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COATINGS FOR LONG TERM-INTERMEDIATE TEMPERATURE PROTECTION OF COLUMBIUM ALLOYS

J. F. NEJEDLIK and J. D. GADD
TRW Inc.

TECHNICAL REPORT AFML-TR-68-170
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COATINGS FOR LONG TERM-INTERMEDIATE TEMPERATURE PROTECTION OF COLUMBIUM ALLOYS

J. F. Nejedlik and J. D. Gadd

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FOREWORD

This Final Summary Report was prepared by the Equipment Laboratories at TRW Inc. under the Air Force Contract AF 33(615)-5121. The program was administed by the Air Force Materials Laboratory, Wright-Patterson AFB, Ohio with Mr. N. M. Geyer (MAMP) acting as Project Engineer. The manuscript was released by the authors August 30, 1968 for publication.

The report covers work conducted from 1 July 1966 to 31 April 1968. The program was divided into three phases:

Phase I: Synthesize basic coating systems and develop coating application techniques.

Phase II: Identify the most promising system compositions and application techniques.

Phase III: Conduct property evaluation and environmental tests to characterize the potential of the coating-base metal systems.

The experimental work and evaluation results are topically presented.

Dr. J. D. Gadd of the Research Department, Coating Group was program manager and J. F. Nejedlik was the principal investigator.

This technical report has been reviewed and is approved.

I Perlmutter

I. Perlmutter
Chief, Metals Branch
Metals and Ceramics Division
Air Force Materials Laboratory

ABSTRACT

The program objective was to develop protective coatings for columbium alloys that would provide hundreds of hours of protection at temperatures to 2500°F for applications in gas turbine engines and aerospace environments. This work was intended to advance the research findings developed previously under contract AF 33(615)-1598.

The coating systems under consideration were basically silicides and aluminides, with improvements to be achieved by modification with elements such as V, Al, Mo, Cr and Ti. Specifically, a ductile coating was sought that would improve upon the Cr-Ti-Si coating system, the standard of comparison for this program. Coating systems which evolved from the studies included Mo-CrTi-Si, Mo-V-CrTi-Si, V-Al-CrTi-Si and V-CrTi-Si for low to high-temperature applications, and Ti-Al and Ti-Al-Si for low-temperature applications.

The V-CrTi-Si system was extensively evaluated on various columbium alloy substrates. It exhibited a potential for 1000 hours of protection at 1600-2200°F in cyclic oxidation tests and over 200 hours at 2400°F. In oxidation-erosion rig tests the coating system protected various columbium alloy substrates for up to 200 hours at 2200°F and 100 hours at 2400°F. The V-CrTi-Si system was superior to the CrTi-Si system only in cyclic oxidation tests. In other tests, such as oxidation-erosion, ballistic impact, and slow thermal cyclic exposure, the two systems performed similarly. However, the V-CrTi-Si coating failures propogated slowly in contrast to the rate observed for the Cr-Ti-Si coating.

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SECTION I

INTRODUCTION

The principal objective of this program was to develop metallic coating systems capable of providing hundreds of hours of oxidation protection for columbium-base alloys at temperatures to 2500°F. This work was intended to advance the research findings of work performed previously under Contract AF 33(615)-1598(1).

Two application categories dictated the environmental performance requirements of the desired coating systems: 1) reusable hypersonic flight or re-entry vehicles, and 2) aircraft gas turbine engines. The maximum temperatures considered in this program were 2500°F for the first application and 2200°F for the latter. In addition, blade root coatings for use in the temperature range 1600-1800°F were also considered.

Specifically, a ductile coating was sought that would be an improvement over the CrTi-Si coating system presently available. This coating should be capable of providing reliable protection against oxidation in a variety of severe environments without causing significant degradation of the substrate material.

A basic weakness with the present coatings is the lack of low temperature ductility. The approach taken in this program was to provide at least one intermediate layer in the coating with reasonable ductility to protect the underlying material from damaging strains or from the pest oxidation phenomenon. The systems considered were basically modified silicides or aluminides, with improvements to be achieved by the introduction of elements such as V, Mo, Cr, and Ti into the systems. Severe problems were previously(1) encountered in coating columbium base alloys with molybdenum and vanadium. Therefore, the initial efforts in this program were devoted principally to the development of vanadium and molybdenum deposition techniques.

The program was eighteen months in duration and divided into three major phases: 1) synthesize basic coating systems and develop coating application techniques, 2) identify the most promising system compositions and application techniques, and 3) conduct property evaluation and environmental tests to characterize the potential of the coated materials.

Phase I entailed six specific areas related to the formation of complex coatings on columbium alloy substrates: 1) develop techniques for the deposition of molybdenum, 2) develop techniques for the deposition of vanadium, 3) investigate potential aluminide coating systems, 4) investigate various silicide coating systems, 5) evaluate the various coating systems for further study.

Phase II involved three tasks related to several promising coating systems selected from Phase I: 1) a parametric study to establish processing parameters for reproducible deposition of appropriate elements, 2) coating composition optimization, and 3) evaluation of the coatings. After selection of the preferred coating systems, three additional substrates were coated and evaluated to assess the influence of the substrate material on coating properties.

