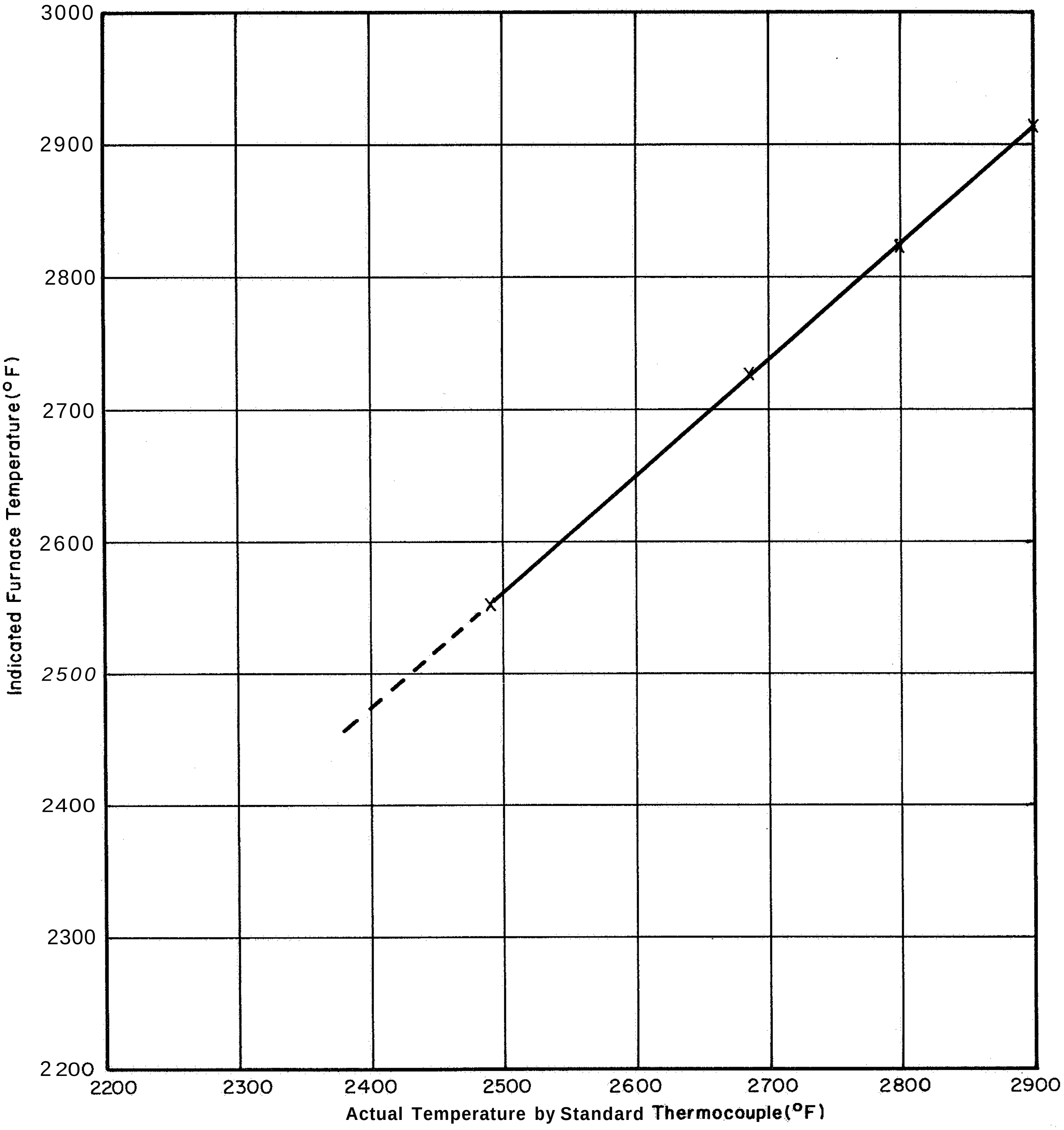


FIGURE 1

PERENY TUBE FURNACE TEMPERATURE CALIBRATION

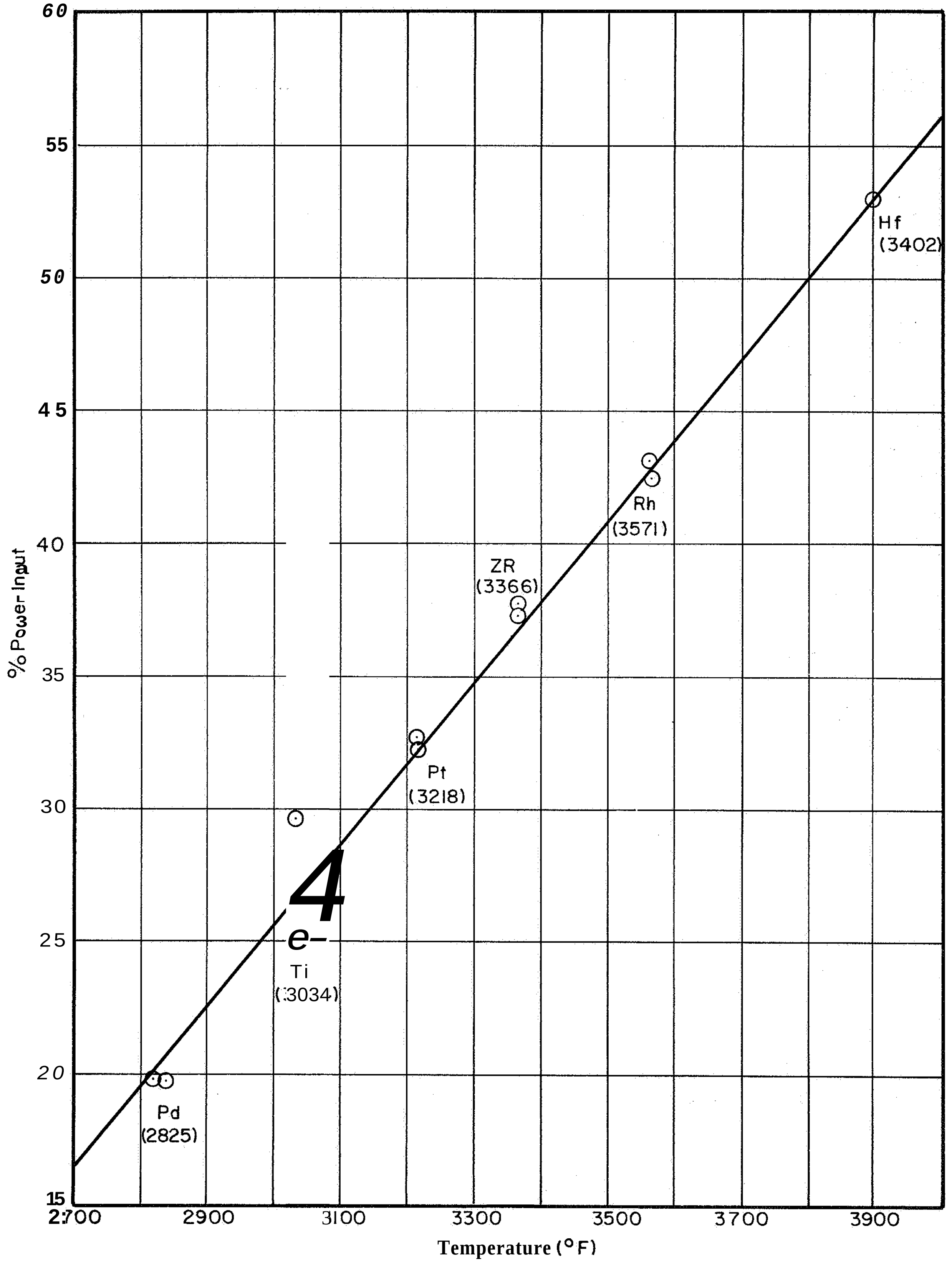


FIGURE 2
TEMPERATURE CALIBRATION FOR BREW HIGH VACUUM FURNACE (HIGH RANGE)

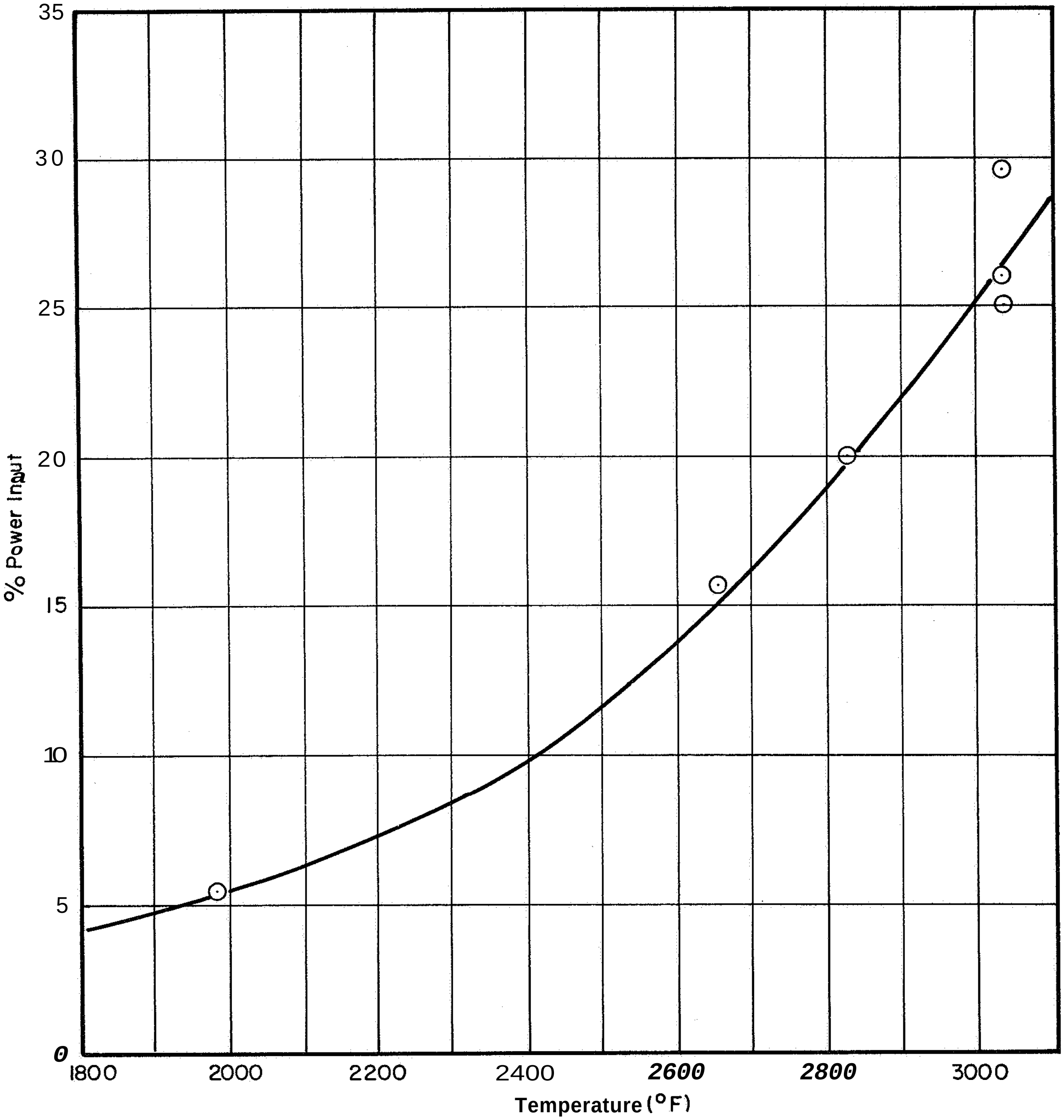


FIGURE 3

TEMPERATURE CALIBRATION FOR BREW HIGH VACUUM FURNACE (LOW RANGE)

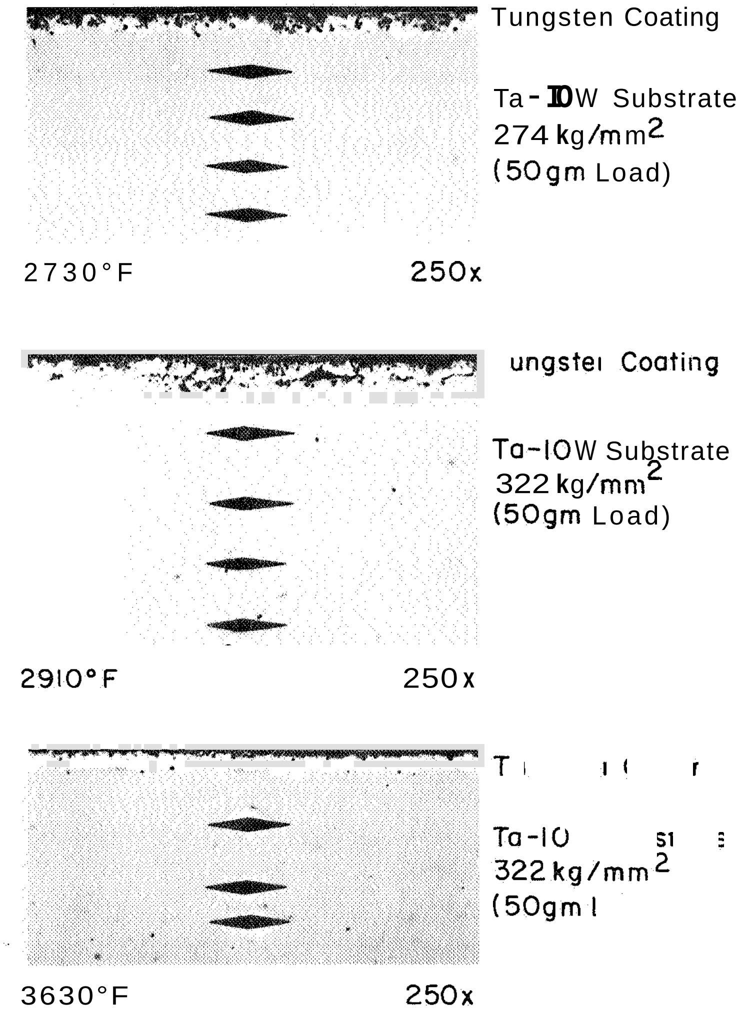
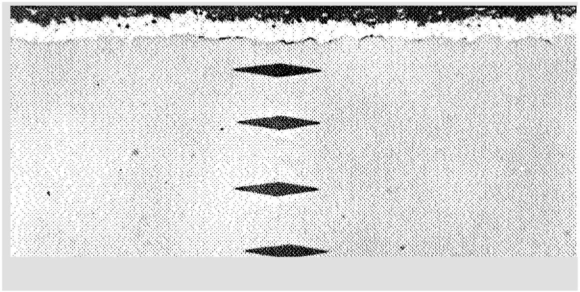


FIGURE 4

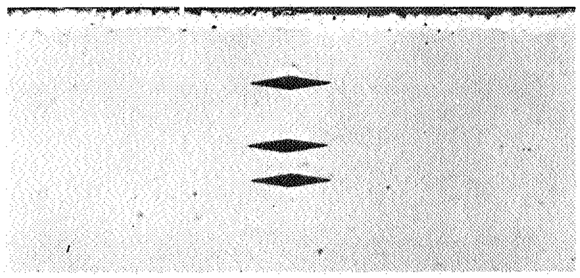
TUNGSTEN COATINGS ON Ta-10W SINTERED FOR 7 HOURS
UNDER REDUCED PRESSURE (0.01 micron)
AT VARIOUS TEMPERATURES



Tungsten Coating

Ta-10W Substrate
310 kg/mm^2
(50gm Load)

3Hours 250x



Tungsten Coating

a- Substrate
322 kg/mm^2
(50gm l ad)

7 Hours 25

FIGURE 5

TUNGSTEN COATING ON Ta-10W, SINTERED AT 3630°F UNDER REDUCED PRESSURE FOR VARIOUS TIME INTERVALS (0.01 microns)

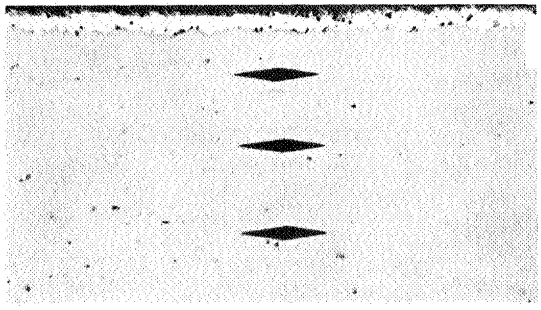
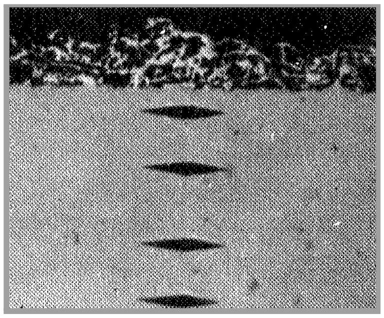
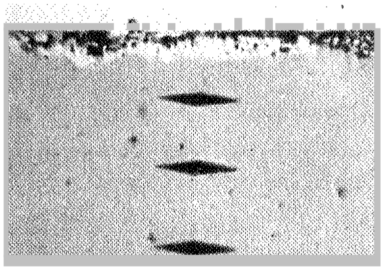


FIGURE 6

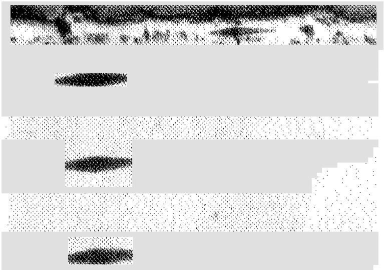
SINTERING EXPERIMENTS FOR SURFACE SILICIDE COATINGS ON TUNGSTEN-COATED TA-10W



2910°F, 7 hrs 250x



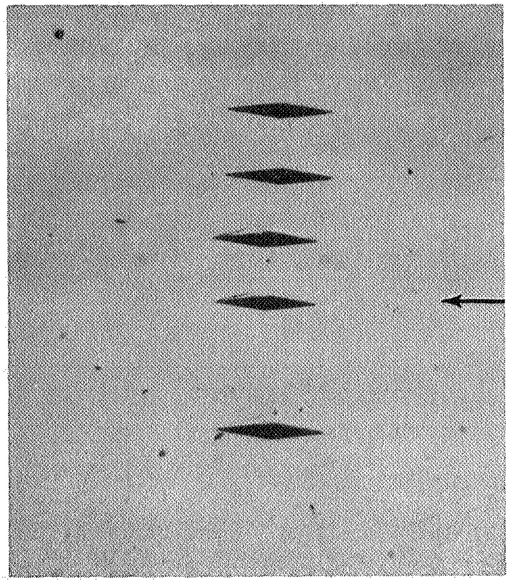
3630" F, 3 hrs 250x



3630°F, 7 hrs 250x

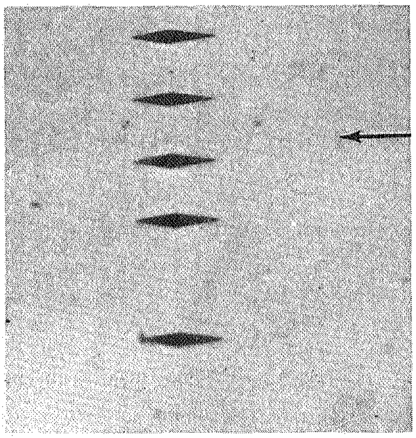
FIGURE 7

RHENIUM COATING ON Ta-10W SINTERED AT 2910°F AND 3630°F UNDER REDUCED PRESSURE (0.01 micron) FOR INDICATED TIME INTERVALS



Microhardness 235kg/mm^2
(50g Load)

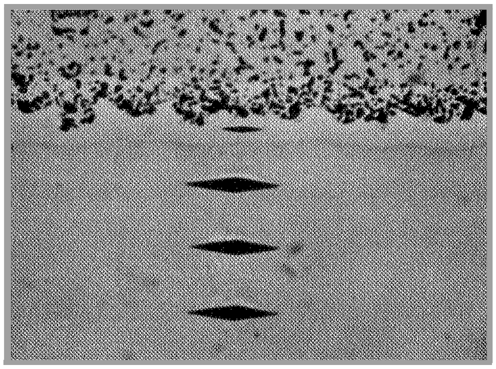
Ta-IOW (As Received)



Heat-Treated, But Uncoated
Ta- IOW Substrate

Hardness=323kg/mm^2 (50g-Load)

Unetched 250x



W Si_2

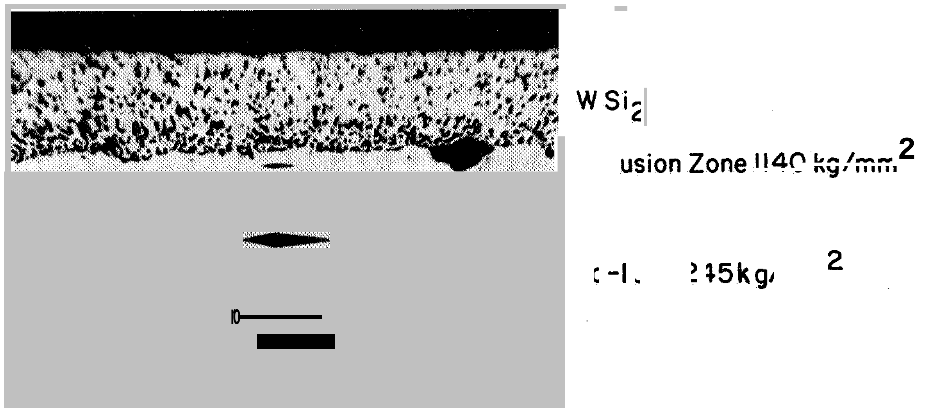
Diffusion Zone 1250 kg/mm^2

Ta-IOW 320 kg/mm^2

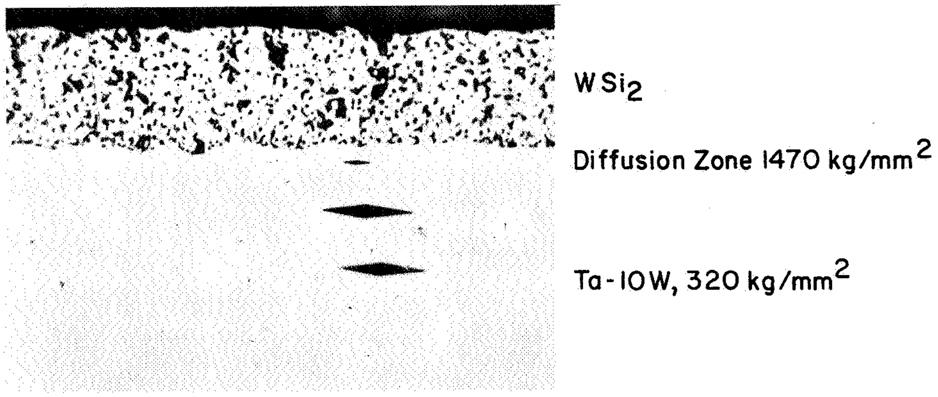
2910°F, 2hrs-Argon 250x, Unetched

FIGURE 8

Ta-10W AS-RECEIVED, AFTER HEAT TREATMENT AT 2550°F, AND AFTER COATING WITH WSi_2 AND SINTERING AT 2910°F FOR TWO HOURS UNDER ARGON



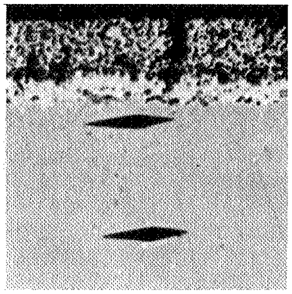
Siliconized 1 hr **250x, Unetched**
2460°F **in Argon**



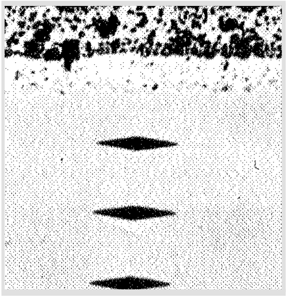
16hr Siliconization **250x, Unetched**
2370°F, < 0.1Torr,