Phase III was a comprehensive property evaluation of the most promising coating system selected from the Phase I and II investigations.

This report describes topically the experimental work and evaluations performed in each phase.

SECTION II

SUMMARY

The principal objective of the program was to develop protective coatings for columbium alloys that would provide hundreds of hours of protection at temperatures to 2500°F for applications in gas turbine engines and aerospace environments. The coating systems under consideration were basically silicides and aluminides, with improvements to be achieved by modification with elements such as V, Mo, Cr, Al and Ti.

This work was intended to advance and capitalize upon the research findings of work performed previously under contract AF 33(615)-1598. Specifically, a ductile coating was sought that would improve upon the Cr-Ti-Si coating system presently available. A basic weakness with present silicide coatings is their lack of low-temperature ductility. The approach taken was to provide at least one ductile intermediate layer in the coating to protect the substrate while relying upon the silicide surface layer for primary oxidation protection. The major effort was spent on the V-CrTi-Si system development and evaluation of the V-CrTi-Si coating system for aerospace and gas turbine applications.

Phase I activity was concerned with the development of techniques for the deposition of vanadium and molybdenum on columbium, investigation of potential aluminide and silicide coating systems, and selection of the most promising systems in screening tests for further study in Phase II. Vanadium deposition was achieved by the use of mixed sodium chloride and vanadium tetrachloride activators, a pure vanadium powder pack, and a 2200°F coating cycle in an argon atmosphere (150mm). The use of either activator alone resulted in low deposition rates. Other halide activators also produced low vanadium rates of transfer. No sintering or adverse effects upon columbium alloy ductility were experienced.

Four approaches were pursued to precoat columbium alloys with molybdenum: 1) pack deposition, 2) molybdenum trioxide-hydrogen reduction, 3) slurry coating and 4) chemical vapor deposition. Pack studies showed that molybdenum transfer rates were very low, thus corroborating previous investigators'findings that pack deposition of molybdenum on columbium is thermodynamically impractical. The use of volatile molybdenum trioxide to effect transfer, and the subsequent reduction of the oxide to molybdenum by hydrogen reduction, yielded severely embrittled columbium alloy substrates. This method was also abandoned.

Slurry coating experiments showed that sintering of particulate molybdenum to the columbium surface could be enhanced by the use of metallic additives such as titanium and nickel. Five w/o titanium hydride and 0.6w/o nickel additions at sintering temperatures of 2700°F and 2400°F produced adherent molybdenum coatings. The sintering was also catalyzed by the presence of a liquid phase. The use of "fugitive" vehicles such as silver and copper produced sintered coatings at 2400°F. Coating consolidation increased with the use of finer molybdenum powder, but adhesion was impaired, due to the greater shrinkage associated with the use of the finer powder. Molybdenum application by the slurry method resulted in very nonuniform coatings, and the application of thin continuous molybdenum coatings by this technique appeared difficult to accomplish.

Molybdenum deposition by chemical vapor deposition was employed as an expedient means to coat various columbium substrates. Molybdenum was deposited by reducing molybdenum pentachloride with hydrogen at 1800-1900°F. The specimens were contained in rotating barrel coater during the deposition process.

Silicide modification studies by introduction of the elements Cr,Ti, Mo, V and Al showed that of 19 systems selected for study, only 9 systems were readily formed without gross coating defects. These systems were:

Ti-V-Si
Mo-Cr,Ti-Si
Mo-V-Cr,Ti-Si
Mo-V-Si
V-CrTi-Si
V-Si
Mo-Ti-Si
V-Ti-Si
V-Al-CrTi-Si

Cyclic oxidation tests at 1600 and 2400°F showed that of the above systems, only the following had protective capabilities equivalent to the Cr-Ti-Si standard (over 400 hours at 1600°F and 200 hours at 2400°F): Mo-CrTi-Si, Mo-V-CrTi-Si, V-Al-CrTi-Si and V-CrTi-Si.

Aluminide system studies showed that the Ti-Al and Ti-Al-Si systems had protective capabilities for times up to 1000 hours at 1600°F, but were not oxidation resistant at 2400°F. The silicide system Ti-Si showed the same capabilities and limitations as the aluminide systems. Considerable difficulty was experienced in siliciding the systems containing large titanium concentrations because of coating spalling.

For Phase II development of compositions, the Mo-CrTi-Si, Mo-V-CrTi-Si, V-CrTi-Si and V-Al-CrTi-Si systems were selected for low (1600°F) and high (2400°F) temperature evaluation, and the Ti-Al, Ti-Al-Si and Ti-Si systems were selected for low-temperature evaluation. Each system was formed within a broad range of coating compositions.

Cyclic oxidation evaluations at 1600-2400°F indicated that the following were preferred compositions (where the numbers represent deposition levels in mg/cm^2):

7V-10Al-18CrTi-17Si
7V-21CrTi-16Si
15Mo-18CrTi-12Si
12Mo-8V-20CrTi-12Si
25Ti-5Al
22Ti-4Al-1Si
22Ti-5Si

Lifetimes in excess of 300 hours at 1600°F and 200 hours at 2000°-2400°F were obtained with the silicides. The V-Al-CrTi-Si system developed porosity in the coating after the Cr-Ti coating step as a consequence of aluminum loss. Lifetimes in excess of 500 hours were obtained with the Ti-Al-Si system at 1600°F. The Ti-Si system showed poor performance because of silicide spalling problems The Ti-Al coating failed at titanium sinter points.

Ballistic impact testing of the Phase II coatings at a velocity of 340ft/sec and an impact energy 4.6 ft-lb showed that all systems remained protective for 2 hours or more when cyclicly exposed at 2400°F after impacting. Impact at 2000°F resulted in substantially less coating damage than impact at room temperature.

The V-CrTi-Si, V-Al-CrTi-Si and Mo-CrTi-Si coatings, along with the standard Cr-Ti-Si system, were subsequently selected for assessing the influence of substrate on coating behavior in cyclic oxidation, erosion-oxidation, and ballistic impact tests. The alloys coated were Cb752, D43, Cb132M and C129Y. Electron probe traces were also obtained on as-applied coatings and on coatings after cyclic exposure at 2400°F.

In cyclic oxidation tests the V-CrTi-Si system showed a consistent protective capability on all substrates of over 350 hours at 1600-2400°F. The standard CrTi-Si system also displayed a consistent protective capability of over 280 hours at 1600-2200°F and over 160 hours at 2400°F. This system had a shorter life than the V-CrTi-Si system because of a thinner coating (less Cr-Ti). The V-Al-CrTi-Si and Mo-CrTi-Si systems showed erratic behavior because of porosity formed during the Cr-Ti coating cycle. Loss of aluminum from the V-Al precoat, and the lack of adhesion of the chemically vapor deposited molybdenum are the apparent causes of porosity formation.

In erosion-oxidation rig tests in the combustion gases of fuel containing 0.4w/o sulfur, the V-CrTi-Si and CrTi-Si standard coatings showed a protective capability of over 200 hours at 2200°F plus 100 hours at 2400°F. The Mo-CrTi-Si and V-Al-CrTi-Si coatings showed poor performance, again owing primarily to the lack of coating adherence.

Ballistic impact testing of these systems at room temperature and 2000°F showed that, with exception of the V-Al-CrTi-Si system, the coatings demonstrated a capability to protect the impacted substrates at 2200°F for 1 to over 15 hours. The CrTi-Si system displayed a longer protective life than the V-CrTi-Si system.

The V-CrTi-Si system was selected for comprehensive evaluation in Phase III because of its relative ease of formation and its consistent performance.

In Phase III the performance of the nominal 7V-21CrTi-16Si coating system was evaluated on the alloys Cb 752, D 43, Cb 132M and XB 88 in a series of tests designed to judge its applicability to advanced gas turbine engine components and reentry vehicles. Evaluation consisted of cyclic oxidation, low pressure exposure, thermal fatigue, oxidation-erosion, ballistic impact and post oxidation, and reentry simulation tests. In addition, tensile and stress oxidation tests were conducted to evaluate the effect of the coating on substrate mechanical properties.

Flaking was observed on some of the Phase III specimens after siliconizing, and was probably associated with the growth of a titanium-rich silicide which has a relatively large volume expansion in comparison with the chromium-rich silicide which normally forms on a Cr-Ti precoated surface

Cyclic oxidation tests, although variable, indicated a potential of over 1000 hours at 1600 to 2200°F and over 200 hours at 2400°F for the various coating-substrate systems. Thermal profile oxidation tests, which simulated a typical reentry vehicle flight condition, were conducted to a peak temperature of 2400°F. In these tests V-CrTi-Si coated Cb 752, XB 88 and D-43 alloys showed a capability of being cycled up to 25 times or more without failure.

Low pressure exposure at 0.1 to 5 mm for 1 and 4 hours at 2400°F and for 1 hour at 2600°F followed by post cyclic oxidation testing at 2400°F, indicated that no coating degradation occurred on any of the coated substrates after low pressure exposure at 2400°F. After the 2600°F low pressure exposure coating degradation was not observed on the Cb 752 and XB 88 alloys. However, V-CrTi-Si coated Cb 132M and D 43 were adversely affected.

Thermal shock tests were performed by heating the coated substrates to peak temperatures of 2000° and 2200°F for Cb 132M and XB 88 alloys, and 2200° and 2400°F for D 43 and Cb 752 alloys, with an oxyacetylene flame followed by a cooling in an ambient air blast. The heating and cooling cycles were 15 seconds. All coated alloys displayed a tolerance up to 1000 cycles without serious coating degradation.