FIGURE 9

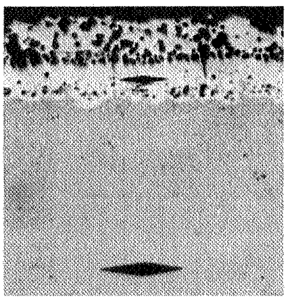
EFFECT OF SILICONIZATION PROCEDURE ON WSi_2 COATING ON Ta-10W, SINTERED AT 2910°F



2550°F 250x



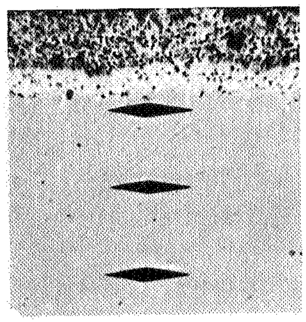
2730° F 250x



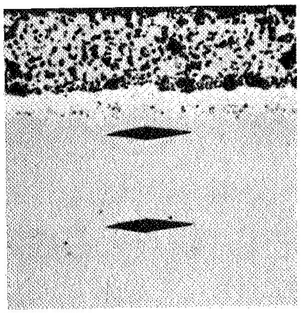
2910° F 250x

FIGURE 10

$MoSi_2$-1% VSi_2 COATINGS ON W/Ta-10W SINTERED FOR 2 HOURS UNDER ARGON AT VARIOUS TEMPERATURES



2550°F 250%

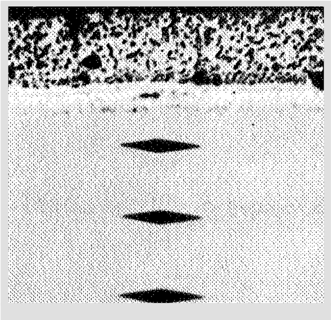


2730°F 250x

2910"F 250x

FIGURE 11

MoSi$_2$ - 3% VSi$_2$ COATINGS ON W/Ta-10W SINTERED FOR 2 HOURS UNDER ARGON AT VARIOUS TEMPERATURES



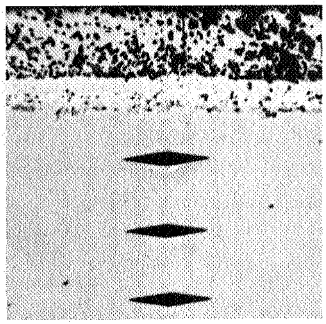
$MoSi_2$-1% $TiSi_2$ Coating

W-Si Barrier

Ta-10W Substrate

309 kg/mm^2 (50 gm Load)

2550°F 250x



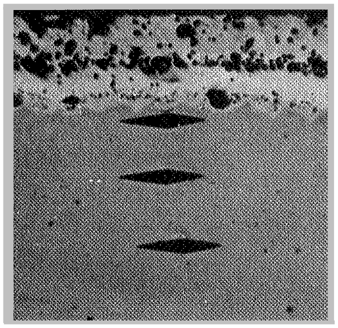
$MoSi_2$-1% $TiSi_2$ Coating

W-Si Barrier

Ta-10W Substrate

322 kg/mm^2 (50 gm Load)

2730°F 250x



$MoSi_2$-1% $TiSi_2$ Coating

W-Si Barrier

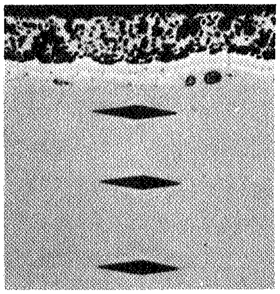
Ta-10W Substrate

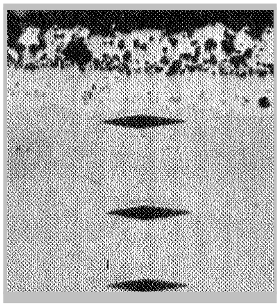
322 kg/mm^2 (50 gm Load)

2910°F 250x

FIGURE 12

$MoSi_2$ -1% TiSi, COATINGS ON W/Ta-10W SINTERED FOR 2 HOURS UNDER ARGON AT VARIOUS TEMPERATURES





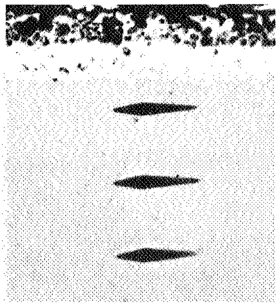


FIGURE 13

$MoSi_2$-3% $TiSi_2$ COATINGS ON W/Ta-10W SINTERED FOR 2 HOURS UNDER ARGON AT VARIOUS TEMPERATURES

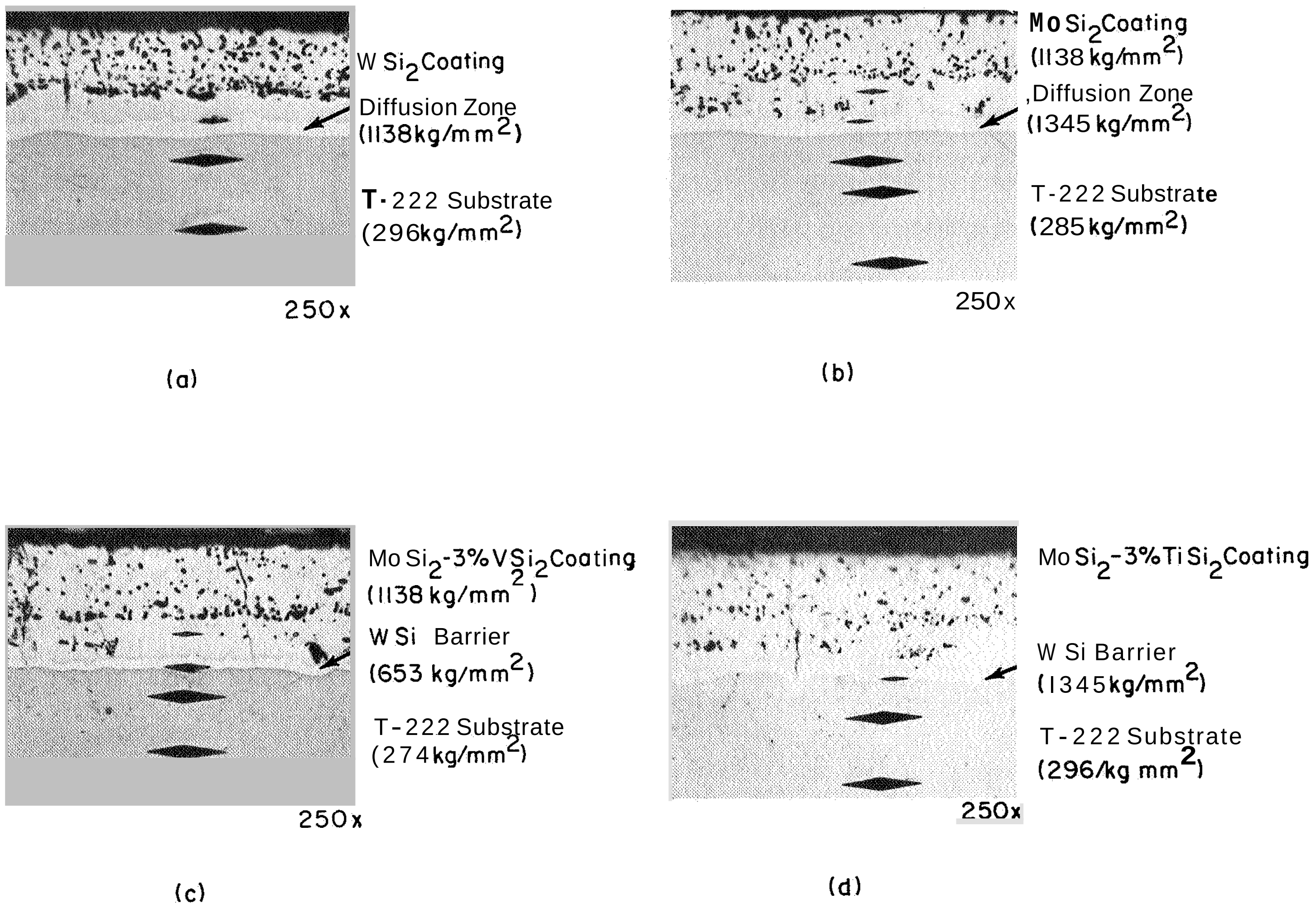


FIGURE 14

PREOXIDIZED SILICIDE COATINGS ON T-222 AND W/T-222

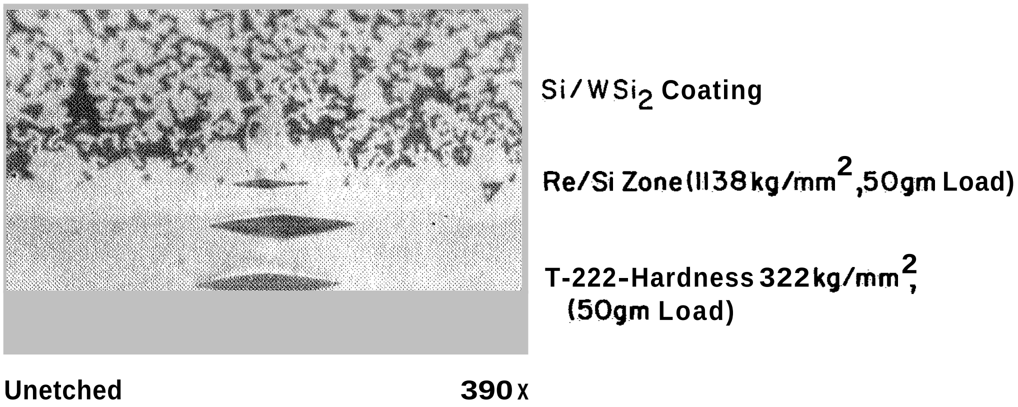


FIGURE 15

SILICONIZED WSi_2 ON RHENIUM-COATED T-222 ALLOY

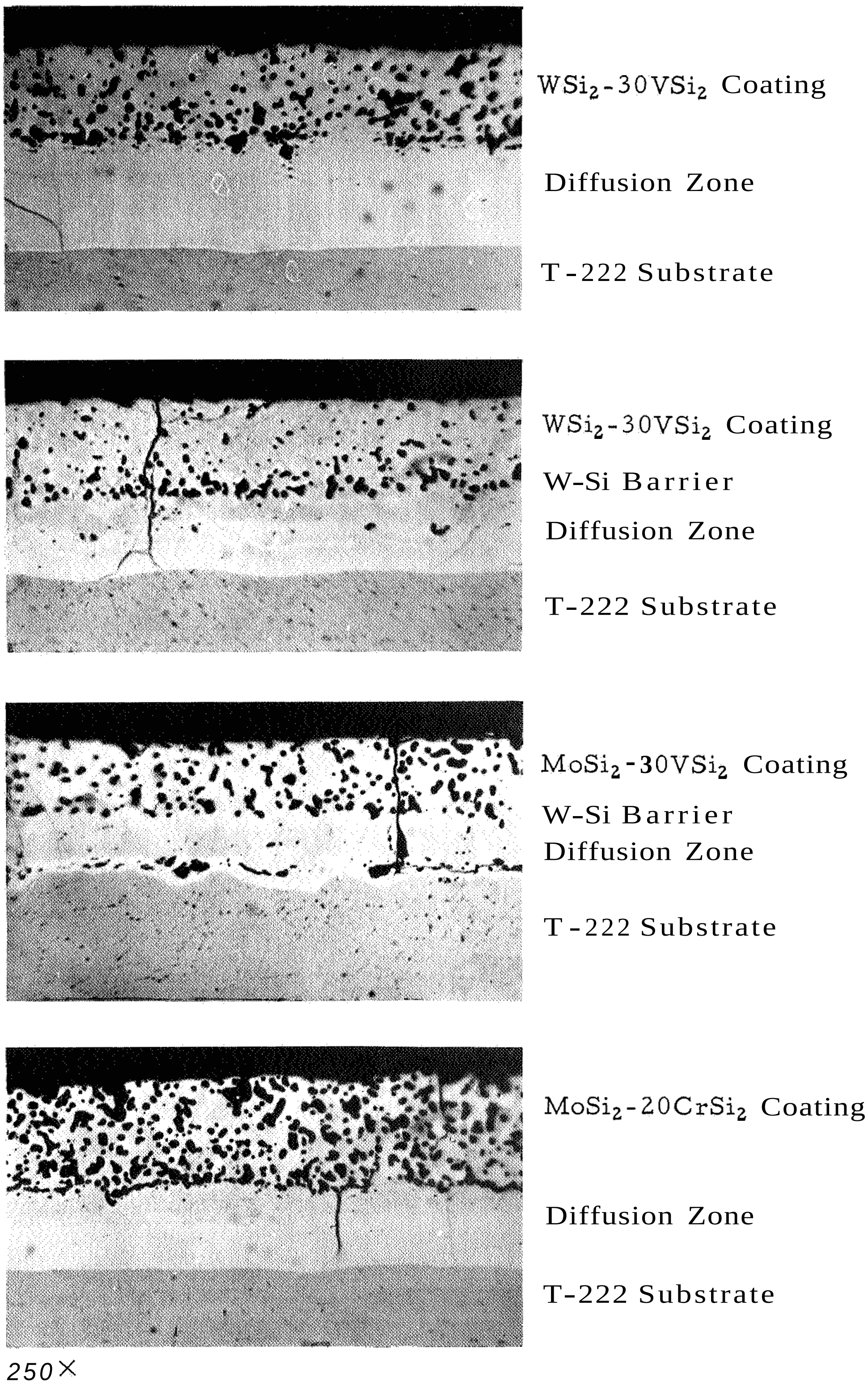


FIGURE 16

HIGHLY MODIFIED SILICIDE COATINGS ON T-222 AND W/T-222

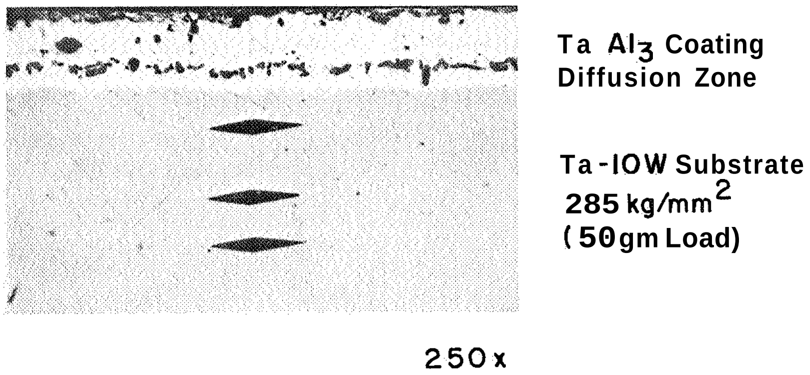
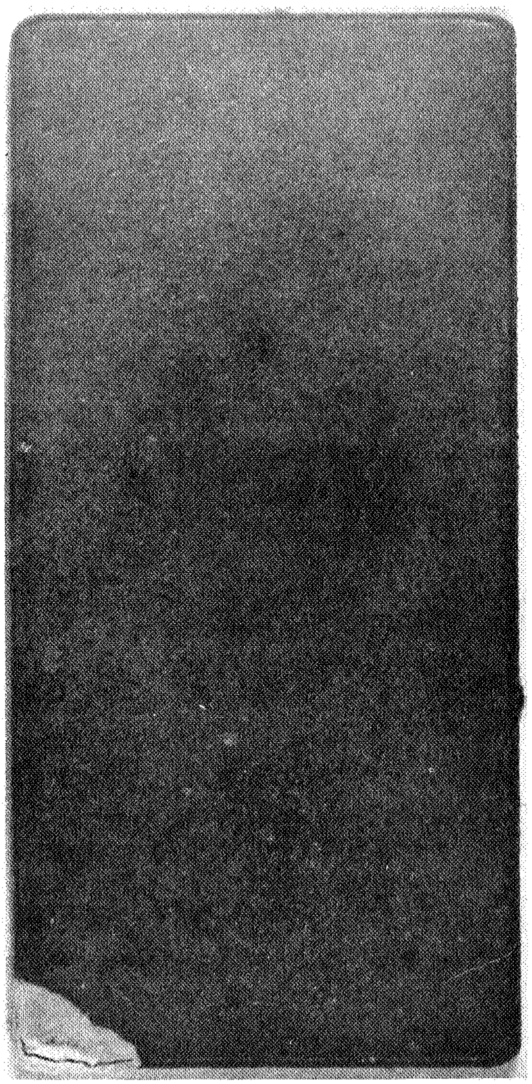