Ballistic impact tests (4.6 ft-lb) at a projectile velocity of 340ft/sec were conducted at room temperature, 1600° and 2000°F. Coating damage was most pronounced at room temperature and generally decreased with increasing temperature. The Cb 132M substrate cracked at all impact temperatures, while the Cb 752 and XB 88 substrates cracked only at room temperature. Post cyclic oxidation of the impacted specimens at 2200°F showed that in the absence of substrate cracking, the V-CrTi-Si was protective for 16 hours or more after impact damage.

Erosion rig tests utilizing fuel containing 0.4 w/o sulfur showed that the V-CrTi-Si coating was capable of protecting the various substrates for over 100 to 200 hours at 2200°F. At 2400°F the bars developed spot failures after 54 hours, however these localized failures exhibited no appreciable growth on proceeding to 100 hours of exposure.

Tensile tests performed in air with coated Cb 752, D43 and XB 88, and in vacuum with uncoated specimens showed that the coating had an adverse effect on the properties of the columbium alloys. The Cb 752 and D 43 alloys showed approximately a 20 and 30% loss in yield and ultimate strengths at temperatures to 2400°F, respectively. With both alloys, elongation was a minimum at 1600°F and was generally lower than uncoated material at elevated temperatures. The coated XB 88 alloy showed a drastic reduction in strength at room temperature and displayed notch sensitivity. At 2000°F the reduction in yield and ultimate strength was about 20%, while the elongation was about 70% less than uncoated material.

In stress oxidation tests at 2200°F and 2400°F the Cb 752 and D-43 coated alloys showed rupture strengths that were equivalent to uncoated material. In contrast, the coated XB 88 showed a significant reduction in rupture strength at stress levels over 50,000 psi, while at lower stress levels the coating influence was nil. Total elongations measured after specimen failure showed that extensive creep occurred prior to rupture. This indicates that the V-CrTi-Si system is able to tolerate considerable plastic flow at elevated temperatures without loss of protection.

In comparing the V-CrTi-Si coating system with the standard CrTi-Si system, the V-CrTi-Si system appeared to be superior in cyclic oxidation tests. However, in oxidation-erosion tests at 2000°F and 2400°F, ballistic impact, and slow thermal cycle (19) tests both systems were comparable.

In general, most data from this program indicate that the benefits derived from vanadium modification of the Cr-Ti-Si chemistry may not justify the introduction of a third coating cycle. One perceptible difference in the two systems was the mode of oxidation failure. Although the time of failure initiation in the V-CrTi-Si system was not significantly different from that of the Cr-Ti-Si coating in most tests, growth of a localized failure was noticeably slower in the vanadium modified system suggesting a beneficial self-healing influence of the vanadium addition.

SECTION III

REVIEW AND ANALYSIS OF THE PROBLEM

The Cr-Ti-Si coating system is generally recognized as one of the best coating composition available for protecting columbium base alloys. The major short coming of this system, and other coatings for refractory metals, is the characteristic lack of low-temperature ductility. As with most silicide coatings, cracks inherent in the coating as a result of the thermal expansion mismatch between the silicide and the substrate, or cracks induced in the coating by external stress or foreign object impact, can promote premature loss of coating protection.

The inability of the duplex Cr-Ti-Si coating to tolerate significant strains at low temperatures is attributed to two factors:

1) The formation of the intermetallic Laves phase $(Cb,Ti)Cr_2$. This phase is extremely hard, quite brittle, and incapable of arresting the high energy propagation of cracks which initiate in the brittle silicide coating.

2) The interstitial sink effect of the titanium in the solid solution region of the columbium matrix. The gettering effect of the titanium, both from the inward diffusion of oxygen and from the egress of interstitials from the columbium matrix, eventually embrittles this region until it will no longer sustain plastic deformation at low temperatures. Cracks emanating from the silicide can then propagate through this layer to the unaffected substrate core. In addition, the coating constituents are gradually depleted from this region by oxidation and by inward and outward diffusion, thereby progressively reducing the oxidation resistance of this zone.

The general approach taken by Solar (1) to overcome these problems was to modify the chemistry, and yet retain the desirable characteristics of the Cr-Ti-Si coating. The modification was based on the formation of a coating sublayer that would have "effective" ductility and, thus, would be able to absorb deformation strains. This coating would also display good low temperature (below 1800°F) oxidation resistance, while relying upon an inherently brittle surface layer (such as a silicide or aluminide) to provide high temperature oxidation protection. The intermediate layer could be either a solid solution zone of the coating elements in the substrate, or an independent layer formed by a duplex coating operation.

Based on these two apparent problems with the Cr-Ti-Si coating system, Solar's approach to the design of new coating systems was directed towards elimination of the titanium getter (interstitial sink) on the one hand, and elimination of the chromium or suppression of the Laves phase formation on the other. Silicides and aluminides were accepted as the only intermetallic compounds capable of providing the high temperature oxidation resistance required of the surface layer. Elimination of the brittle, chromium-rich Laves phase appeared to be a sound approach to lessening the susceptibility of coatings to crack propagation: and the problems associated with the high vapor pressure of chromium (vaporization at both one atmosphere and at reduced pressures) provided further justification for seeking a substitute for chromium in the Cr-Ti-Si system. Elimination of the gettering agent titanium in the matrix region adjacent to the coating had distinct drawbacks, however. In the absence of this interstitial sink, oxygen which permeates the silicide layer, (by slow diffusion at high temperatures through compositionally heterogeneous paths, down cracks, etc.) would continue into the substrate matrix and progressively alter the mechanical properties of the base material (raise the ductile-to-brittle transition temperature). Of the potential coating elements for columbium alloys, only titanium and tantalum appeared to have this very effective scavenging capability.

The major findings of the Solar(1) work are summarized below:

1. At 1600°F the oxidation resistance of commercial columbium alloys varies by a factor of 20 or more, and prealloying with titanium improves this by a factor of three.

2. Of several binary and ternary M_5Si_3 silicides evaluated at 1500-2400°F, only the $(Cb,Ti,Cr)_5Si_3$ or $(Ti,Cr)_5Si_3$ exhibit good oxidation resistance.

3. Titanium and tantalum in coatings act as powerful interstitial sinks for oxygen and carbon.

4. Tungsten and molybdenum are effective elements in retarding the inward diffusion of chromium and titanium in columbium, while vanadium is not as effective in promoting the diffusion of chromium into columbium as is titanium.

5. The expansion of $(Ti,Cr)Si_2$ compositions is 50-70% greater than that of columbium alloys, and this differential can be reduced to 20-25% by substantial replacement of the chromium with molybdenum.

6. Disilicides containing chromium exhibit poor oxidation resistance at 2400°F, whereas substitution of tungsten or molybdenum for chromium substantially improves the oxidation resistance of these compounds.

7. Solid solution compositions in the Cb-Ti-Mo and Cb-V-Cr systems exhibit low-temperature oxidation resistances comparable to that of the Cb-Cr-Ti prealloyed surface layer, which is the basis for the Cr-Ti-Si coating.

8. Solid solution alloys in the system Cb-(50-60)Ti-10Al are quite oxidation resistant to 2500°F, are very ductile, and exhibit excellent potential as a sublayer beneath a disilicide surface coating. They are susceptible, however, to internal oxidation.

9. The substitution of the transition elements Cb, Ta, Cr, Mo and W for Ti in the gamma phase TiAl markedly improves the oxidation resistance of this compound. Tantalum is superior to columbium, and the group VI elements (Mo, Cr, W) are more effective than the group V elements (Cb, Ta). Chromium depresses the melting point of aluminides below 2500°F, leaving the most promising systems as those of the type (Ti,Cb, Mo)Al and (Ti, Cb, Ta)Al. Additions of Zr, Hf and V have an adverse effect on the oxidation resistance of the gamma phase.

10. Substitutions of the transition elements Mo,W and Ta for Cb in the compound $CbAl_3$ again have a beneficial effect on the oxidation resistance of this phase.

11. The (Ti,Cr)-Si system may be modified by substitution of vanadium for the titanium and molybdenum for the chromium. These elements are introduced to eliminate the brittle Laves phase, and increase the free energy of formation of oxygen and carbon solutions in the modified zone.

12. The V-(Cr,Ti)-Si coating shows excellent oxidation resistance at 1600 and 2400°F. The vanadium, in addition to the above modifications, also improves the oxidation resistance of the disilicide. Vanadium deposition on the order of 7 mg/cm^2 is necessary.

13. Barium borosilicate glass impregnated (95 Mo-5 Ti)-Si coating exhibits excellent oxidation resistance at 1600 and 2400°F.

In summarizing these findings, Solar selected two coating systems which exhibited potential advantages over the Cr-Ti-Si coating, the (Ti,Mo)-Si and V-(Cr,Ti)-Si systems. The Ti-Mo-Si was not successfully formed because of the difficulty of depositing molybdenum. The latter system was evaluated as a potential turbine blade and aerospace coating, but was not optimized as to coating chemistry.

This program was intended to pursue, advance and capitalize upon the research findings reported by Solar under contract AF 33(615)-1598, to attain coatings with an overall protective performance superior to that afforded by the Cr-Ti-Si system.

SECTION IV

MATERIALS

Five columbium substrate alloys were included in the program: Cb752, D43, C129Y, Cb132M and XB88. Chemical analyses of these alloys are shown in Table I. The D-43 alloy was used in two conditions, 0.030 inches thick sheet in the duplex heat treated condition (solution at 2900 to 3000°F followed by 25 percent cold reduction and aging at 2650°F) and 0.5 inches diameter bar in the recrystallized condition. The Cb752 alloy 0.030 inches thick sheet was also used in the duplex heat treated condition (solution at 2800°F followed by 40 percent cold reduction and aging at 2450°F). The Cb132M (0.5 inches diameter bar only) was used in the as-extruded condition. The XB88 alloy (0.5 inch diameter bar only) was used in the extruded, swaged and annealed at 3090°F condition.