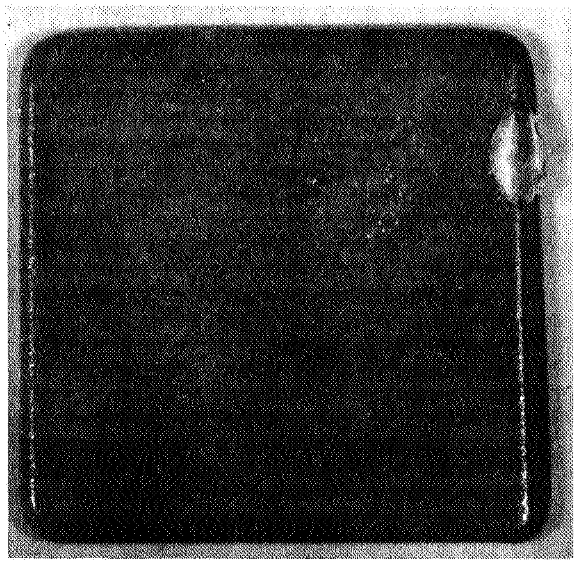
FIGURE 17

$TaAl_3$ COATING ON Ta-10W
SINTERED FOR 2 HOURS
UNDER ARGON AT 2910°F



Corner Failure 5 x

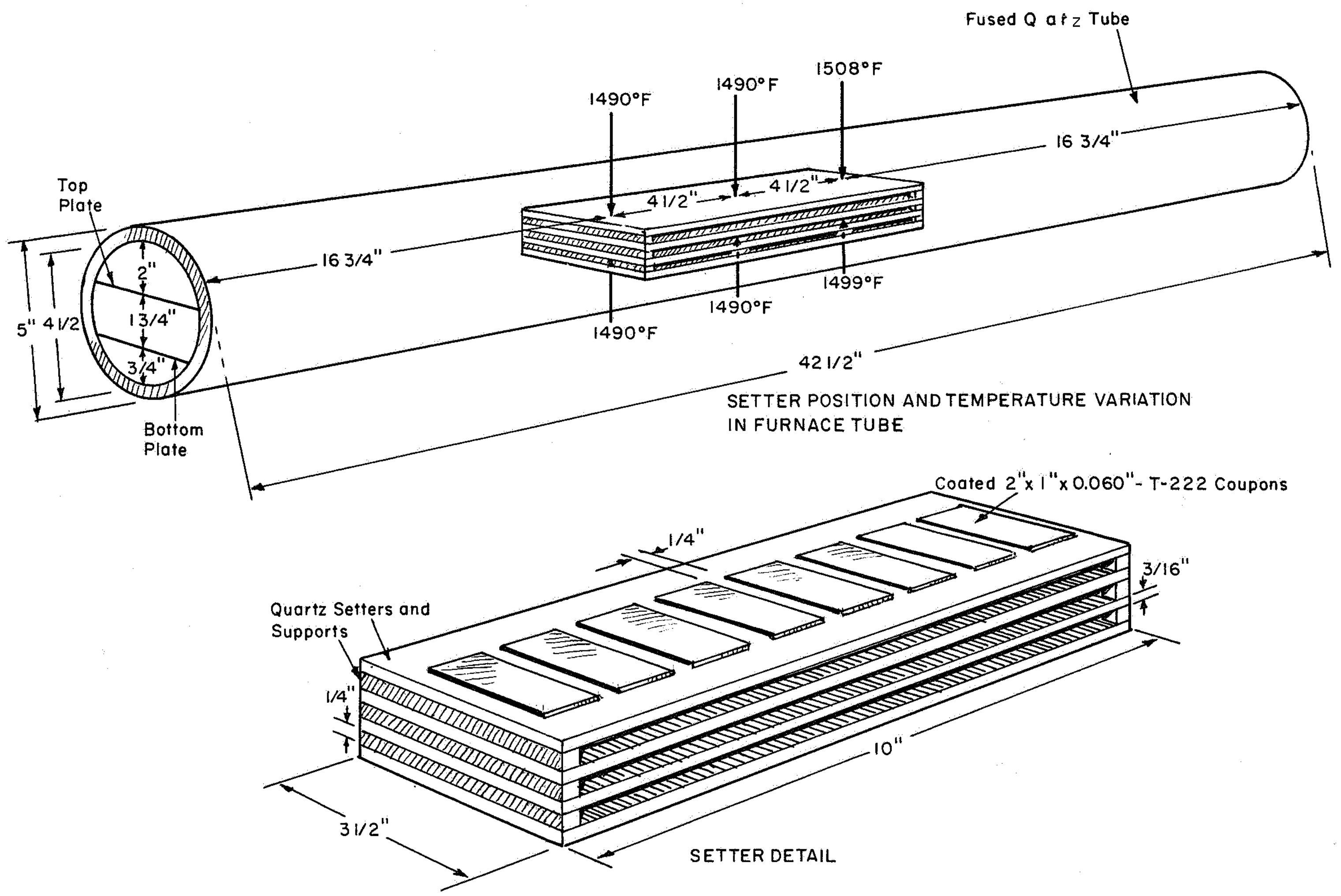
General Failure 5 x



Edge Failure 5x

FIGURE 18

TYPICAL OXIDATION FAILURES AT 1500°F AND 2400°F OF SILICIDE-COATED W/Ta-10W TEST COUPONS

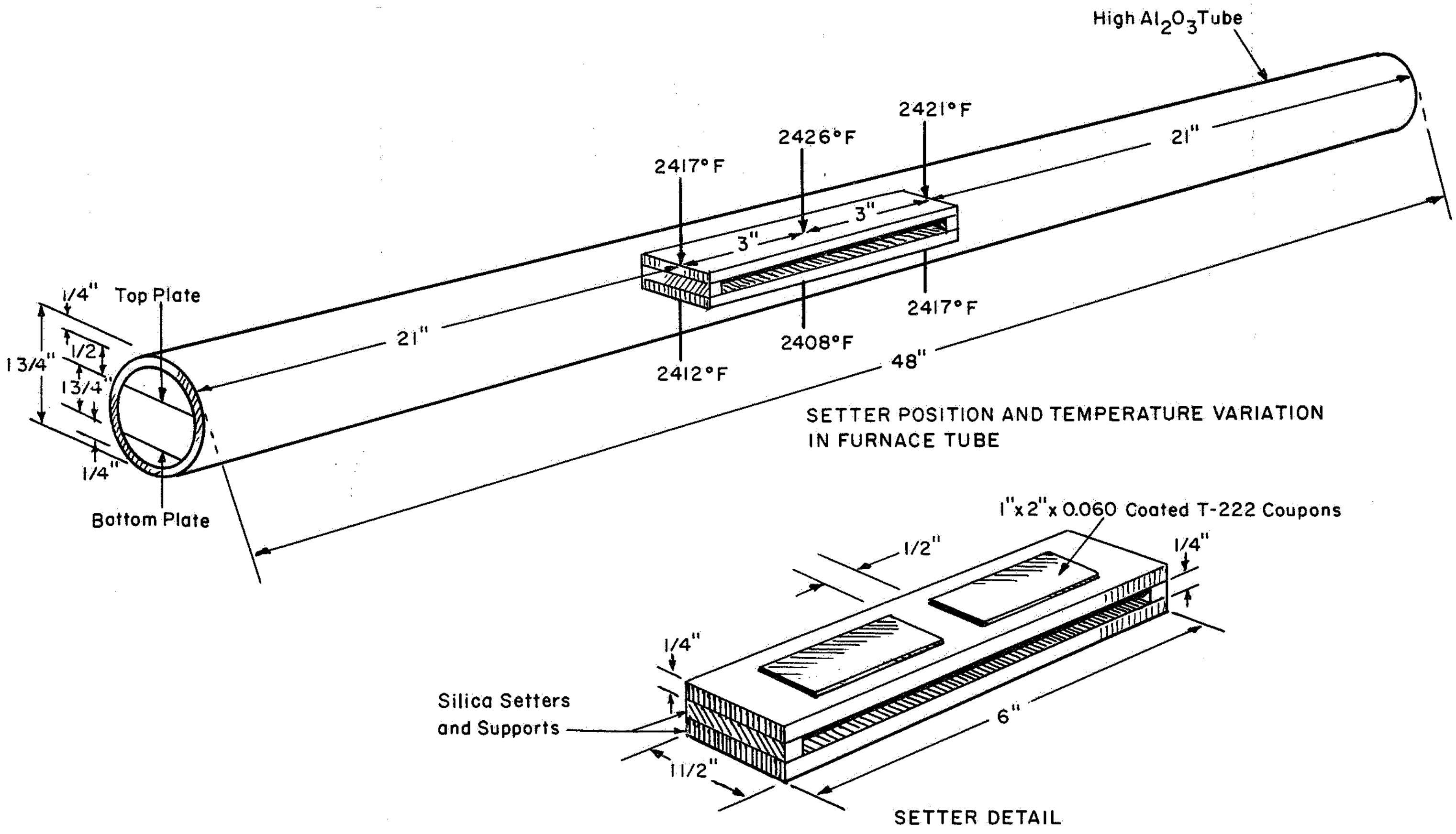


SETTER POSITION AND TEMPERATURE VARIATION IN FURNACE TUBE

SETTER DETAIL

FIGURE 19

SPECIMEN ARRANGEMENT - 1500°F OXIDATION TEST



SETTER POSITION AND TEMPERATURE VARIATION IN FURNACE TUBE

SETTER DETAIL

FIGURE 20

SPECIMEN ARRANGEMENT - 2400°F OXIDATION TEST

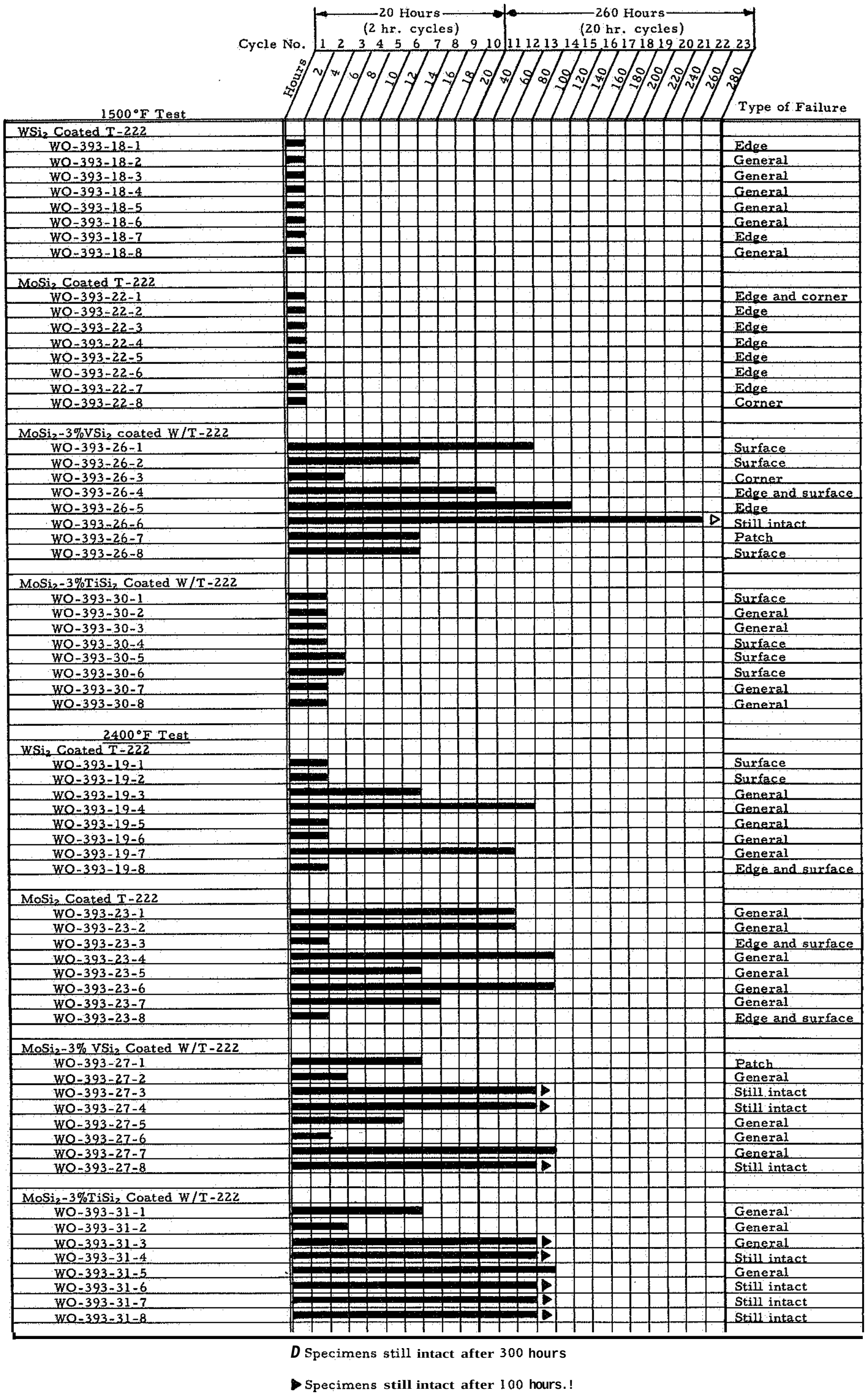
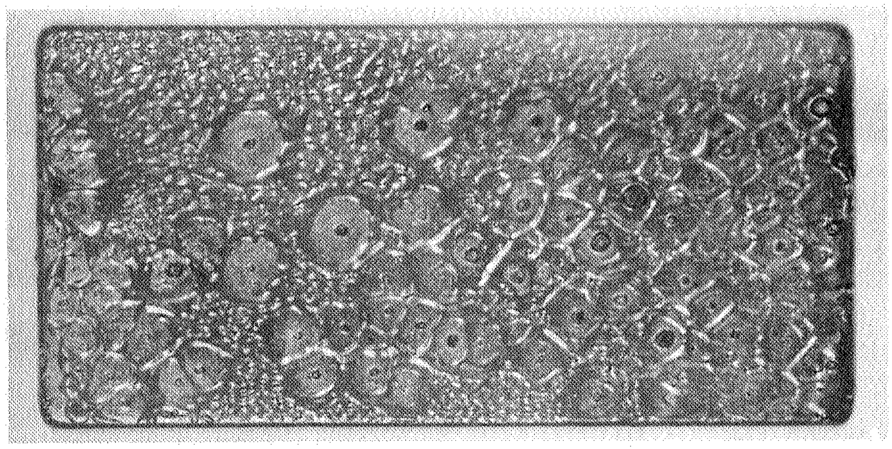
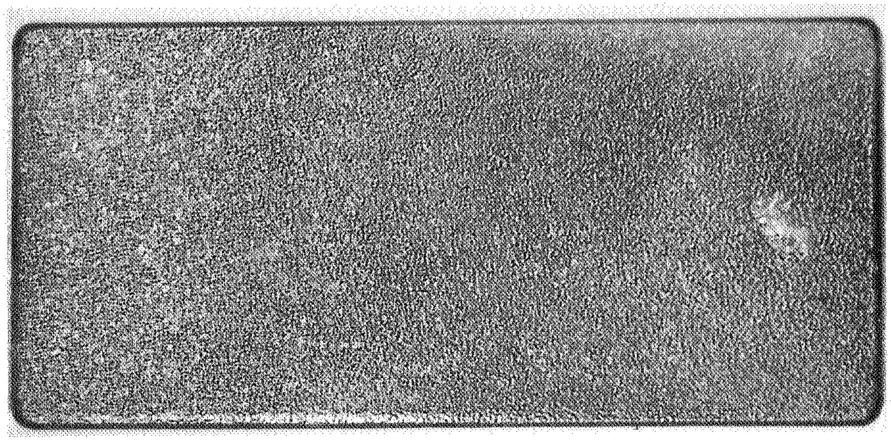


FIGURE 21

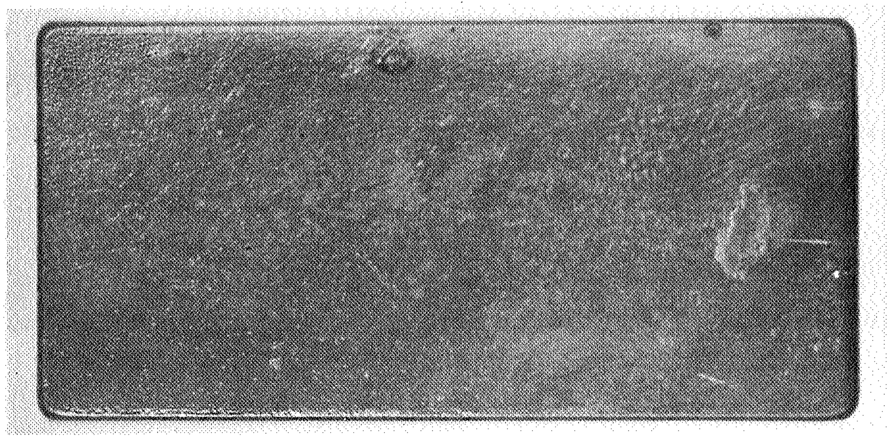
CYCLIC AND STATIC OXIDATION TESTS OF SILICIDE SURFACE COATINGS ON T-222 AND W/T-222



(a) Specimen Rested on Contaminated 33 HD Alumina Setter



(b) Specimen Rested on a Thoria Pellet Interposed Between Contaminated 33 HD Alumina and Specimen