TABLE I

COMPOSITIONS OF COLUMBIUM BASE ALLOYS

Alloy	Heat Number	Thickness, in.	Elements, w/o							
			W	Zr	Ta	C	O	H	N	Others
Cb 752	UMC-1	0.030	9.97	2.5	---	.0010	52	.0006	.0042	
Cb132M	-	0.50 dia	13.5 to 16.5	0.75 to 1.25	18 to 20	.08 to .12	.04 max	.002 max	.01 max	Mo 4.5 to 5.5
Cb132M	132M1868	0.50 dia	14.95	1.49	20.15	.11	.013	.0005	.001	
D-43	5091	0.030	9.36 to 9.56	1.07 to 0.96	---	.107 to .123	.005 to .006	.00027	.0035 to .0025	
C129Y	610-57259	0.040	9.8 to 10.0	---	---	.0060 to .0090	.0070	.0037 to .0038	.0025 to .0042	Hf 9.0 to 9.6 Y 0.08 to 0.15
D-43	387-23	0.030	9.4	1.0	---	0.107	.0136	.0003	.0040	
D-43	387-32	0.030	1h.2	0.96	---	0.102	.0188	.0002	.0034	
D-43	43-188	0.030	9.8	1.0	---	0.0994	.0366	.0001	.0038	
D-43	43-372	0.50 dia	10.0	1.1	---	0.0828	.0050	.0002	.0030	
D-43	43-409	0.50 dia	11.0	0.97	---	0.0863	.0116	.0008	.0031	
D-43	43-423	0.50 dia	9.6	0.91	---	0.0945	.0056	.0009	.0033	
XB 88	VAM91-A	0.50 dia	27.5 to 28.0	---	---	.072 to .071	.0015 to .0022	---	.0045 to .0077	Hf 1.79 to 1.88
Cb 752	52529	0.50 dia	10.05	2.34	- -	.002	.0033	0004	.0070	

SECTION V

PHASE I: COATING COMPOSITION STUDY

In the initial stages of the program two parallel efforts were conducted to develop techniques for the deposition of molybdenum and vanadium on columbium alloy substrates. A study of aluminide and silicide coating systems was subsequently undertaken.

5.1 VANADIUM PACK DEPOSITION STUDIES

Previous studies (1) indicated that vanadium introduced into the Cr-Ti-Si protective coating on columbium base alloys improved coating ductility by: 1) eliminating or reducing the brittle Laves phase (Ti,Cb)-Cr_2, 2) modifying the interstitial sink effect of the titanium and 3) proving the oxidation resistance of the disilicide. However, considerable difficulty was experienced by these previous investigators in depositing vanadium by various pack techniques. Sintering, oxygen embrittlement of the substrate, and low transport rates were the major problems associated with vanadium deposition. The oxygen embrittlement reportedly resulted from the high concentration of oxygen in the vanadium powder and its subsequent transport to the columbium.

The vanadium vacuum pack deposition studies conducted in this investigation are summarized in Table II. Specimens were packed in a columbium retort containing pure vanadium powder and a halide activator. The vanadium powder (-8 + 50 mesh) was purchased from Haynes Stellite Division of Union Carbide Corporation. The oxygen content was less than 1000 ppm based on a vendor analysis.

Various halide activators were investigated at coating temperatures of 1900° and 2200°F to determine the merits of each halide in promoting vanadium transfer. To prevent oxygen contamination, the initial pack runs were made in a composite titanium gettered-double pack. This composite consisted of a small columbium retort (one inch diameter) within a larger columbium retort (2-1/4" diameter), with the intervening space packed with pure titanium sponge. Very little vanadium deposition was achieved in these initial runs (1/2 mg/cm^2) utilizing the individual halide activators. The columbium alloy Cb 752 coupons were clean and ductile, and no sintering of pack material to the coupons was noted.

Microscopic examination of the vanadium coated coupons revealed the existence of a narrow diffusion zone, Figure 1. The coupons from Run 11 were subjected to a microprobe scan to determine the presence of vanadium or titanium. The scan verified the presence of vanadium; however, one side of the coupon was contaminated with considerable titanium from the getter placed in the double pack. The depth of the vanadium diffusion zone was measured at 0.6 mils for the uncontaminated side, while the titanium contaminated side of the coupon evidenced a 0.4 mil diffusion layer. The titanium gettered pack was eliminated in subsequent vanadizing

TABLE II

VANADIUM[a] PACK DEPOSITION RESULTS ON COLUMBIUM ALLOY Cb-752

Run No.	Activator w/o	Temperature °F	Time Hrs.	Pressure mm	Average Weight Gain-mg/cm^2	Remarks
11	2 NaCl	2200	6	10^{-2}	2.4	Runs 11-21 made in titanium gettered-double pack.
12	2KI	2200	6	10^{-2}	0.86	Coupons ductile and clean after run.
14	2 NaF	2200	6	10^{-2}	1.14	
15	2 NaCl	2200	6	1.5	0	
16	2 NaCl	2300	6	10^{-2}	1.28	
17	2 NaCl	2000	6	10^{-2}	0.38	
21	$2NH_4Cl$+ 2 NaCl	2200	6	10^{-2}	0	
24	0	2700	15	10^{-2}	-	T.C. broke; Temperature overshot to at least 2900°F; pack sintered together.
25	0	2600	15	10^{-2}	-2.0	Single pack; specimens brittle and gray. Some sintered spots.
26	2KF	1900	12	10^{-2}	1.1	Vacuum partially lost-broken belts. Specimens brittle.
27	2KF	1900	12	10^{-2}	0.28	Specimens ductile.
48	2NaCl+ 0.2 VCl_4	2200	6	150Ar	6.9	Specimens ductile and clean. Slight sintering.