(c) Specimen Rested on a Silica Setter

FIGURE 22

EFFECT OF VARIOUS SETTER MATERIALS ON PREOXIDIZED WSi_2-COATED T-222 ALLOY AFTER TESTING AT 2400°F

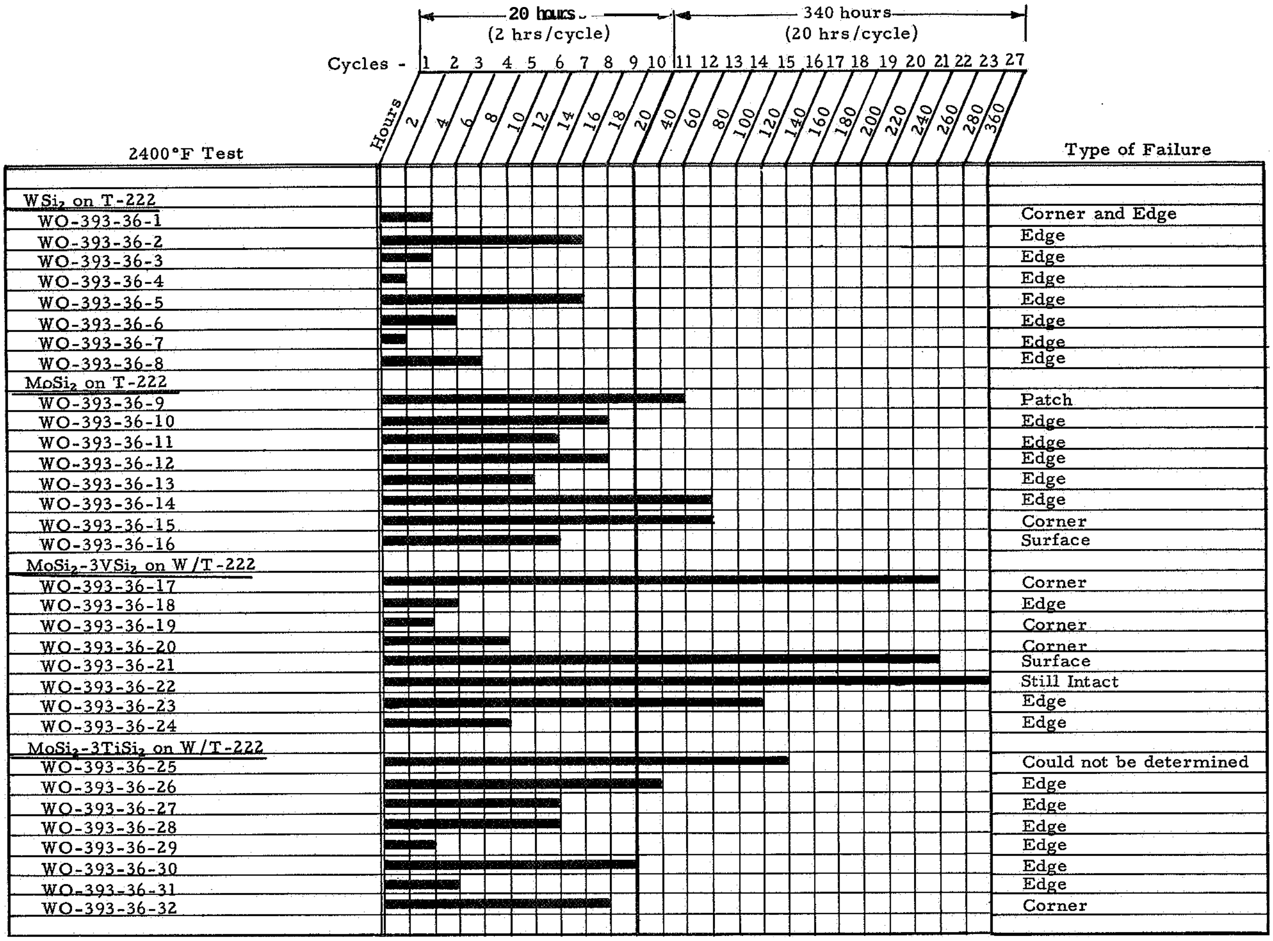


FIGURE 23

2400°F CYCLIC OXIDATION TESTS OF FOUR COATING SYSTEMS ON T-222 USING SILICA SETTERS

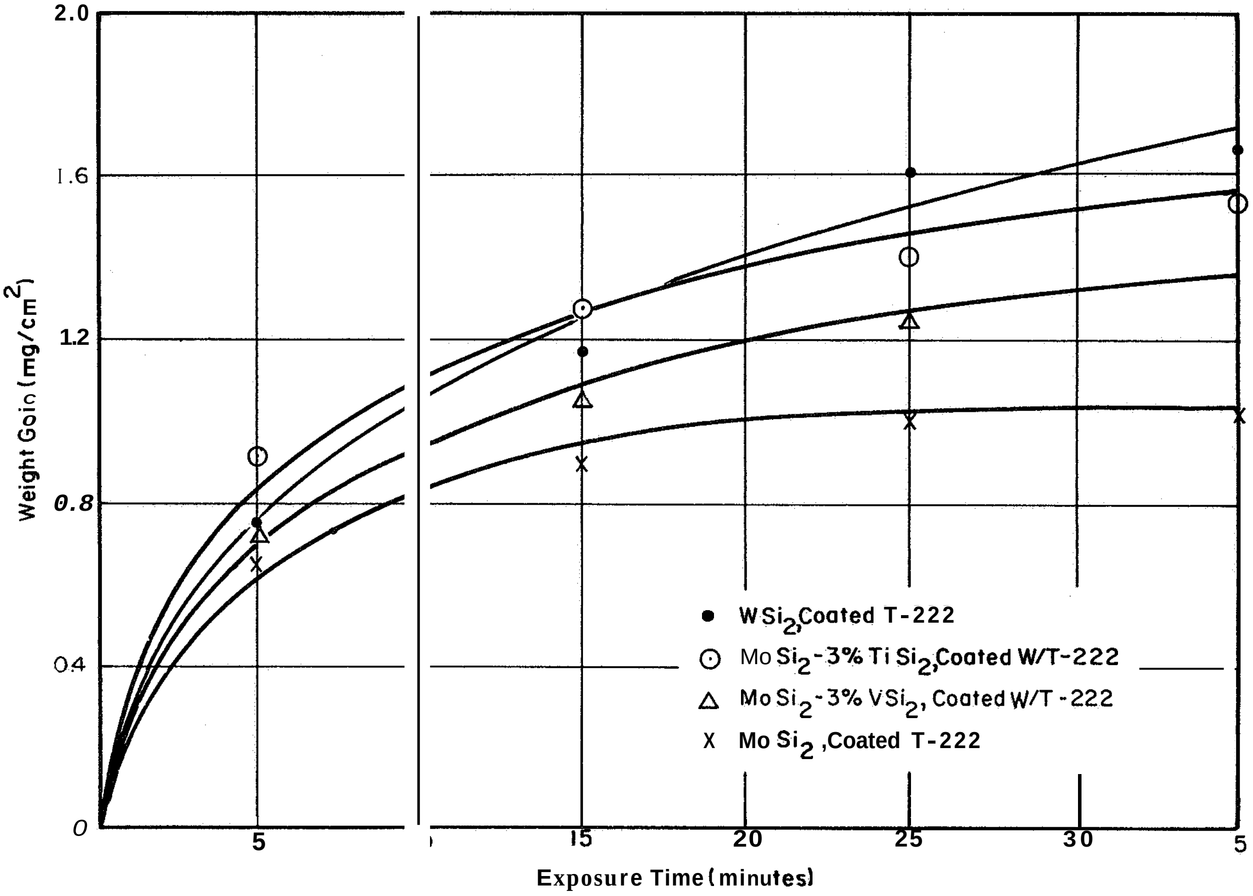


FIGURE 24

PREOXIDATION TIME VS. WEIGHT GAIN OF VARIOUS SILICIDE COATINGS ON T-222 AND W/T-222

a

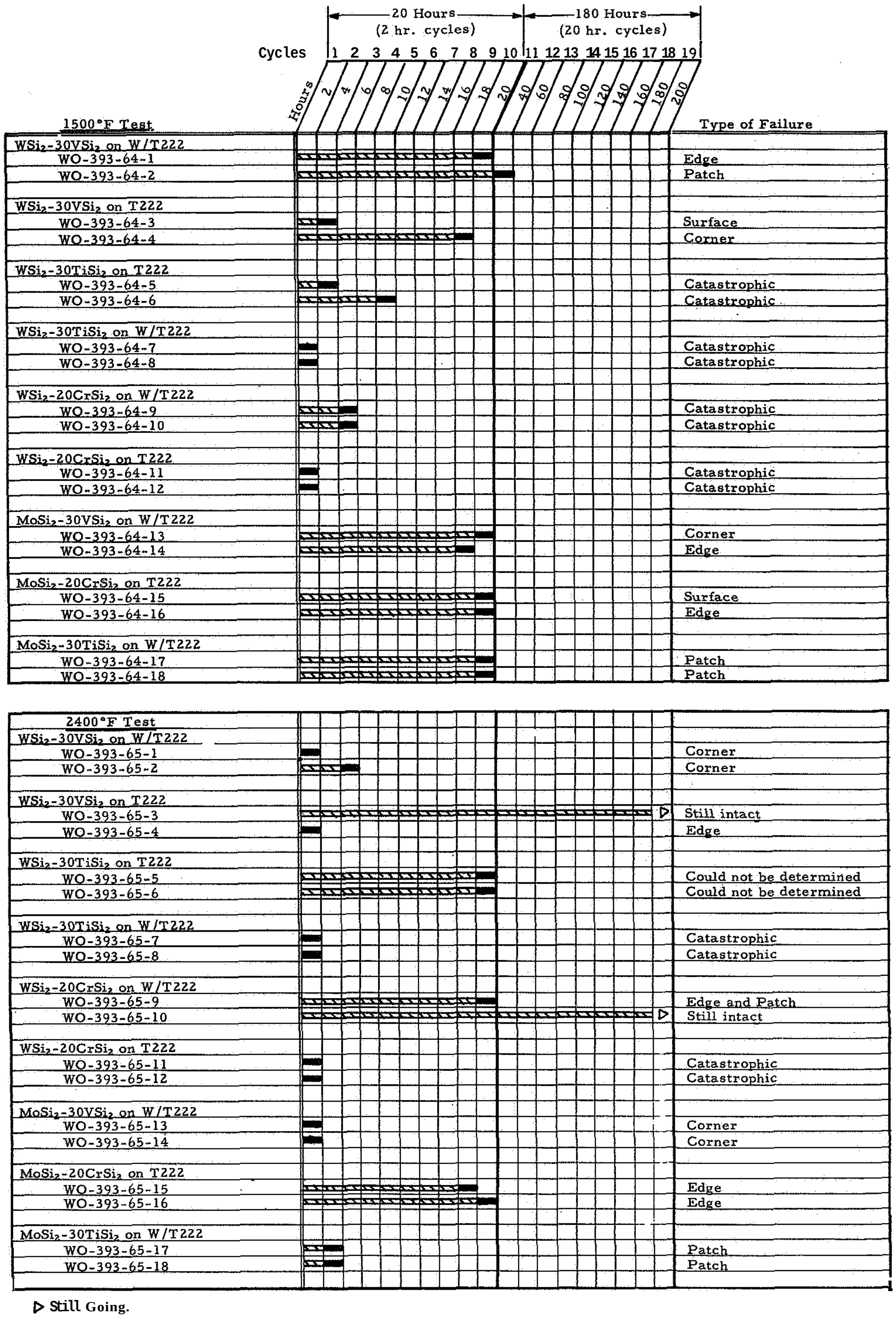


FIGURE 25

OXIDATION SCREENING TESTS OF MODIFIED WSi_2 AND $MoSi_2$-BASE COATING SYSTEMS

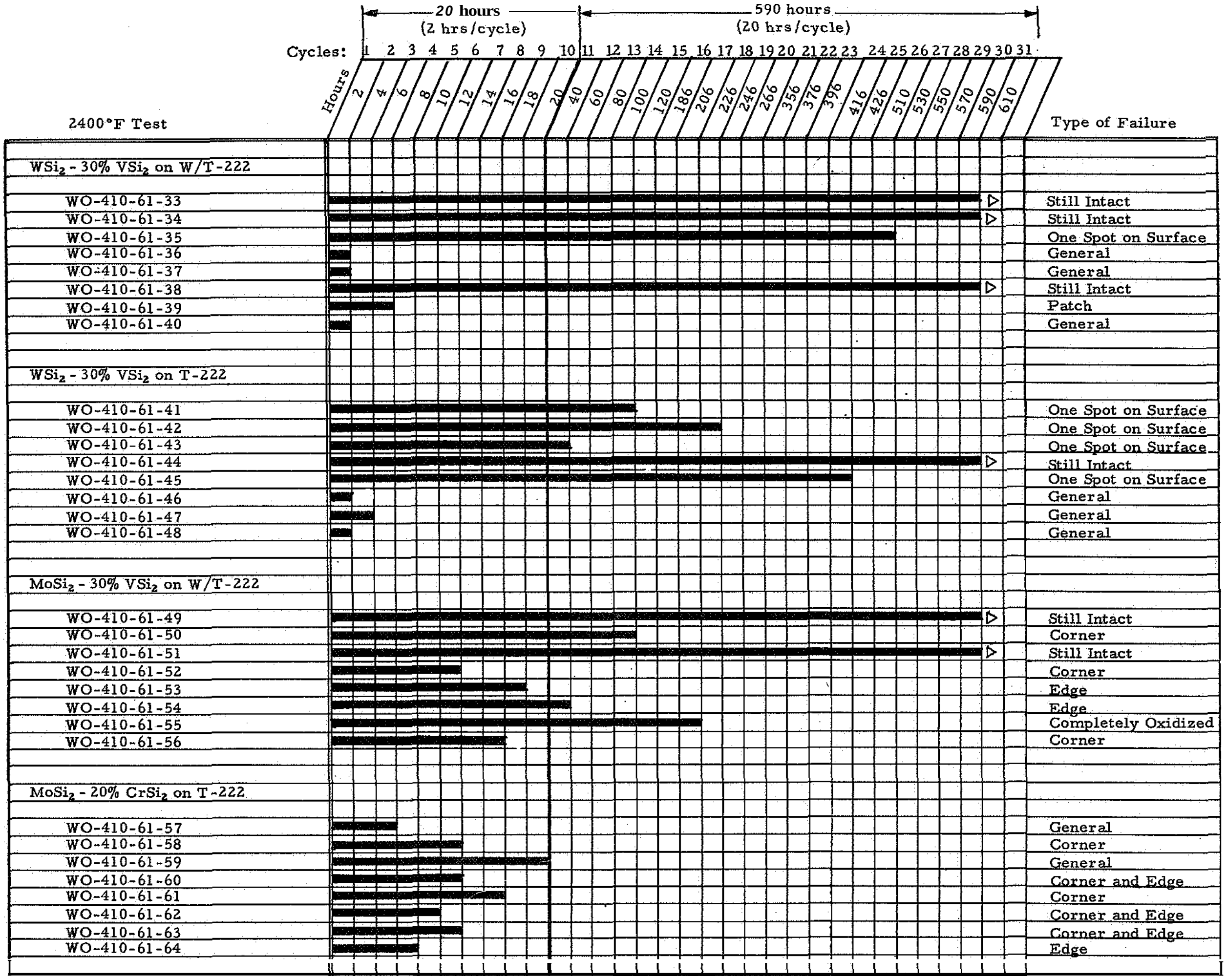


FIGURE 26

FINAL CYCLIC OXIDATION TESTS AT 2400°F OF MODIFIED WSi_2 AND $MoSi_2$-BASE COATING SYSTEMS

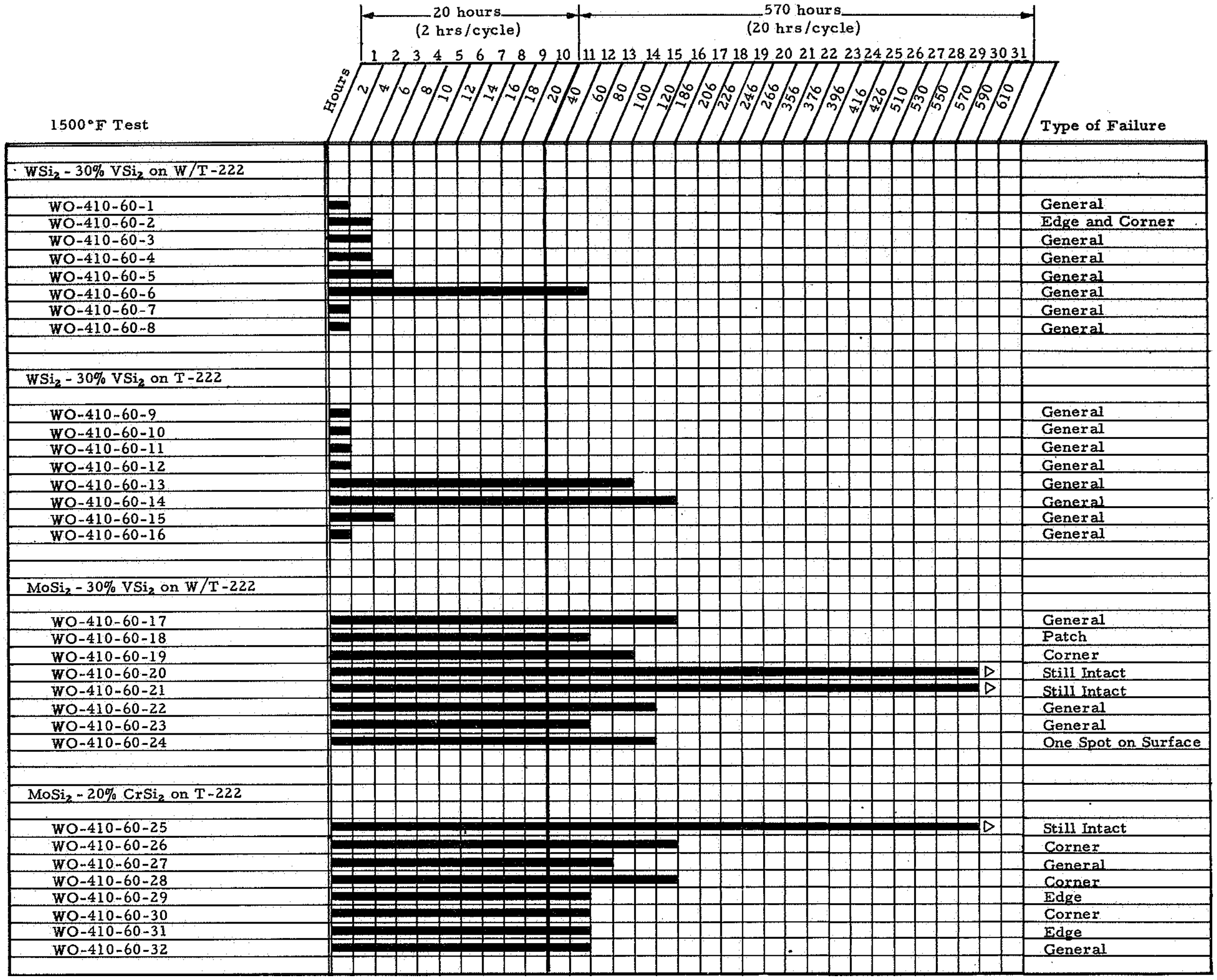


FIGURE 27

FINAL CYCLIC OXIDATION TESTS AT 1500°F OF MODIFIED WSi_2 AND $MoSi_2$-BASE COATING SYSTEMS

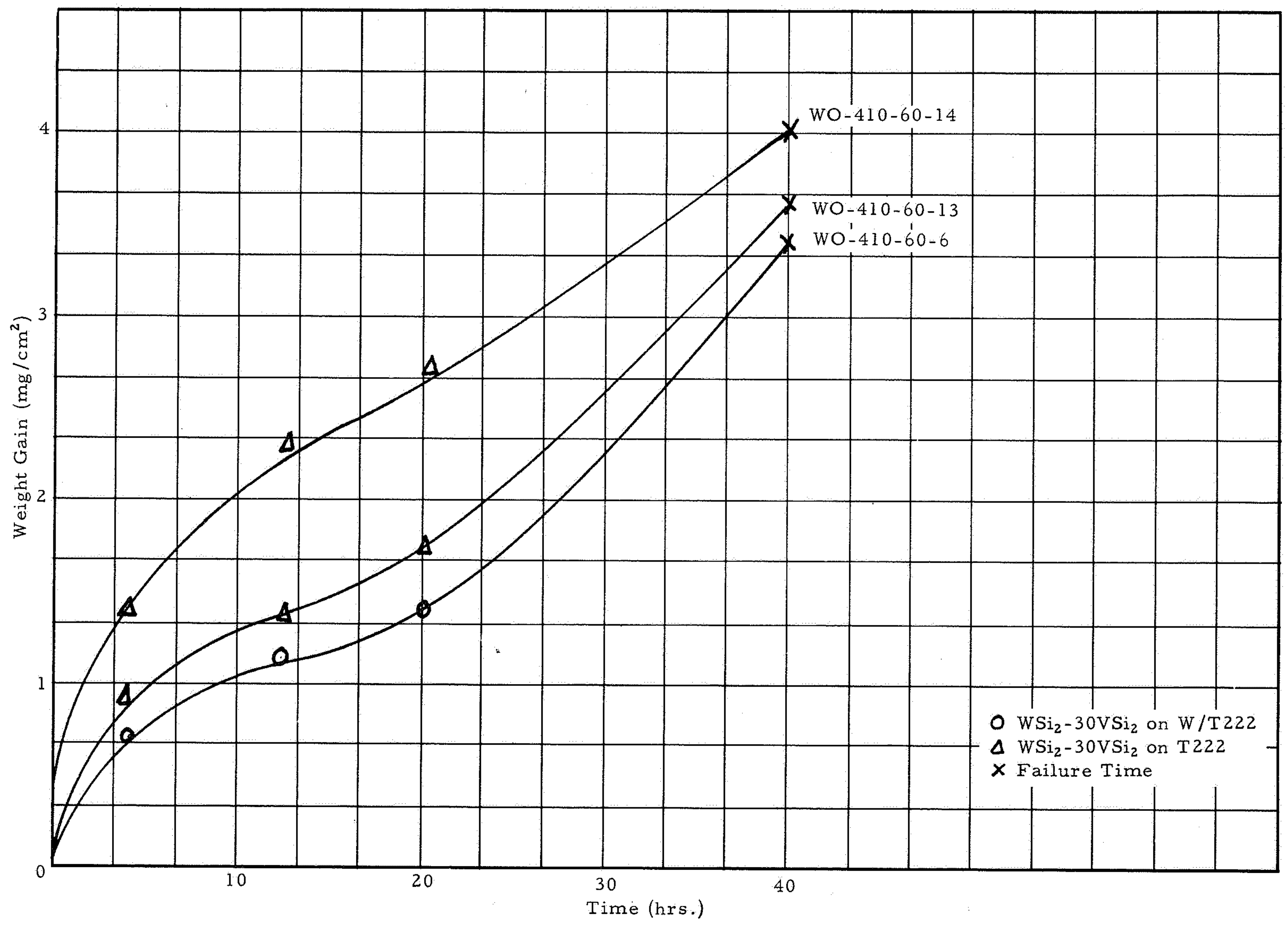


FIGURE 28

OXIDATION RATE OF THE WSi$_2$-30VSi$_2$
COATING ON W/T222 AND T222 AT 1500°F

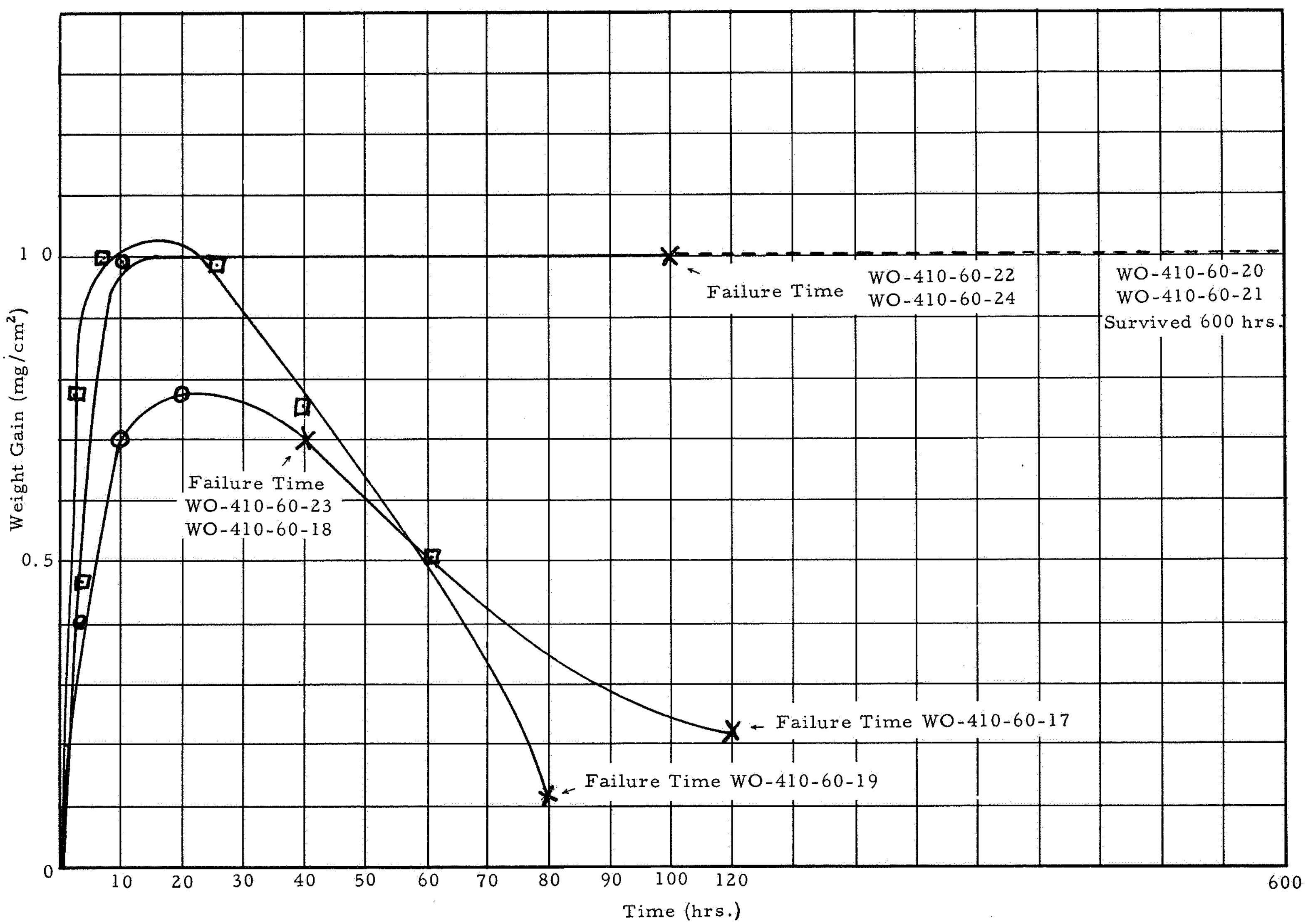


FIGURE 29

OXIDATION RATE OF THE $MoSi_2$-$30VSi_2$
COATING ON W/T222 AT 1500°F

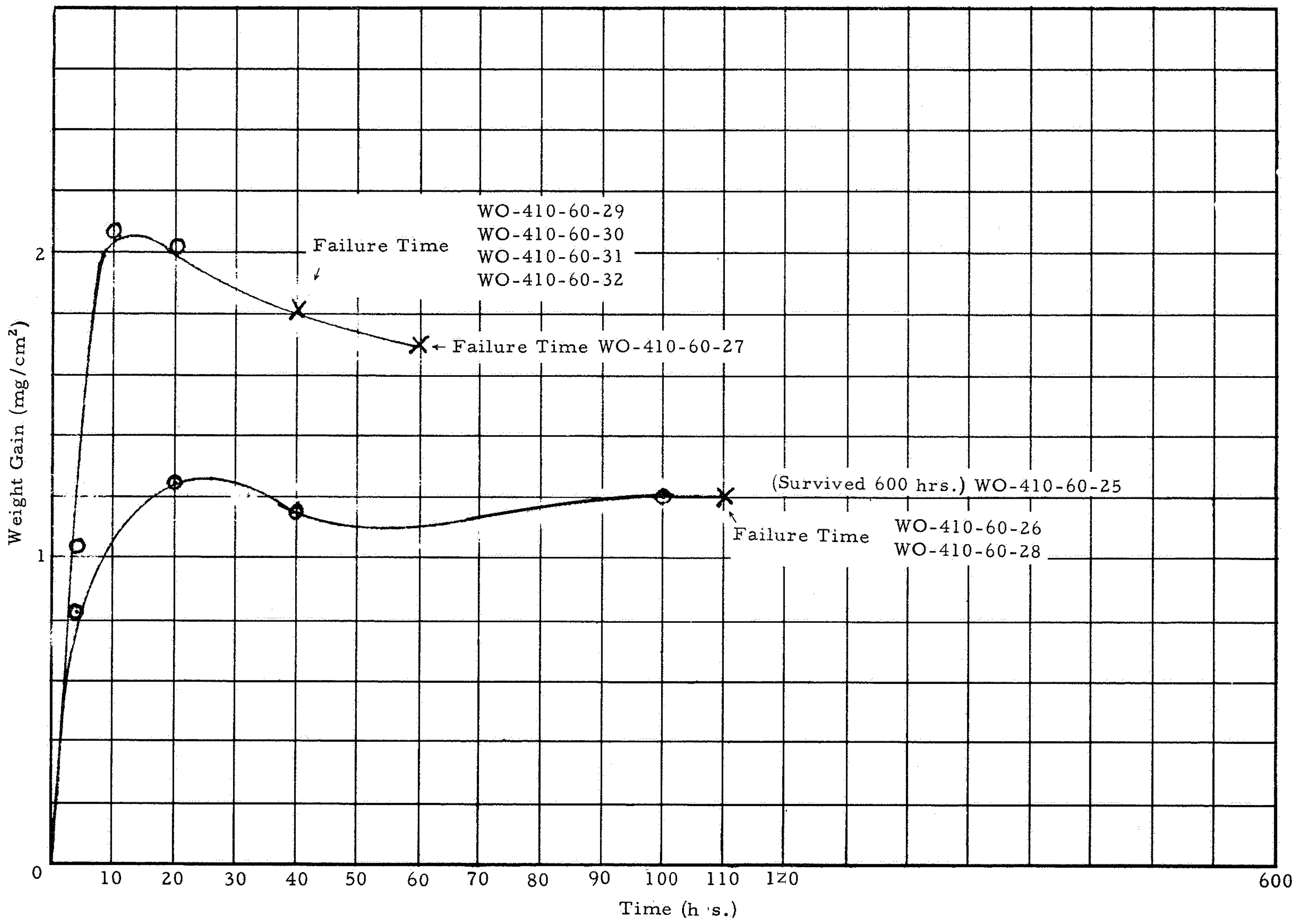


FIGURE 30

OXIDATION RATE OF THE $MoSi_2$-20$CrSi_2$ COATING ON T222 AT 1500°F COATING

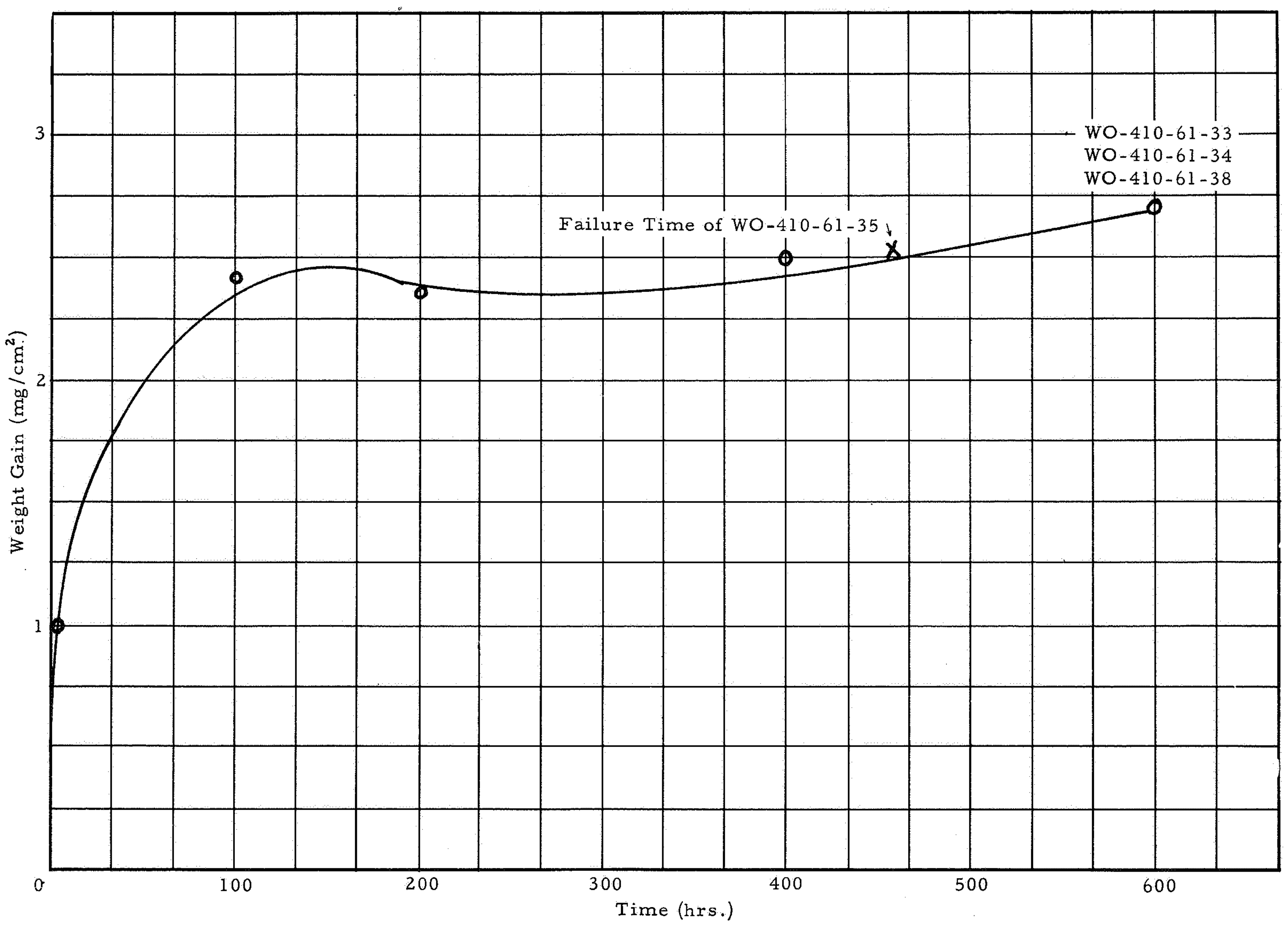


FIGURE 31

OXIDATION RATE OF THE WSi_2-30VSi_2
COATING ON W/T222 AT 2400°F

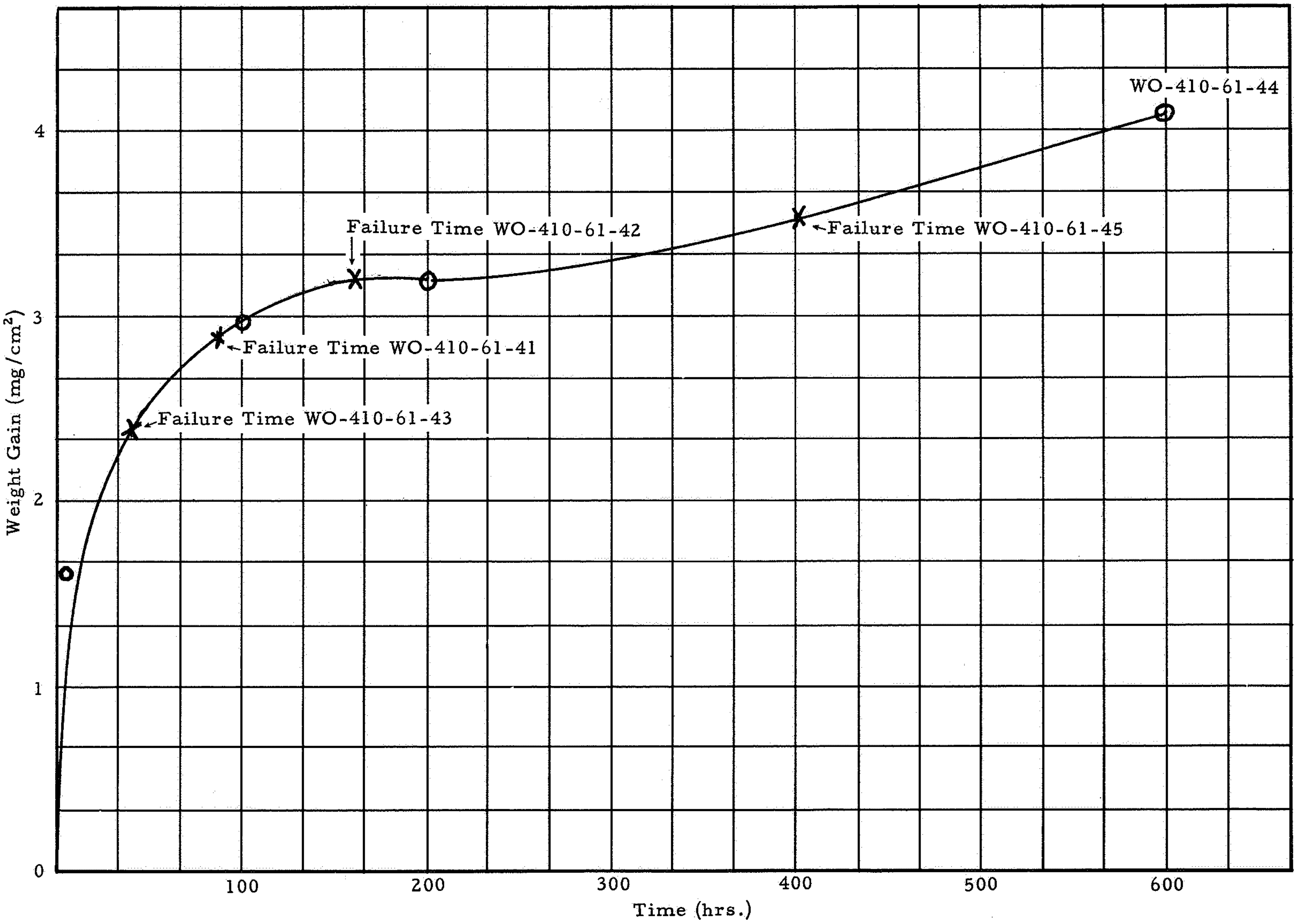


FIGURE 32

OXIDATION RATE OF THE WSi_2-$30VSi_2$ COATING ON T222 AT 2400°F

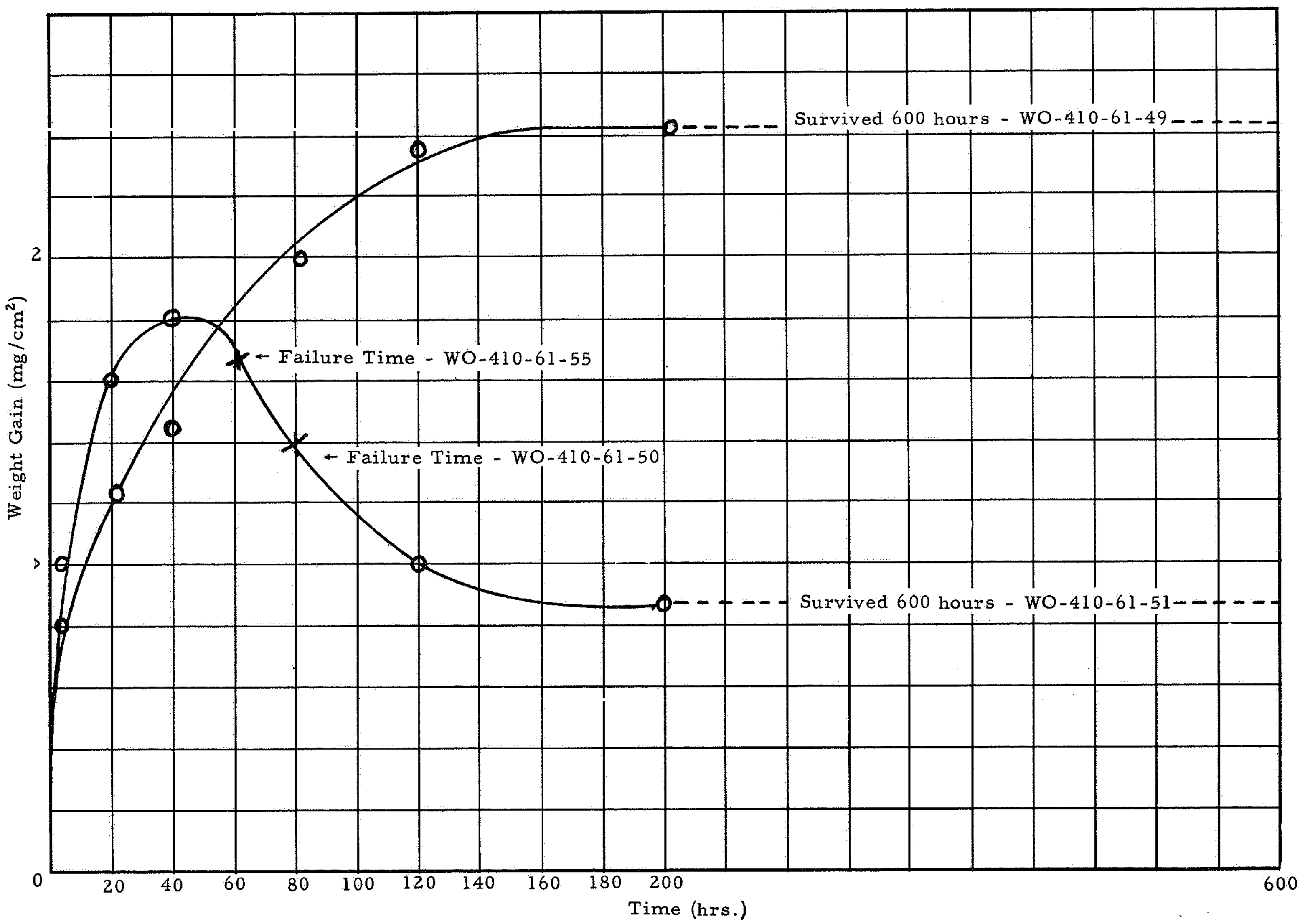
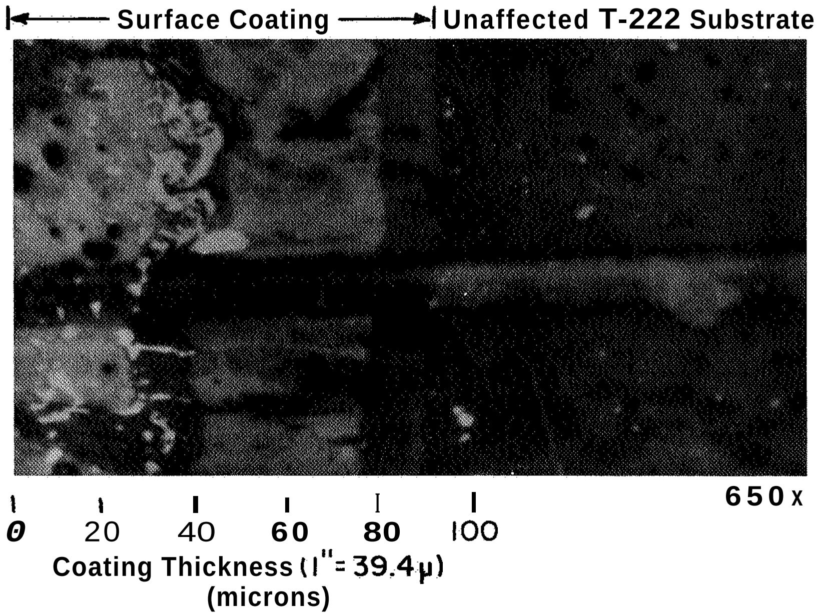


FIGURE 33

OXIDATION RATE OF THE $MoSi_2$-$30VSi_2$ COATING ON W/T222 AT 2400°F

Sample WO-393-17-3A



Sample WO-393-17-38

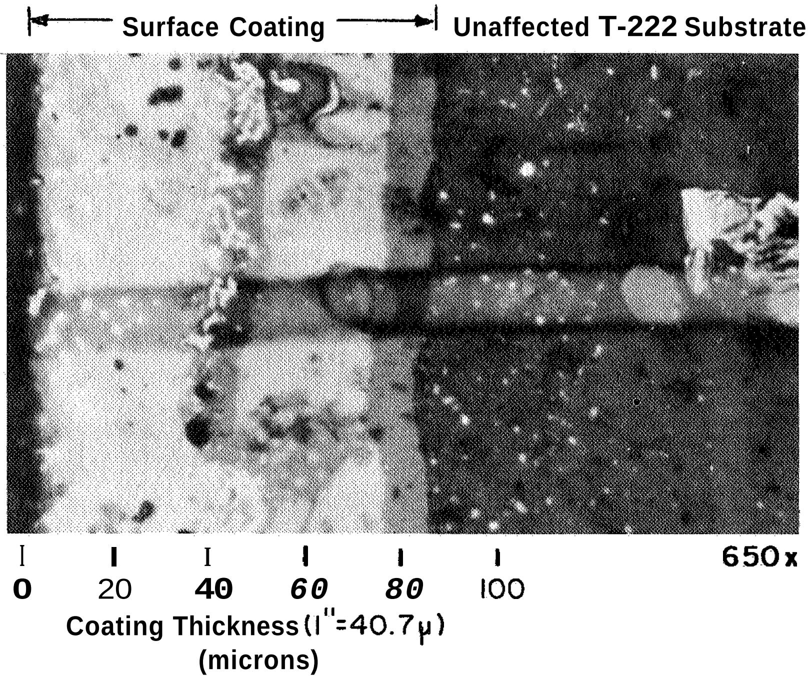


FIGURE 34

PHOTOMICROGRAPH OF WSi_2 ON T-222 BEFORE OXIDATION
(SAMPLE WO-393-17-3)

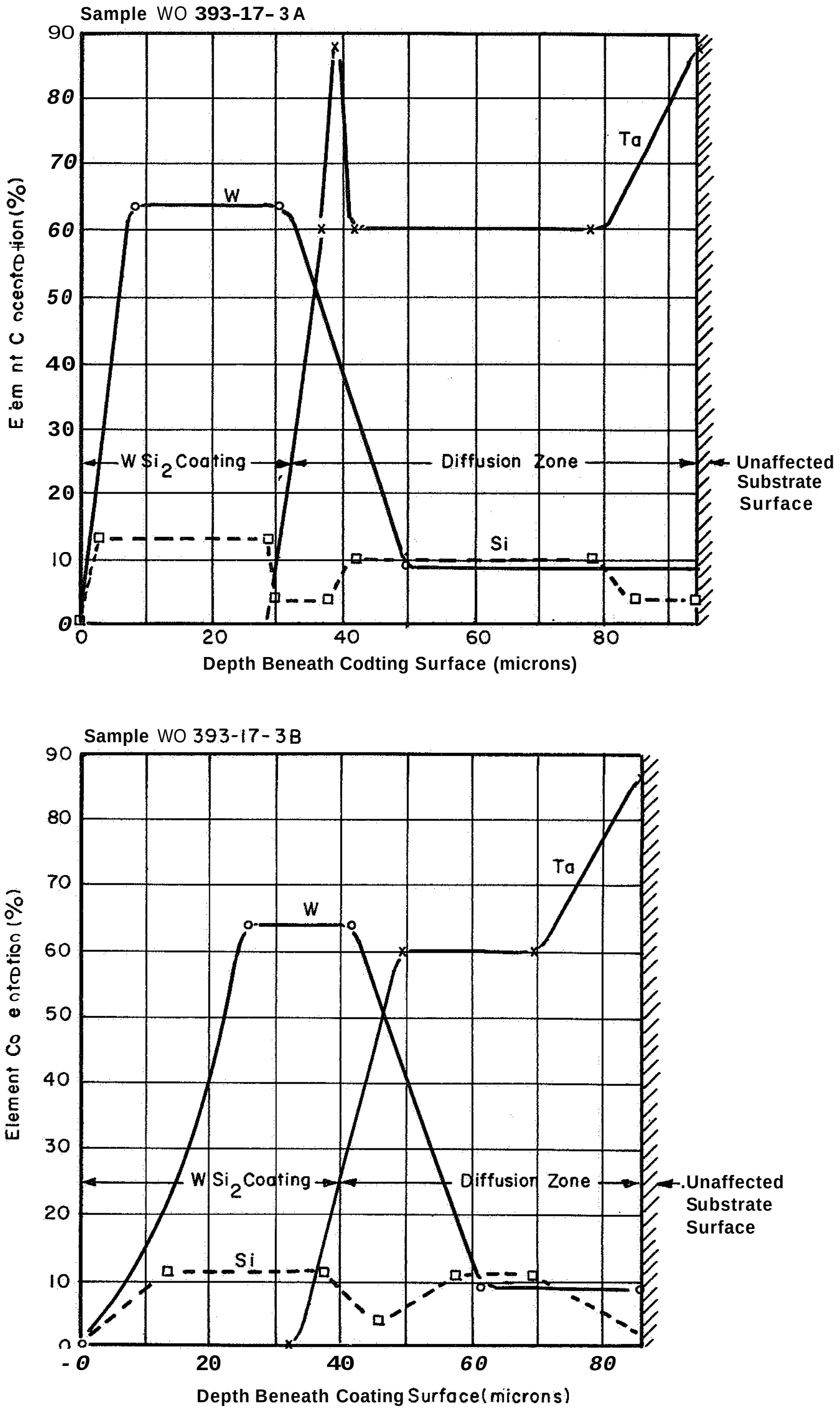
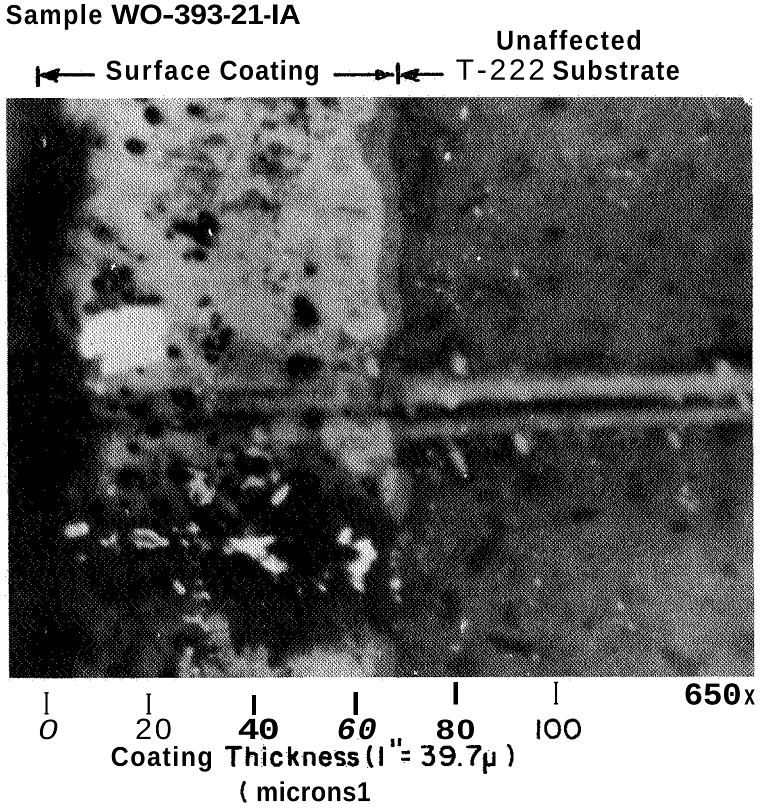


FIGURE 35

ELECTRON MICROPROBE ANALYSIS OF WSi_2 ON T-222 BEFORE OXIDATION (SAMPLE WO-393-17-3)

Sample WO-393-21-IA



Sample WO-393-21-IR

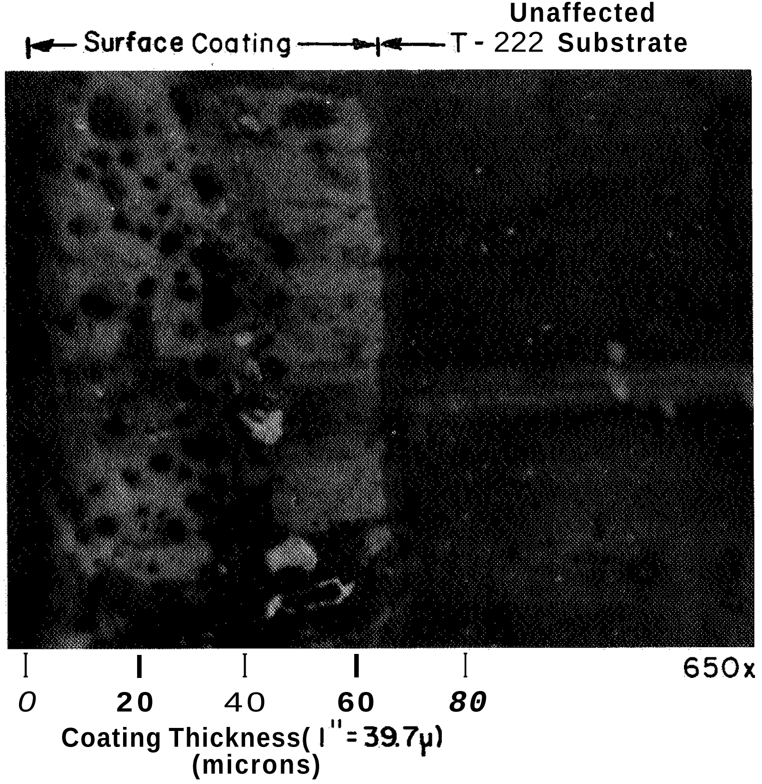


FIGURE 36

PHOTOMICROGRAPH OF $MoSi_2$ ON T-222 BEFORE OXIDATION
(SAMPLE WO-393-21-1)

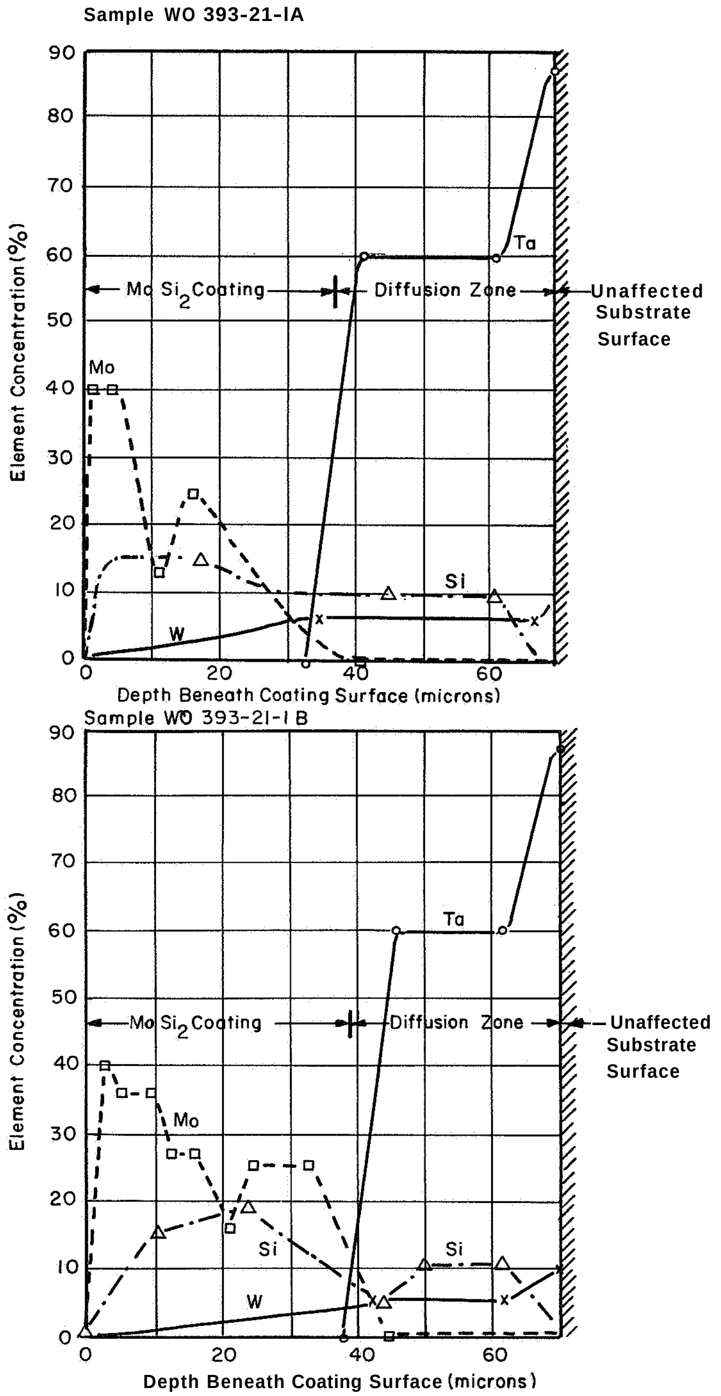
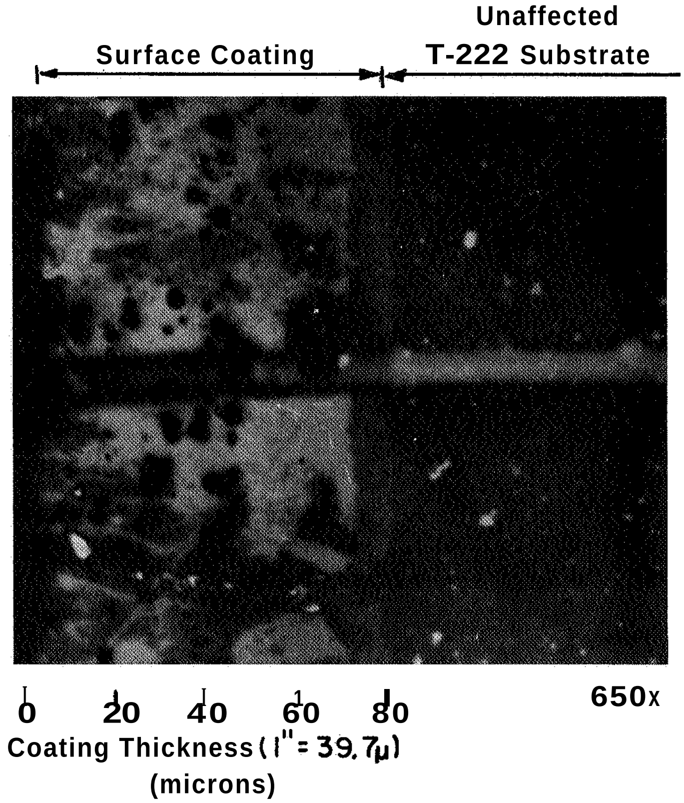


FIGURE 37

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$ ON T-222 BEFORE OXIDATION (SAMPLE WO-393-21-1)

Sample W0-393-25-2A



Sample WO- 393-25-28

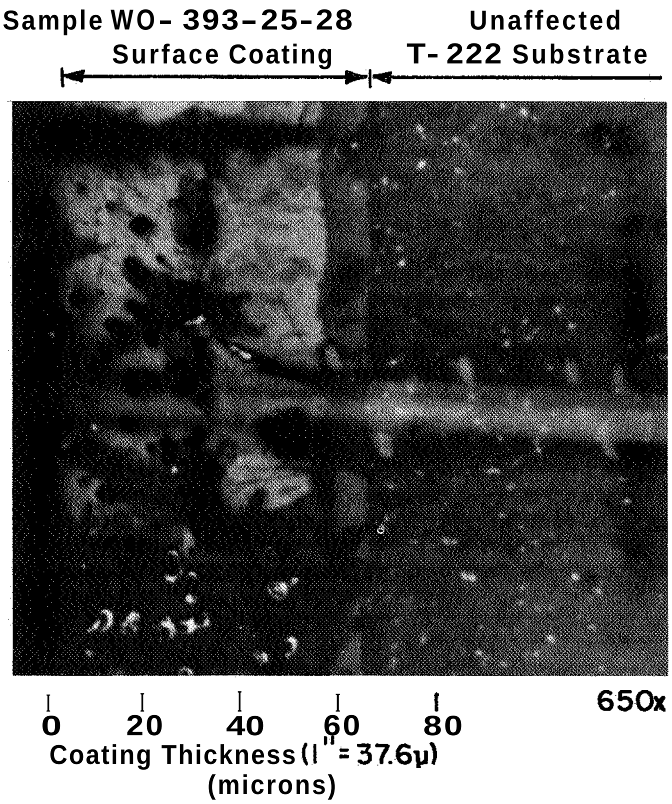


FIGURE 38

PHOTOMICROGRAPH OF $MoSi_2$-3VSi_2 ON W/T-222 BEFORE OXIDATION (SAMPLE WO-393-25-2)