TABLE II

(Continued)

Run No.	Activator w/o	Temperature °F	Time Hrs.	Pressure mm	Average Weight Gain-mg/cm^2	Remarks
49	2NaCl+ 0.2VCl$_4$	2200	6	150Ar	6.1	Specimens clean. Slight sintering. D-43 gained 5.2 mg/cm^2; C-129Y-6.5 mg/cm^2.
52	2NaCl+ 0.2VCl$_4$	2200	12	150Ar	6.8	
54	2NaCl+ 0.2VCl$_4$	2200	12	150Ar	6.0	On molybdenized specimens.
64	0.2VCl$_4$	2200	6	150Ar	1.6	

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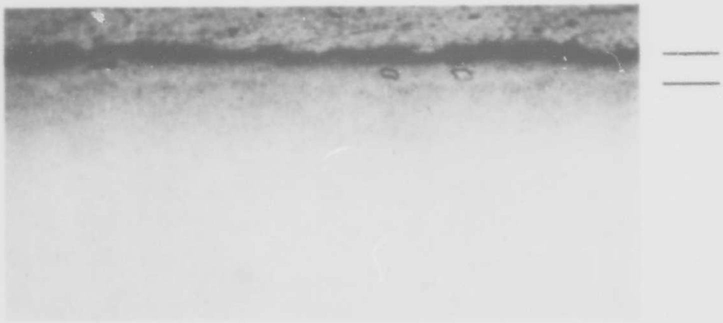
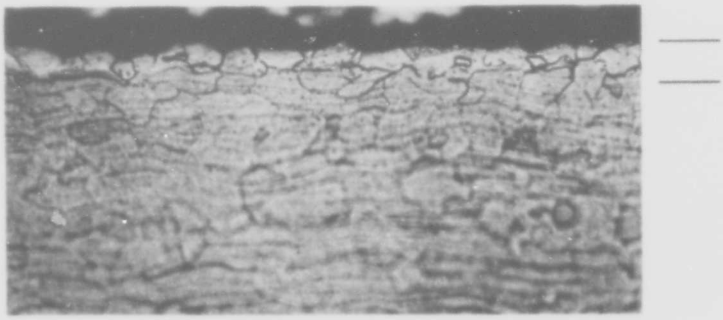
a. Pure vanadium metal powder (-8 + 50 mesh); 1000 ppm O_2.



Unetched



Etched: 15V% H_2SO_4 - 15V% HF - 8V% HNO_3 - H_2O

Figure 1 Microstructure of Vanadium Diffusion Coating on Columbium Alloy Cb-752 - Pure Vanadium Pack Run No. 11 500X experiments because of this contamination.

Vapor pressure data for vanadium from the literature (2) and from experiments at Solar (3) suggested that physical vapor deposition was a feasible method of depositing vanadium on columbium alloys at 2600°-2700°F. Two pack runs were made at 2600 and 2700°F without a halide activator to see if a sufficiently high vapor concentration of vanadium would be established to coat the columbium alloy coupons. No specimen weight gains were experienced in either of the 15 hour runs. Some sintering of pack material to the coupons was noted, and the specimens were brittle. More recent vapor pressure data (4) indicates that a temperature of 3300°F would be necessary to effect metal transport by physical vaporization, using the facilities available for these experiments.

A modification of the halide activated vacuum pack approach was subsequently investigated, and this modification proved to be successful. Vanadium tetrachloride (VCl_4) on the order of 0.2 w/o was added to the NaCl activated pure vanadium pack. Addition of the VCl_4 to the pack was made in a dry box chamber, and transfer of the retort to the coating furnace was accomplished under argon cover. The furnace was flushed with argon prior to loading to prevent interaction of the VCl_4 with moisture, and the loaded furnace was then immediately evacuated to below 10^{-3} torr, blanked-off, and back-filled with 150 mm of argon prior to heating.

Two six-hour vanadizing runs were conducted at 2200°F utilizing the above technique (Run Nos. 48 and 49), and average vanadium depositions of 6.9 and 6.1 mg/cm^2, respectively, were achieved on Cb 752, D-43 and C-129Y alloys. The specimens were shiny and ductile and no sintering of the pack material to the specimens was observed. Increasing the time from six to twelve hours at 2200°F affected no significant increase in the level of vanadium transfer. This latter observation was attributed to the diffusion controlled aspect of the coating deposition mechanism (parabolic), and to the time dependent depletion of the activator from the pack.