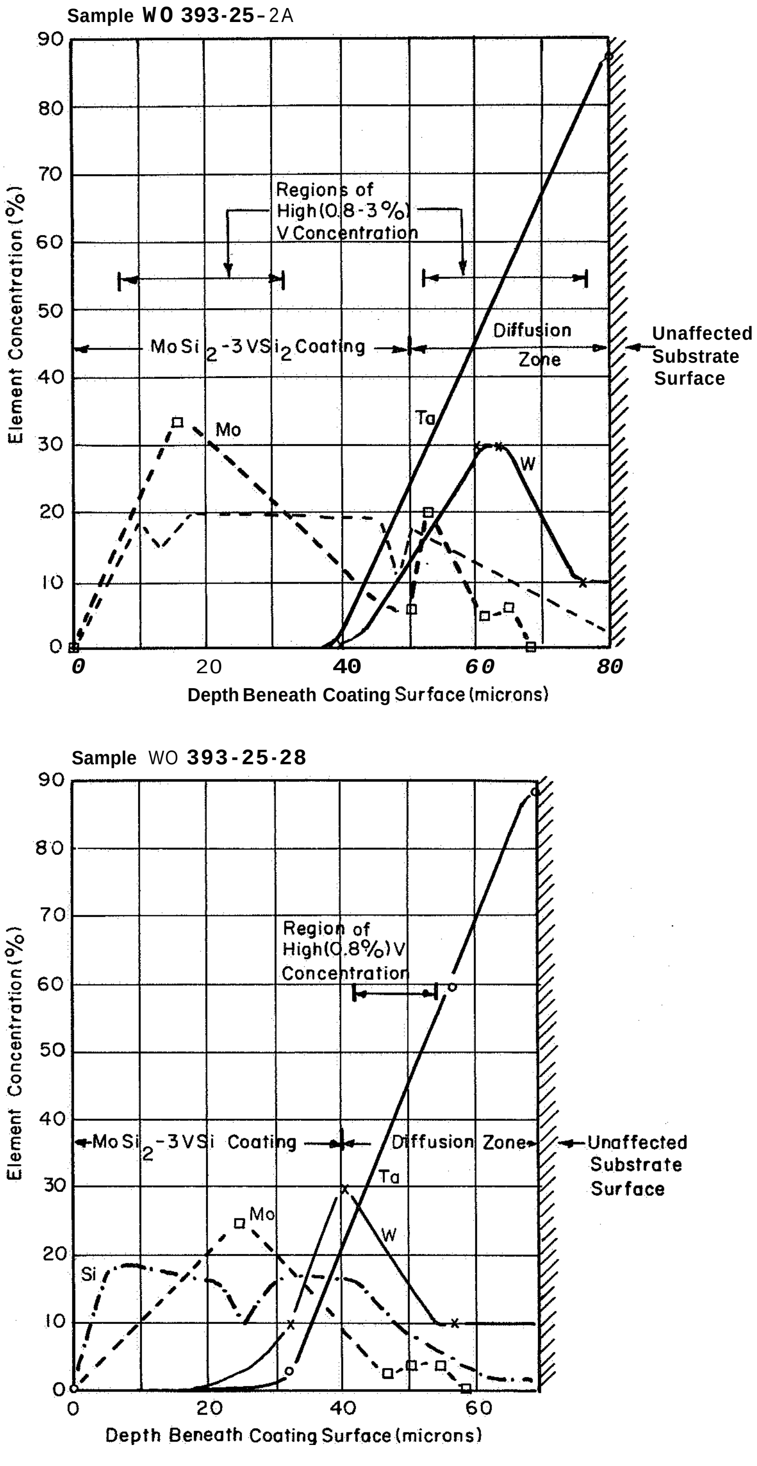
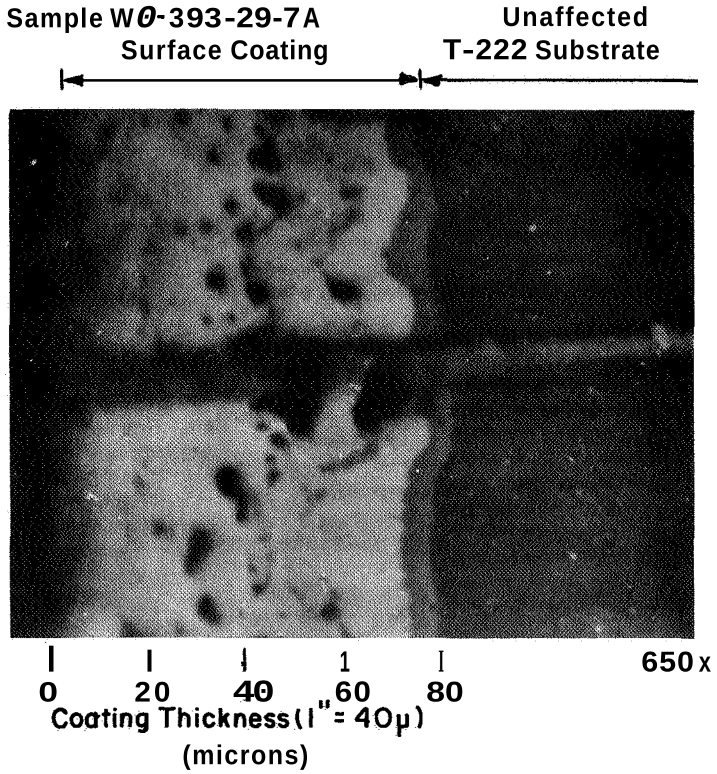


FIGURE 39

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$-$3VSi_2$ ON W/T-222 BEFORE OXIDATION (SAMPLE WO-393-25-2)



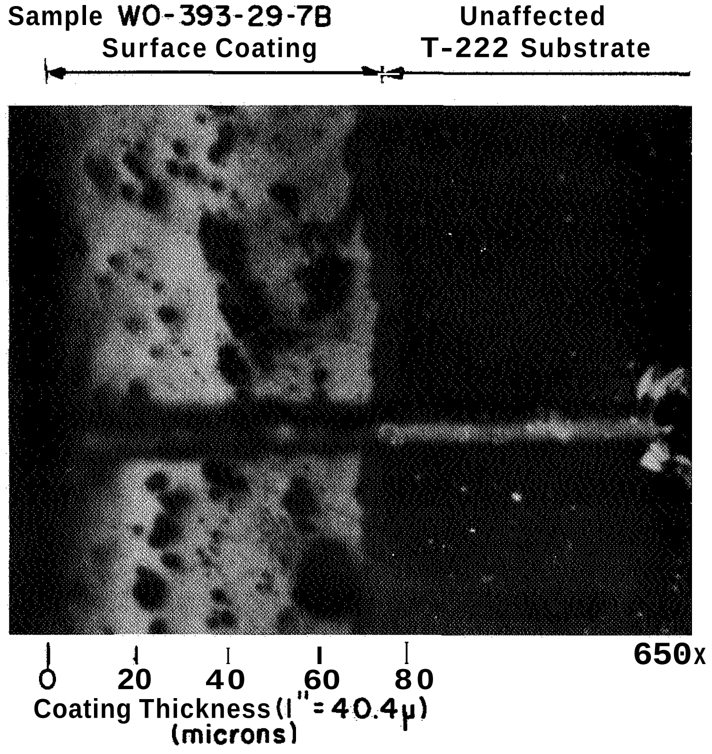


FIGURE 40

PHOTOMICROGRAPH OF $MoSi_2$-$3TiSi_2$ ON W/T-222 BEFORE OXIDATION (SAMPLE WO-393-29-7)

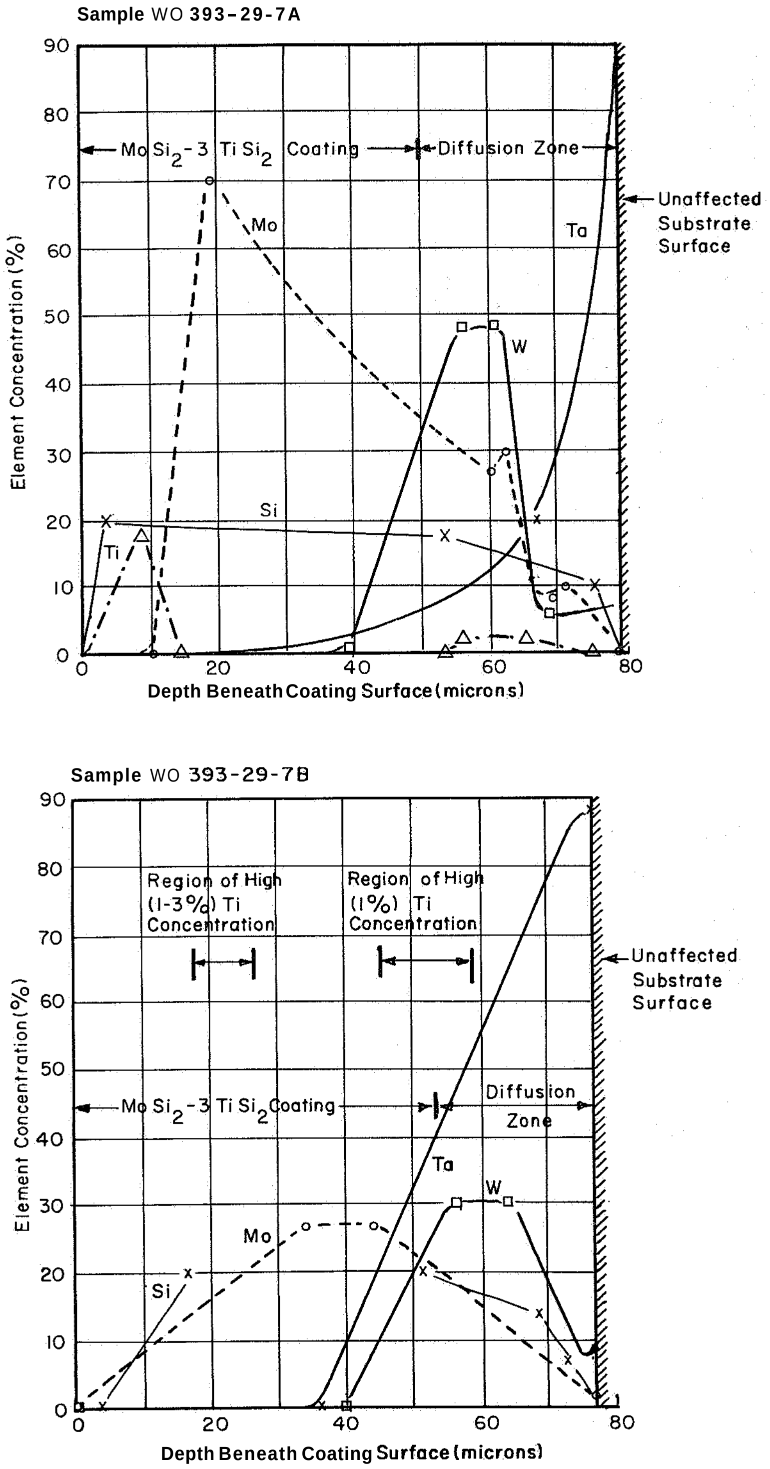
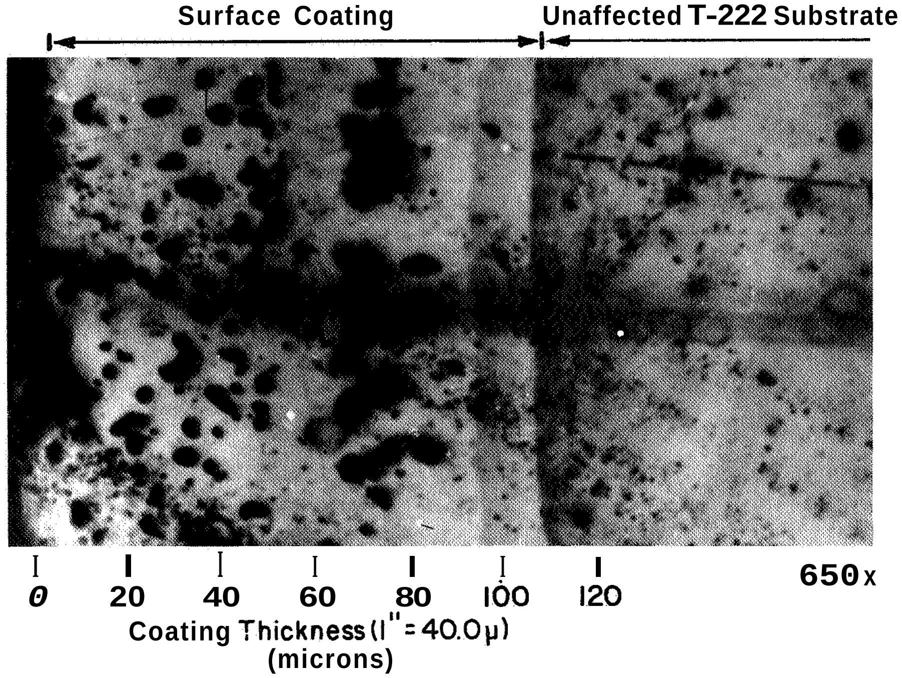


FIGURE 41

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$-$3TiSi_2$ ON W/T-222 BEFORE OXIDATION (SAMPLE WO-393-29-7)

Sample WO-393-36- 13R



Sample WO- 393-36-13 L

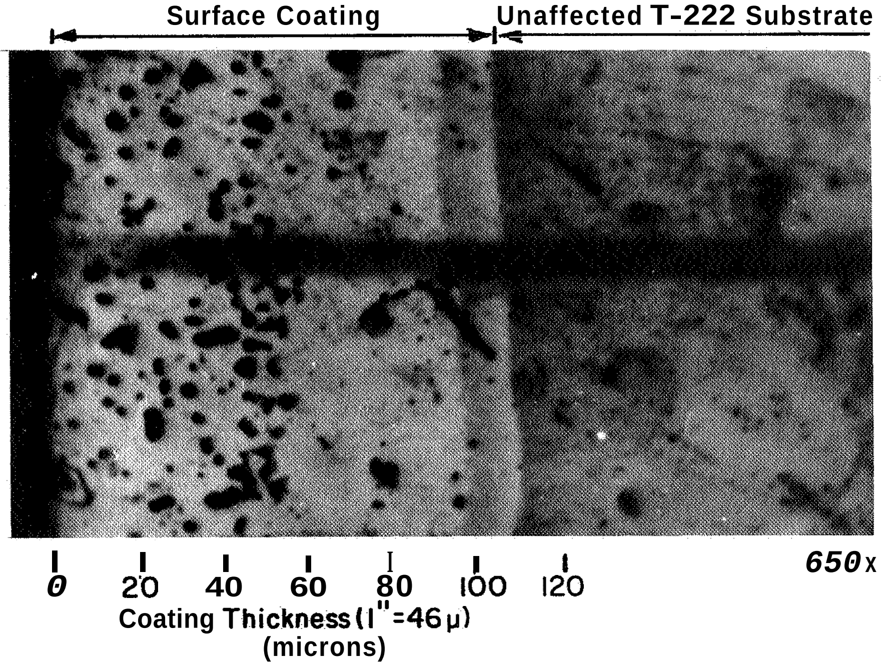
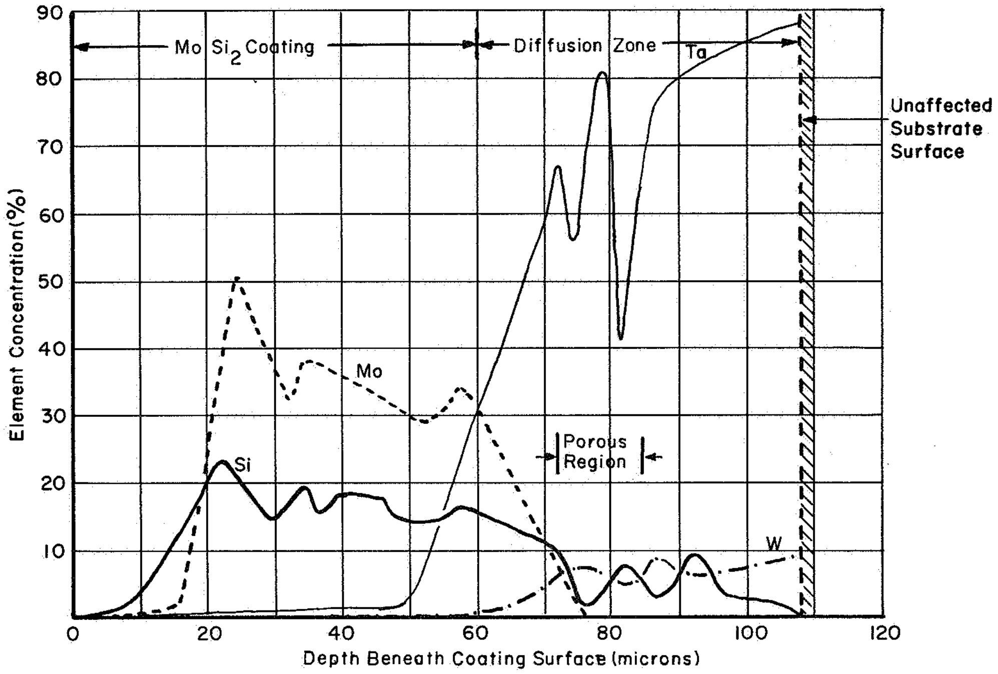


FIGURE 42

PHOTOMICROGRAPH OF $MoSi_2$ ON T-222 AFTER OXIDATION
(SAMPLE WO-393-36-13)
(FAILED AFTER TEN 2-HOUR CYCLES AT 2400°F)

Sample WO-393-36-13 R



Sample WO-393-36-13L

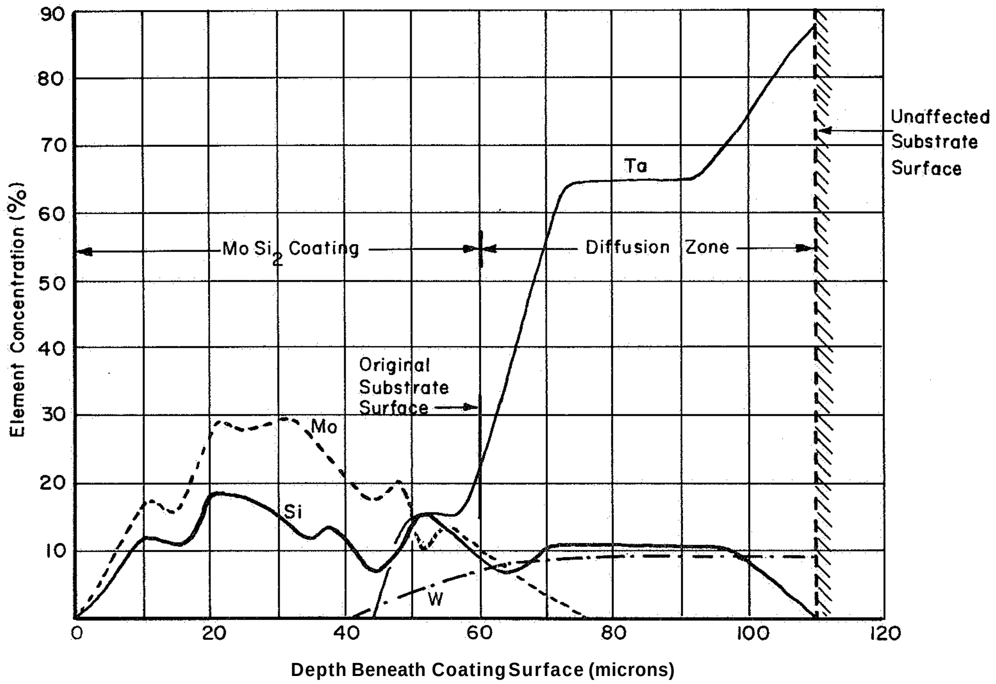
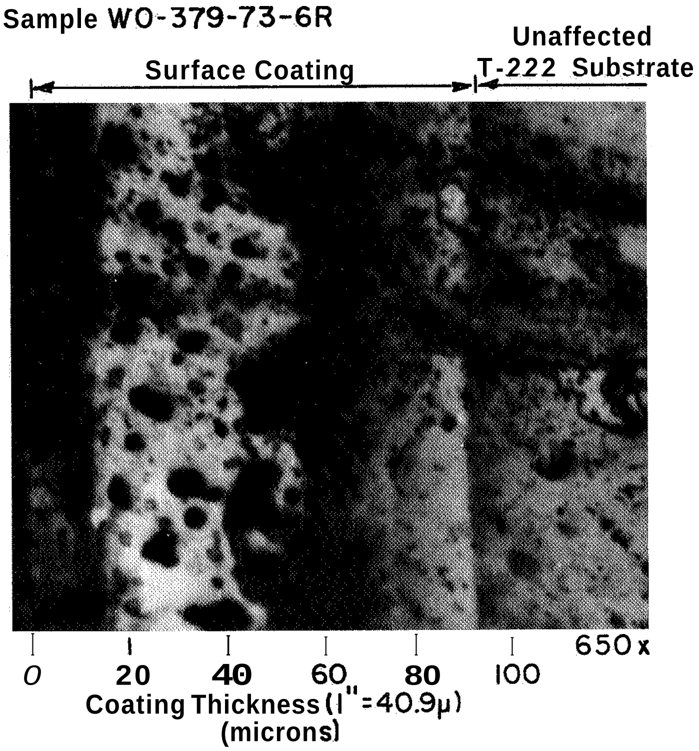


FIGURE 43

MICROPROBE ANALYSIS OF MoSi, ON T-222
(SAMPLE WO-393-36-13)
(FAILED AFTER TEN 2-HOUR CYCLES AT 2400°F)



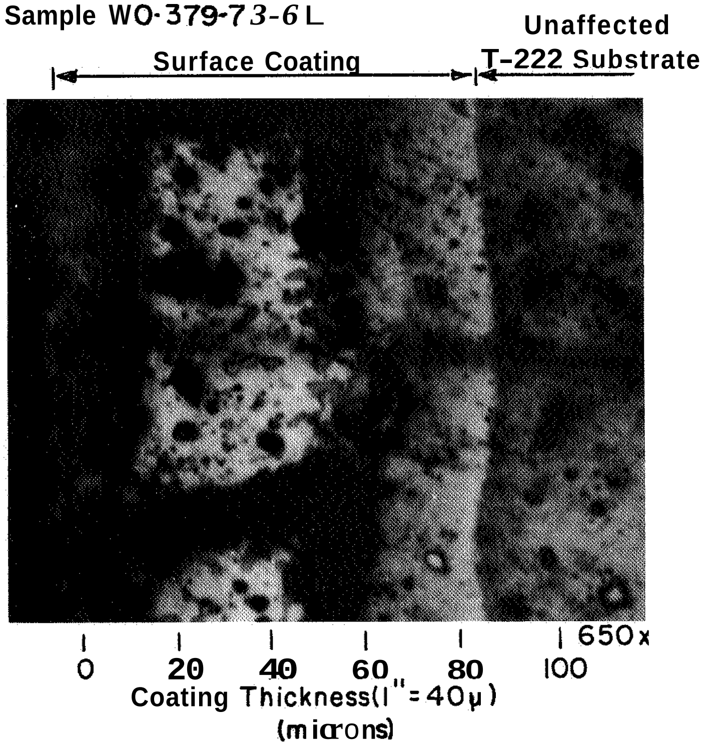
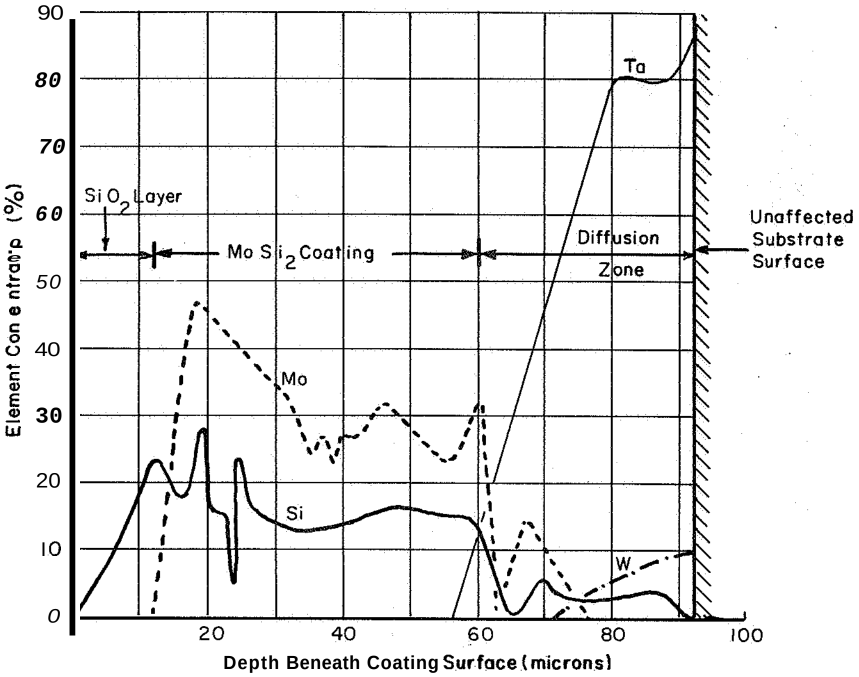


FIGURE 44

PHOTOMICROGRAPH OF MoSi, ON T-222 AFTER OXIDATION
(SAMPLE WO-379-73-6)
(SURVIVED 677 HOURS AT 2400°F)

Sample WO-379-73-6R



Sample WO-379-73-6 L

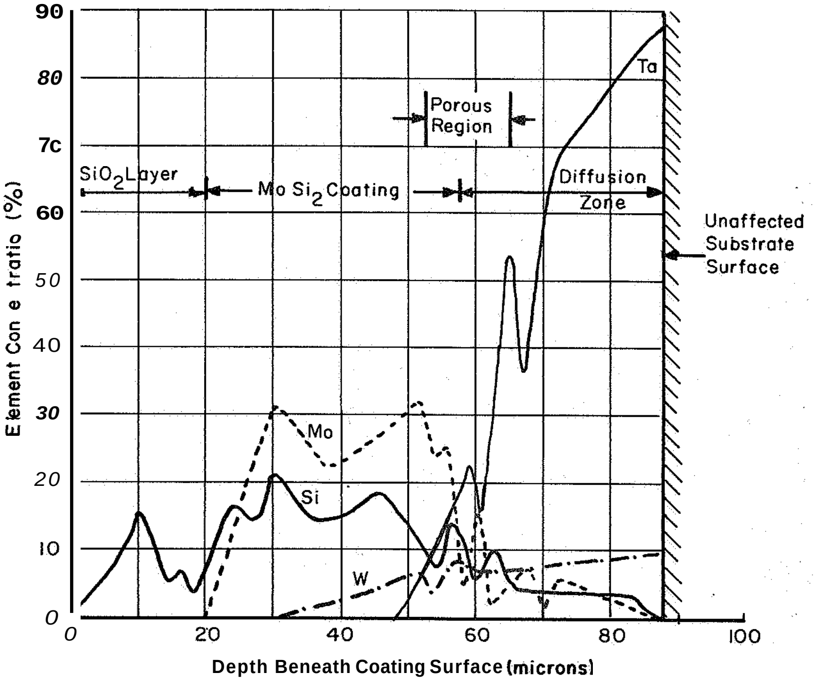
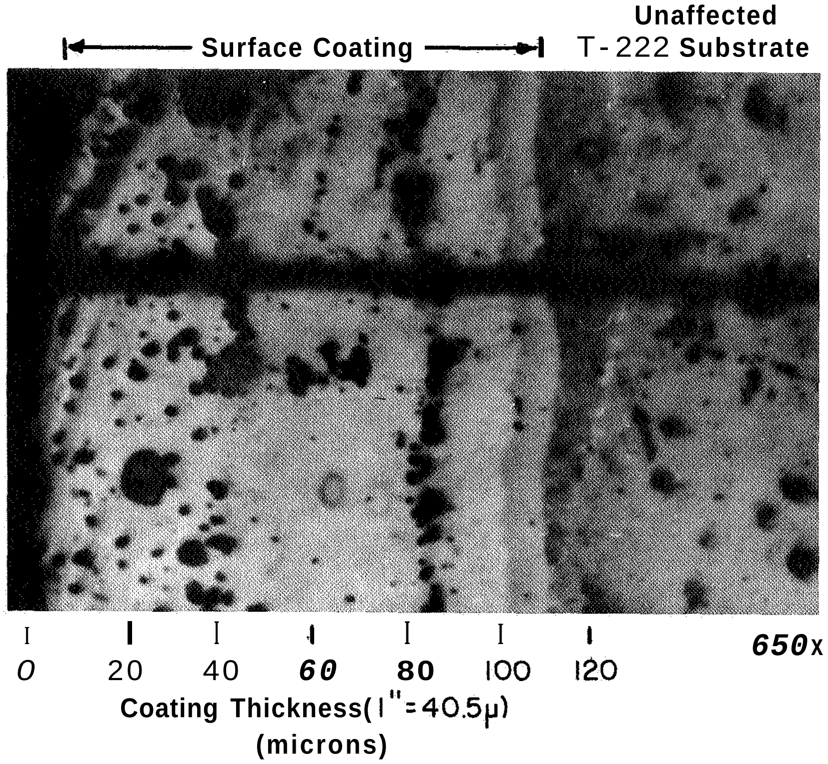


FIGURE 45

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$ ON T-222
(SAMPLE WO-379-73-6)
(SURVIVED 677 HOURS AT 2400°F)

a

Sample WO-393-44-3R



Sample WO-393-44-3L

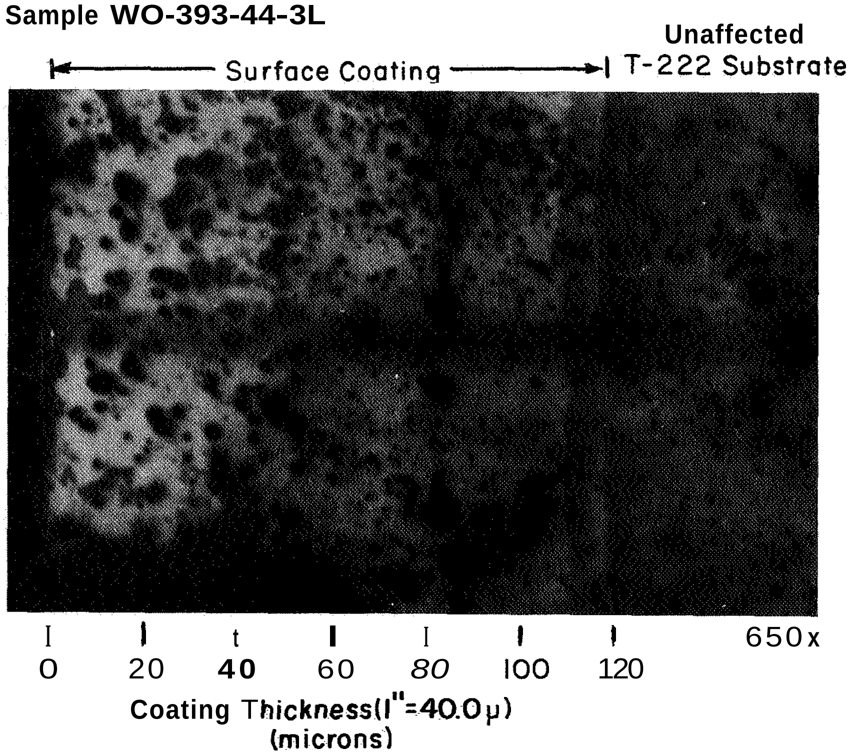
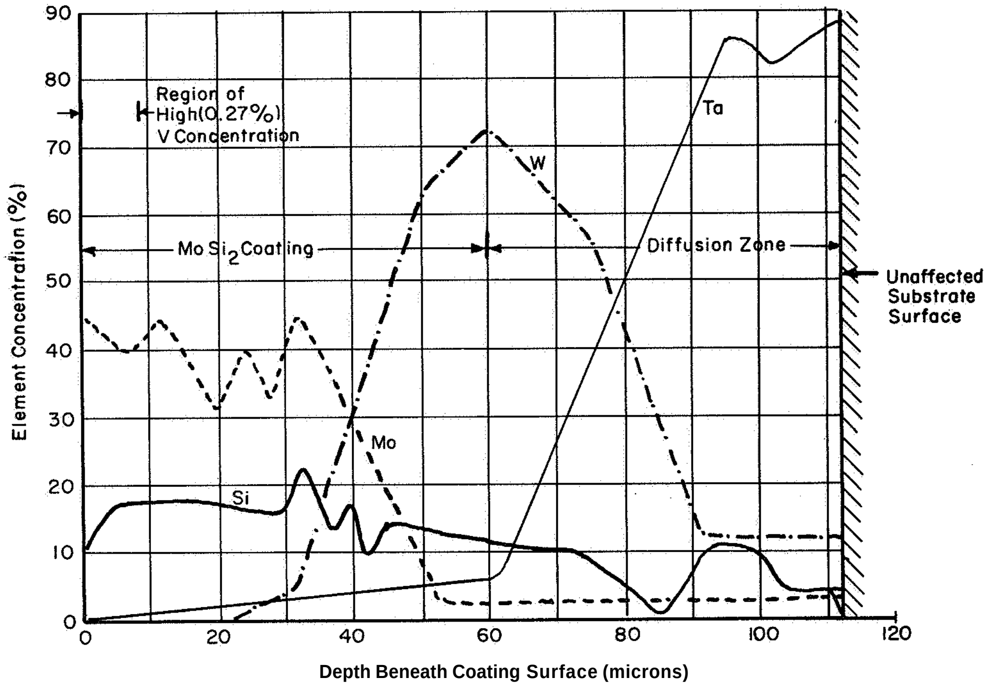


FIGURE 46

PHOTOMICROGRAPH OF $MoSi_2$-3VSi_2 ON W/T -222 AFTER OXIDATION
(SAMPLE WO-393-44-3)
(FAILED AFTER ONE 2-HOUR CYCLE AT 1500°F)

Sample WO-393-44-3R



Sample WO-393-44-3L

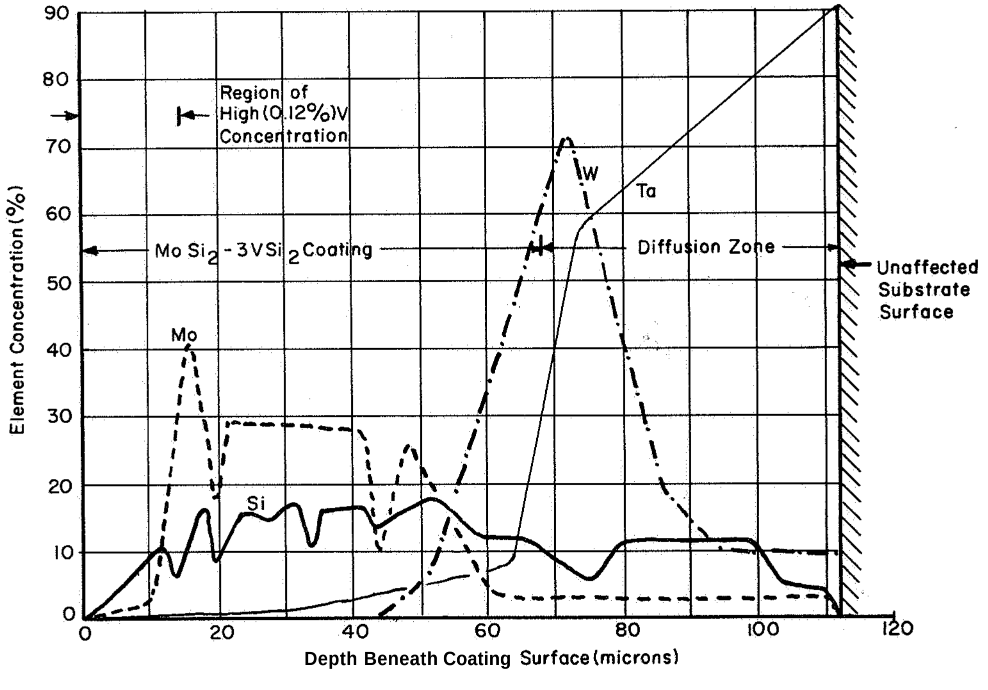
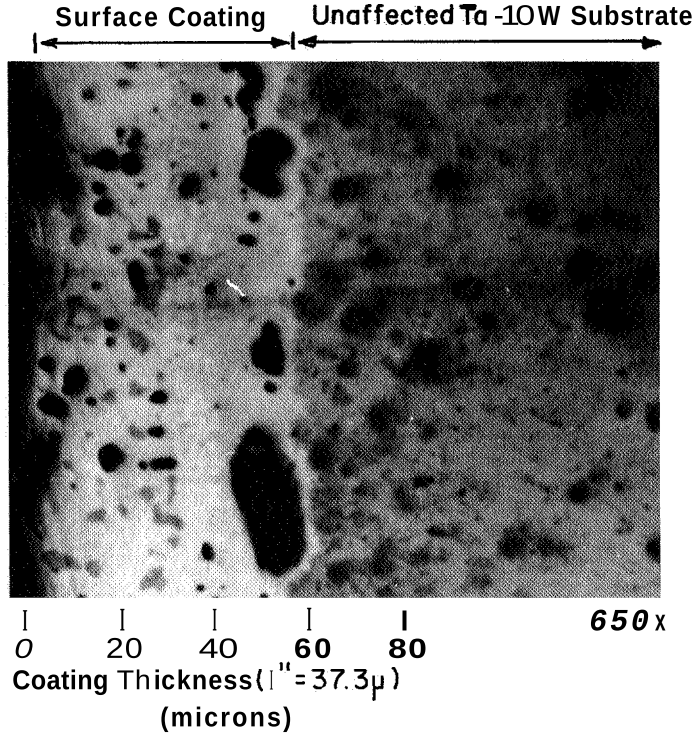


FIGURE 47

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$-$3VSi_2$ ON W/T-222
(SAMPLE WO-393-44-3)
(FAILED AFTER ONE 2-HOUR CYCLE AT 1500°F)

Sample WO-379-100-14R



Sample WO-379-100-14L

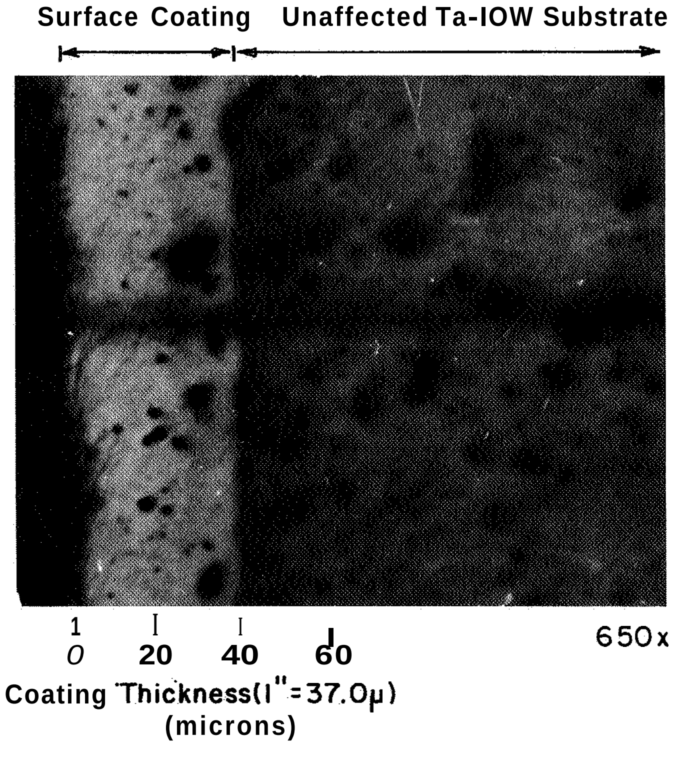
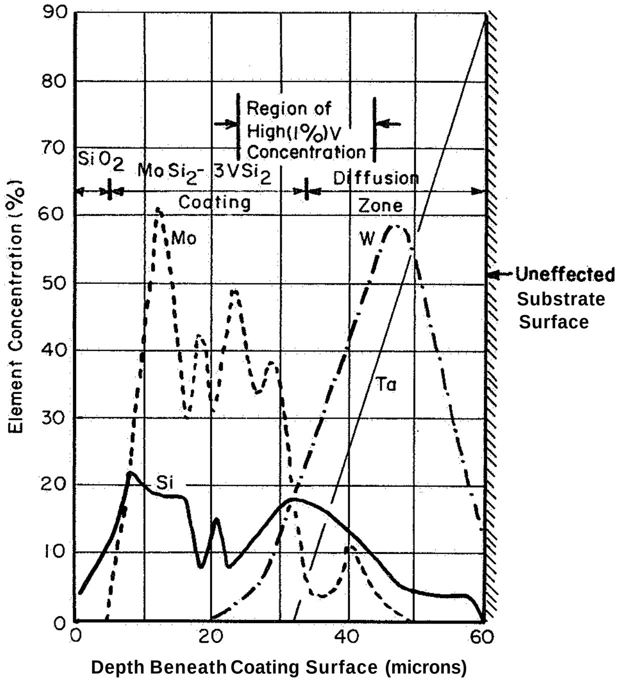


FIGURE 48

PHOTOMICROGRAPH OF $MoSi_2$-$3VSi_2$ ON W/Ta-10W AFTER OXIDATION
(SAMPLE WO-379-100-14)
(SURVIVED 589 HOURS AT 1500°F)

Sample WO-379-100-14R



Sample WO-379-100-14L

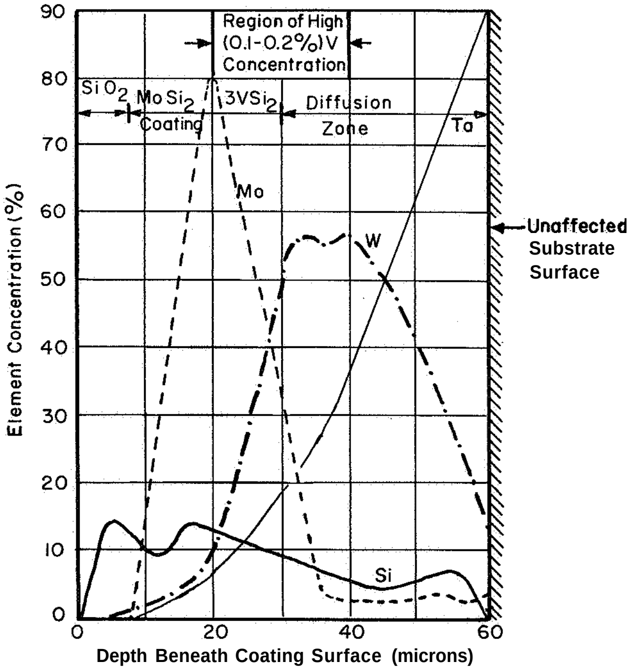
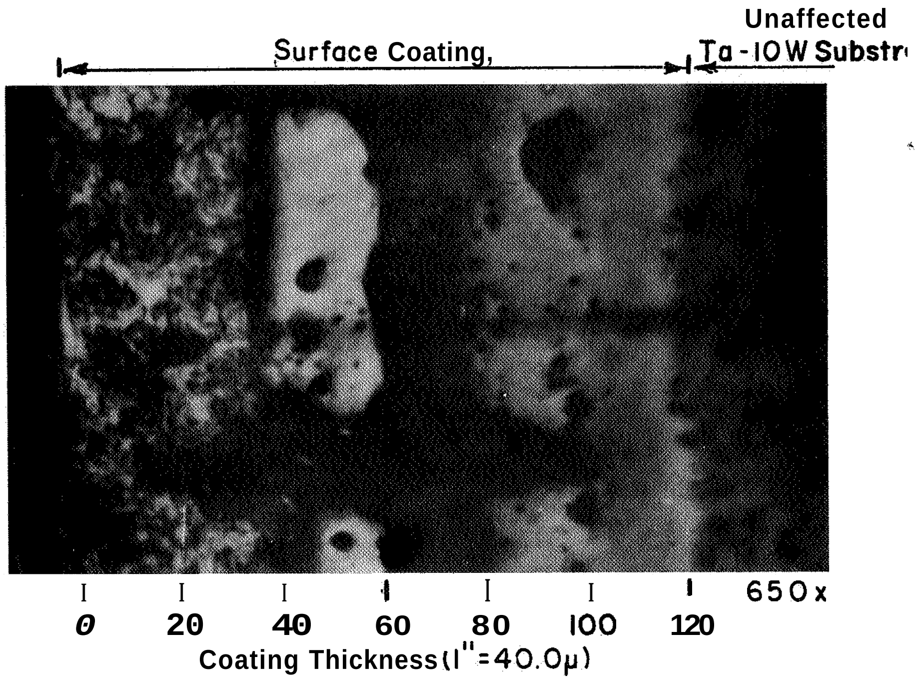


FIGURE 49

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$-$3VSi_2$ ON W/TA-10W(SAMPLE WO-379-100-14)
(SURVIVED 589 HOURS AT 1500°F)

Sample WO-403-12-21R



Sample WO-403-12-21L

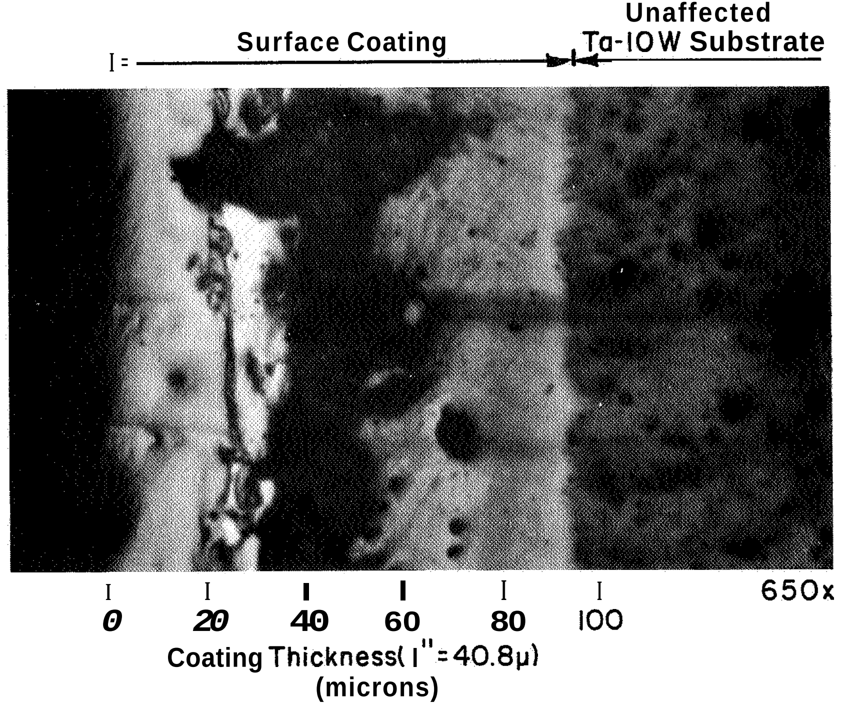
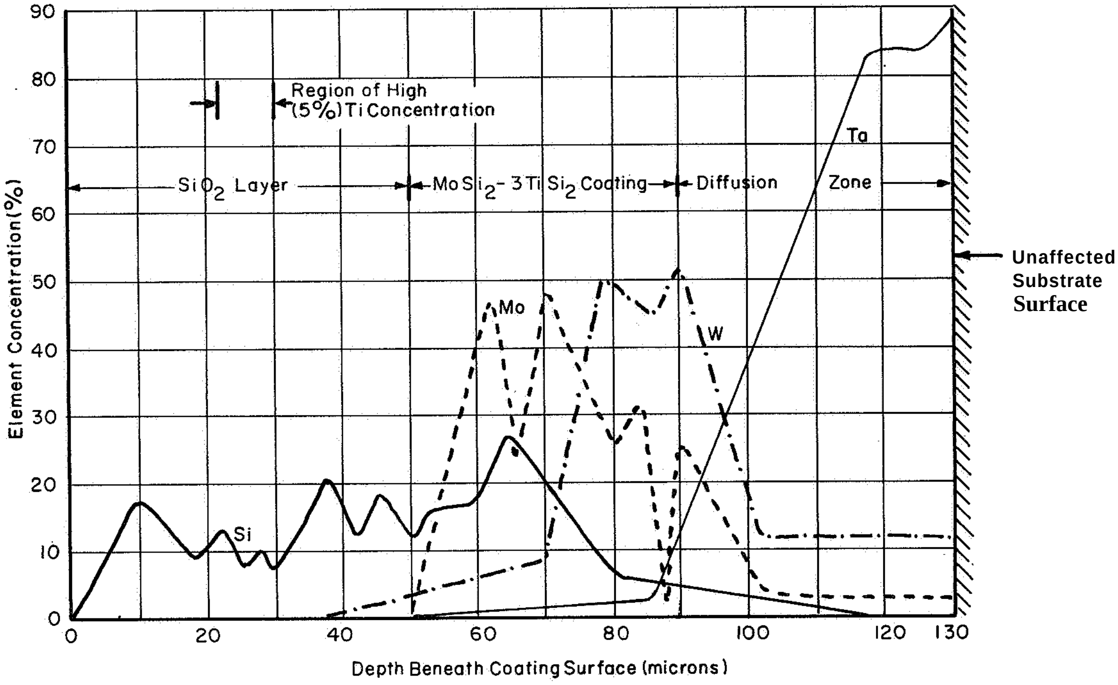


FIGURE 50

PHOTOMICROGRAPH OF $MoSi_2$-3$TiSi_2$ ON W/Ta-10W AFTER OXIDATION (SAMPLE WO-403-12-21) (FAILED AFTER 589 HOURS AT 1500°F AND 541 HOURS AT 2400°F)

Sample WO-403-12-21R



Sample WO-403-12-21L

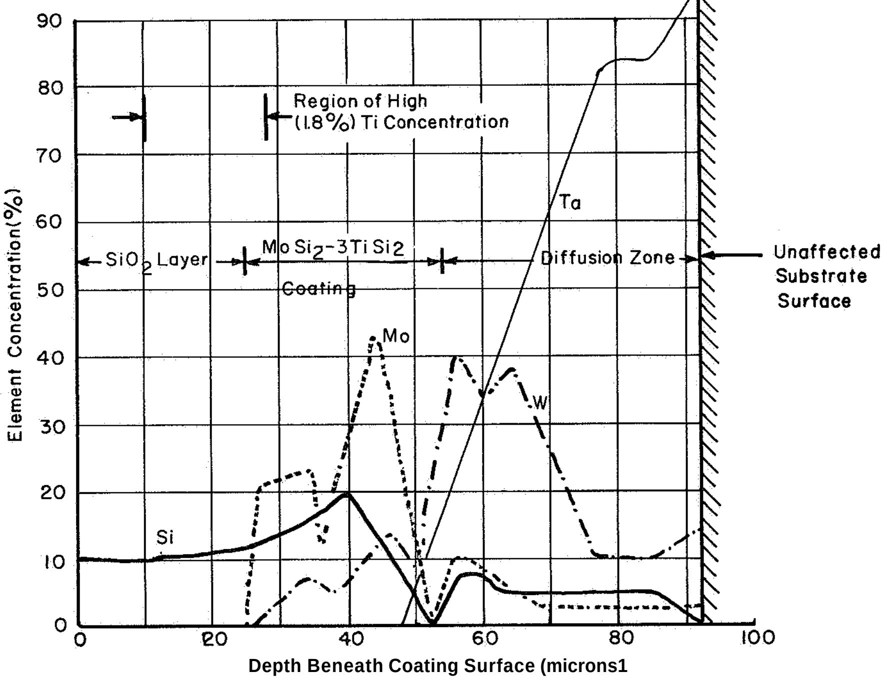
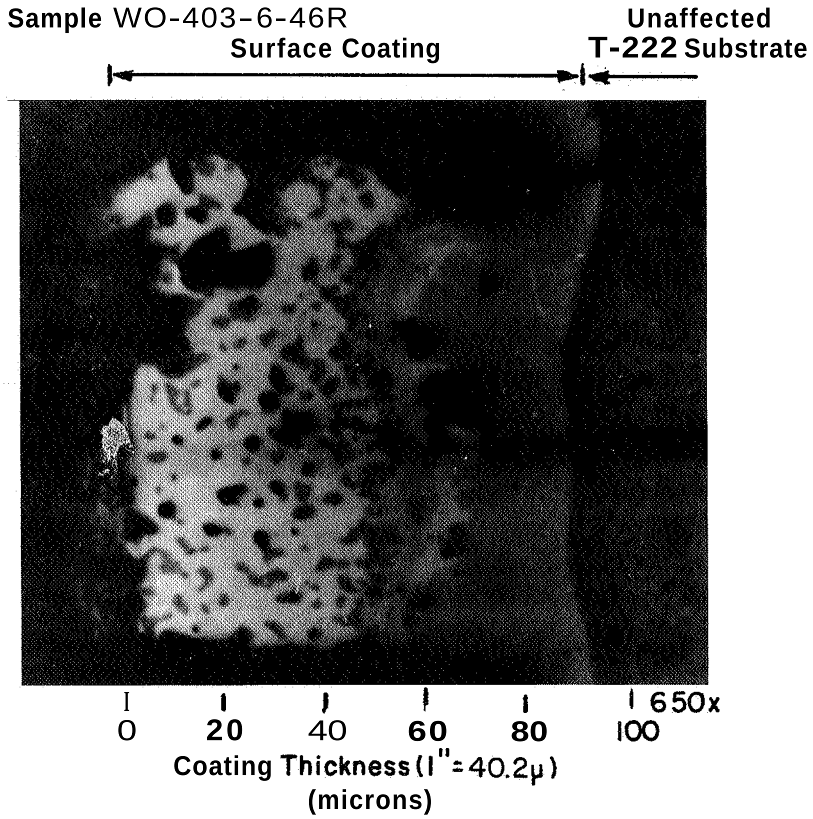


FIGURE 51

ELECTRON MICROPROBE ANALYSIS OF $MoSi_2$-$3TiSi_2$ ON W/Ta-10W
(SAMPLE W0-403-12-21)
(FAILED AFTER 589 HOURS AT 1500°F AND 541 HOURS AT 2400°F)



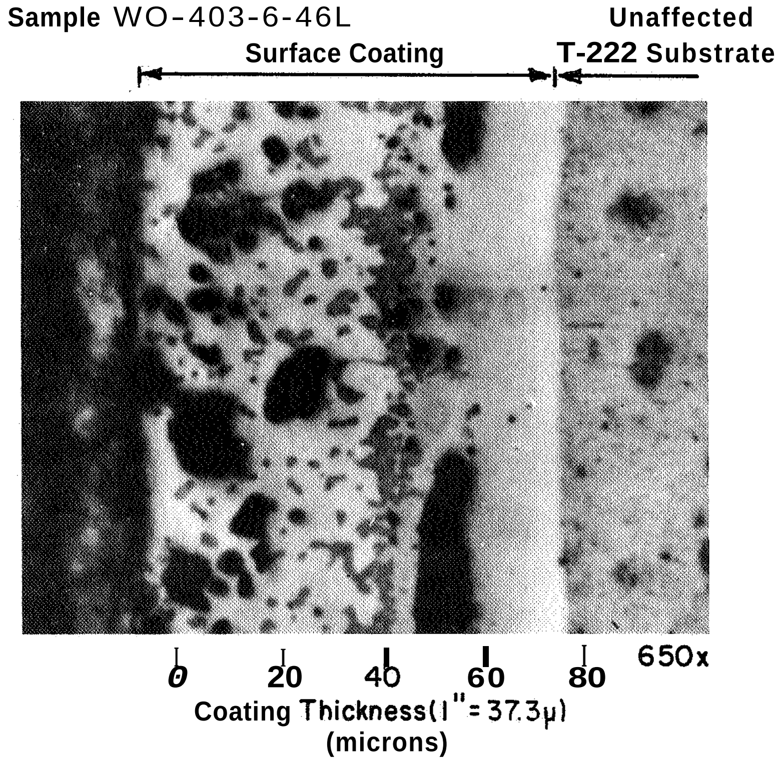
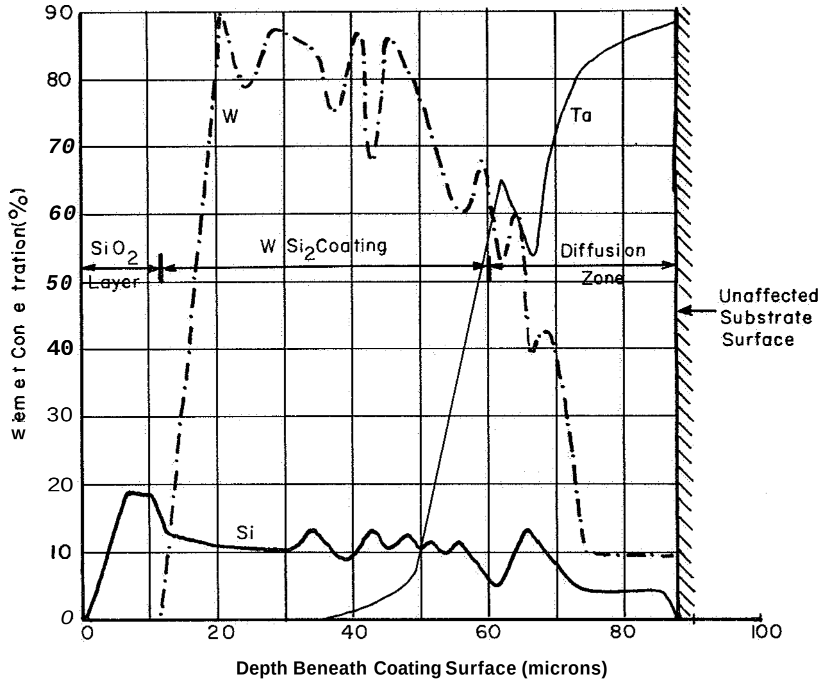


FIGURE 52

PHOTOMICROGRAPH OF WSi_2 ON T-222 AFTER OXIDATION
(SAMPLE WO-403-6-46)
(SURVIVED 597 HOURS AT 2400°F)

Sample WO-403-6-46R



Sample WO-403-6-46L

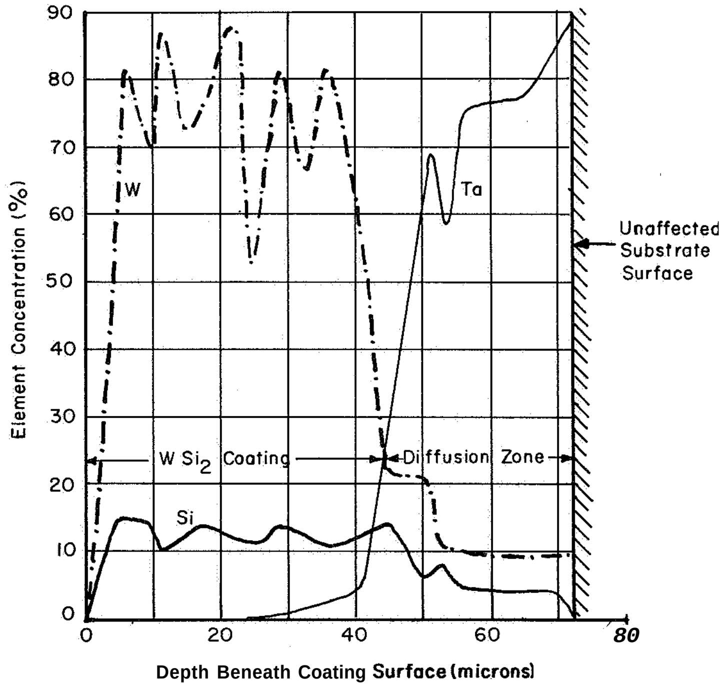


FIGURE 53

ELECTRON MICROPROBE ANALYSIS OF WSi_2 ON T-222
(SAMPLE WO-403-6-46)
(SURVIVED 597 HOURS AT 2400°F)

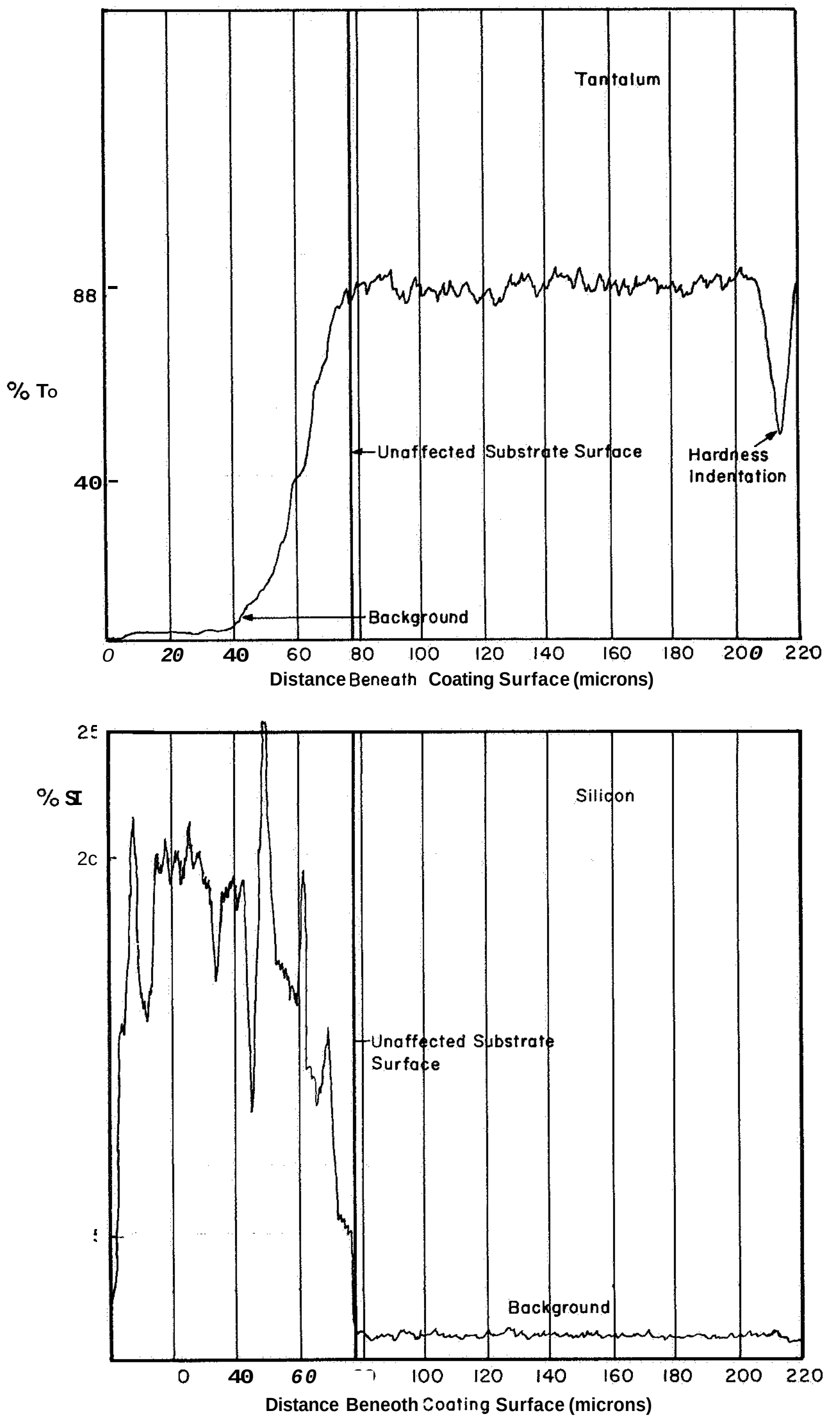


FIGURE 54

ELECTRON MICROPROBE ANALYSIS OF Si AND Ta
(SAMPLE WO-393-25-2A)

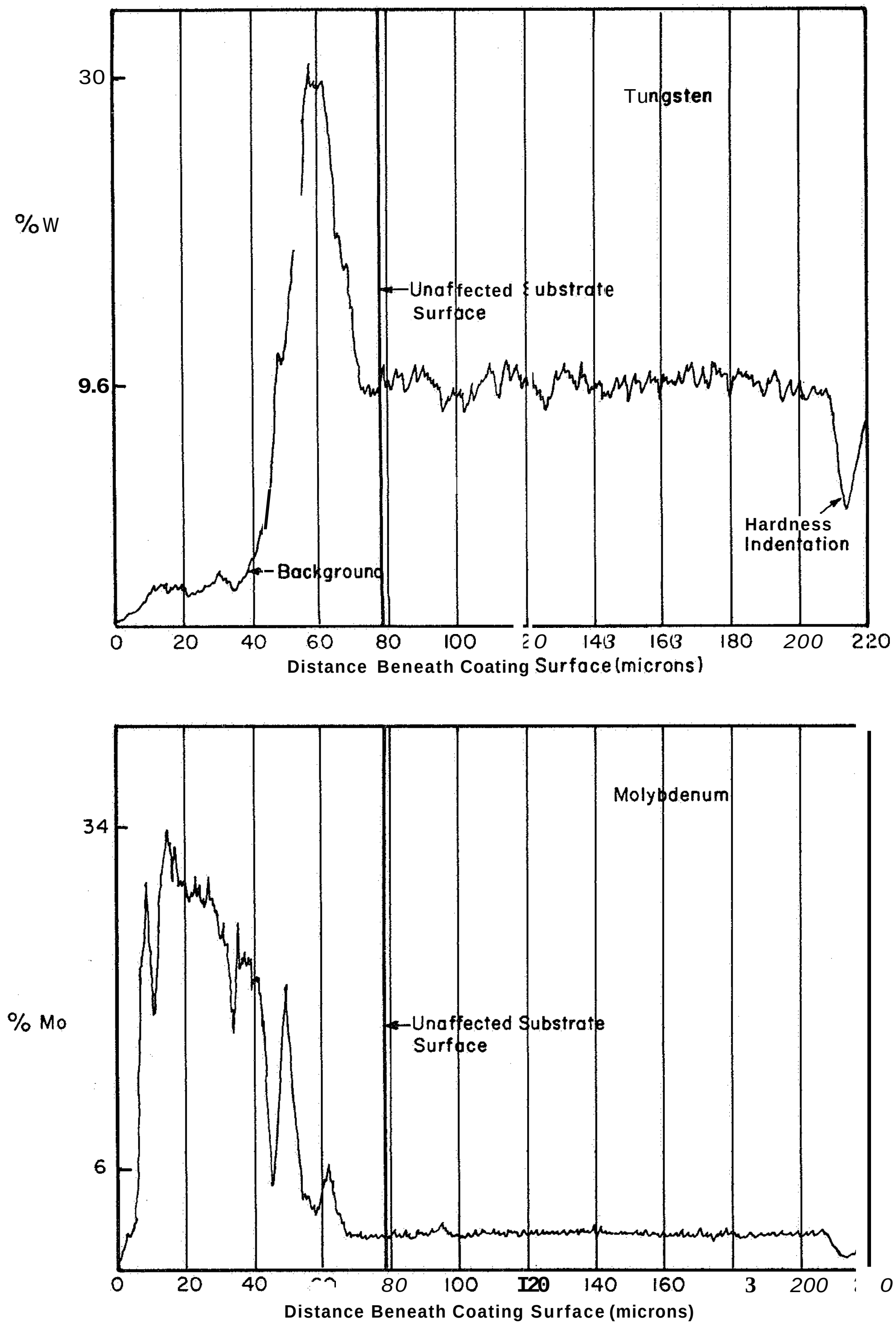


FIGURE 55

ELECTRON MICROPROBE ANALYSIS OF W AND Mo
(SAMPLE WO-393-25-2A)

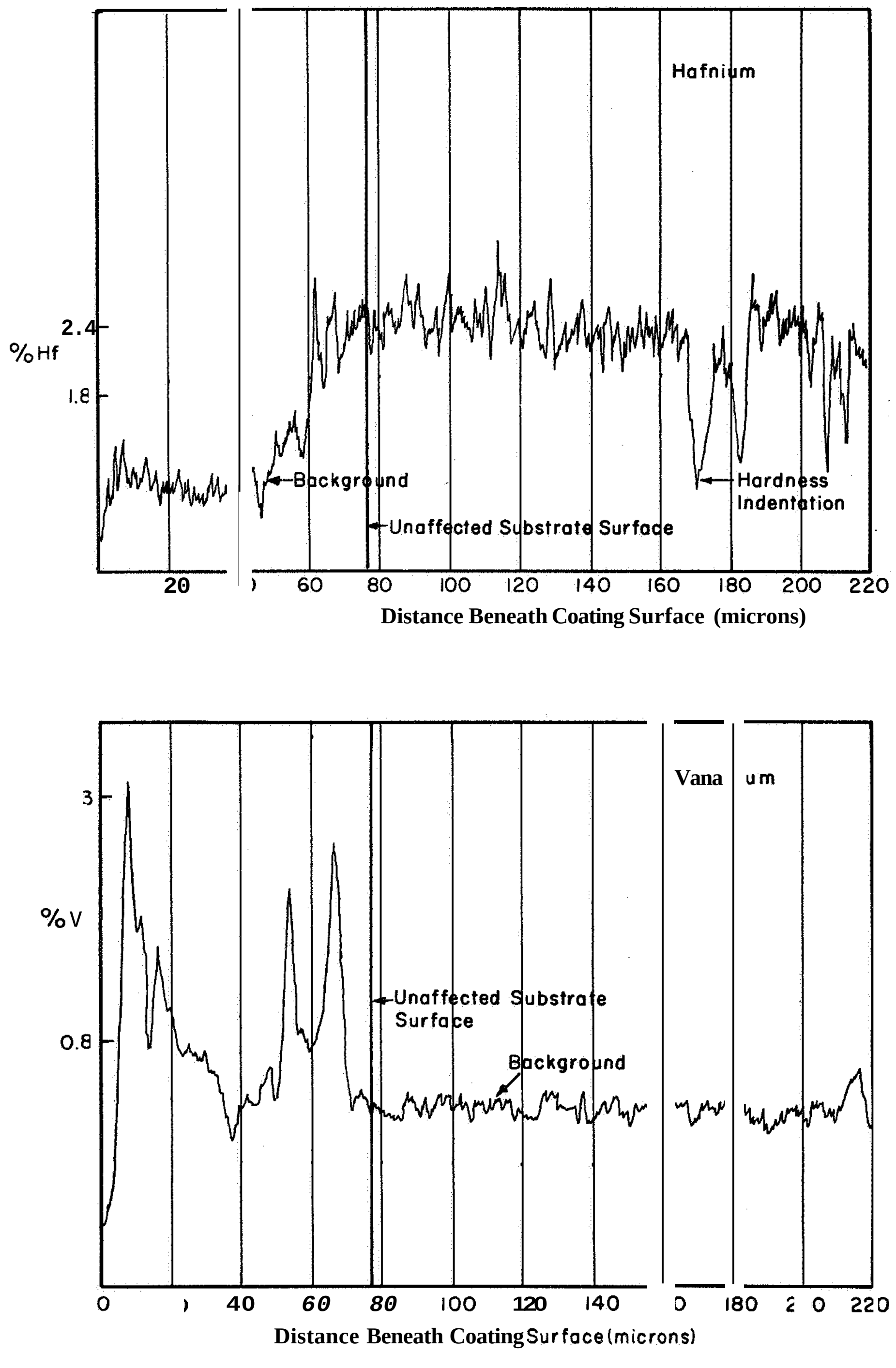


FIGURE 56

ELECTRON MICROPROBE ANALYSIS OF Hf AND V
(SAMPLE WO-393-25-2A)

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Attention: Rodger Turk

29. IIT Research Institute
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30. International Nickel Company
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Suffern, New York 10901
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31. Ling-Temco-Vought
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Dallas, Texas 75222
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32. Lockheed Missiles & Space Division
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33. Materials Research Corp.
Orangeburg, New York 10962
Attention: Vernon E, Adler

34. McDonnell Aircraft Corp.
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St. Louis, Missouri 63166
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35. Melpar, Inc.
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Attention: H. Hahn

36. Narmco Research & Development Division
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3540 Aero Court
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37. New England Materials Lab,, Inc.
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38. North American Aviation, Inc,
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Canoga Park, California 91303
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39. Pratt & Whitney Aircraft
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Attention: E. F. Bradley
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40. Solar Division
International Harvester
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41, Sylvania Electric Products
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42, TRW Inc.
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43. Union Carbide Corporation
Stellite Division
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Attention: (1) Dr. W. Manly, Dir. of Technology
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44. Universal-Cyclops Steel Corporation
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45, University of Dayton
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46. U. S. Atomic Energy Commission
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47. Headquarters, USAF
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Attention: Dr. M. Slawsky

48. Defense Documentation Center (DDC)
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5010 Duke Street
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49. AFML (MAMP)
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50. AFML (MAAE)
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51. AFML (MAAM)
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52. Department of the Navy
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53. Chief, Bureau of Naval Weapons
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54. NASA-Langley Research Center
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55. NASA-Marshall Space Flight Center
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56. Consolidated Controls Corporation
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57. NASA-Manned Spacecraft Center
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58. Department of the Amy
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