Microscopic examination of the vanadized Cb-752 alloy from Run No. 48 revealed a solid solution coating of about 0.8 mil thickness as shown in Figure 2. A microprobe scan was conducted across this specimen, and a graph of the superimposed vanadium and columbium X-ray intensities is shown in Figure 2. The microprobe analysis shows a uniform gradient of vanadium decreasing from approximately 90 w/o at the columbium substrate surface to zero at a depth of approximately 1 mil.

The addition of vanadium tetrachloride (0.2 w/o) to the vanadium pack appeared to catalyze the formation of chlorides, thereby enhancing transport of the coating element. To clarify the role of the sodium chloride in vanadium transfer, one run (No. 64) was made omitting NaCl from the pack. Only VCl_4 (0.2 w/o) was added, and the processing conditions were identical to those employed previously (6 hours at 2200°F with 150 mm of argon). The average amount of vanadium deposited on the Cb 752 coupons was 1.6 mg/cm^2,[1] which was comparable to the amount transferred when NaCl alone was used as

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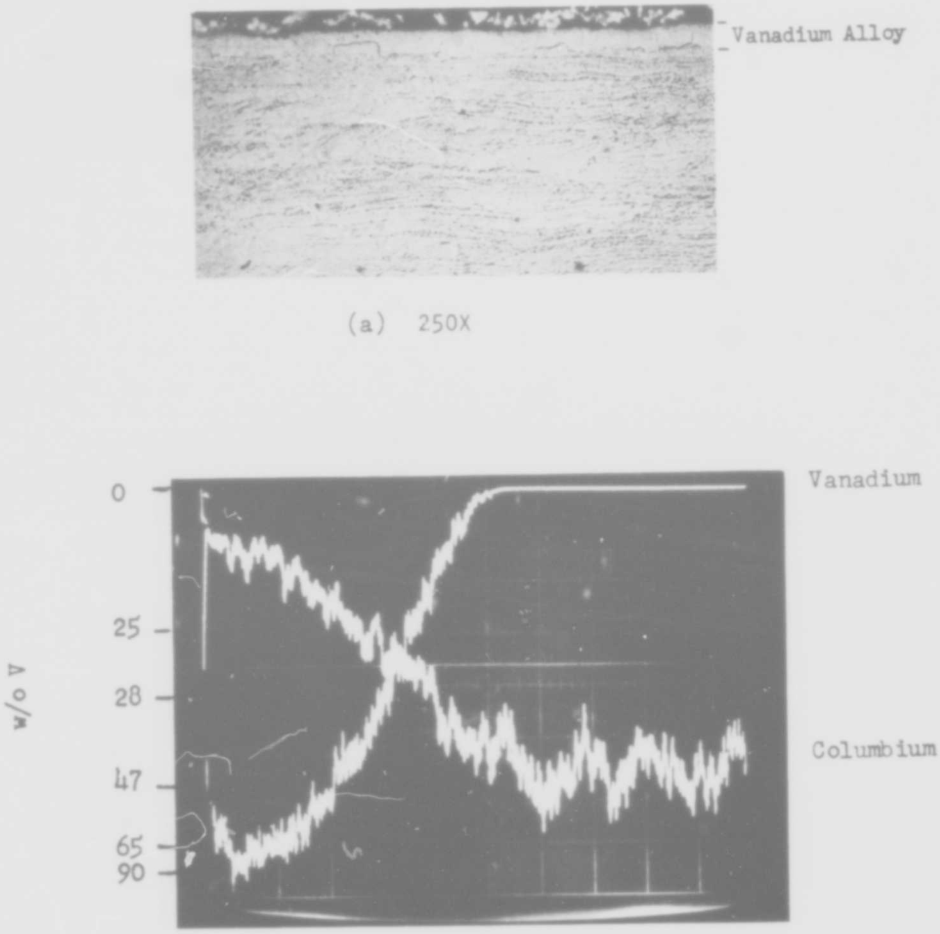
[1] The VCl_4 and NaCl combination yield a vanadium transfer of 7 mg/cm^2 under identical deposition conditions.



(a) 250X

(b) (1cm = 5.33 microns)

Figure 2 Vacuum Pack Deposited (Run No. 49) Vanadium on Columbium Alloy Cb-752: (a) Microstructure and (b) Electron Microprobe Trace.

the activator. Thus, these experiments showed that the VCl_4 and NaCl combination had a synergistic effect on the transfer of vanadium.

To elucidate the mechanism by which vanadium transport was accomplished, the free energy of formation and vapor pressures of the chlorides were plotted as a function of temperature (4,5), as shown in Figures 3 and 4. The curves show that the free energy of formation of vanadium chloride from NaCl and vanadium is thermodynamically unfavorable, thus NaCl alone was not effective in producing vanadium transport. The plots indicate that the VCl_4 will combine with vanadium to form VCl_2, which is a solid at low temperatures. This compound, however, has an appreciable vapor pressure at the coating temperature, as do both the VCl_4 and NaCl. Neither the NaCl or VCl_2 will react with the columbium to form $CbCl_5$, free Na or V, nor does it appear possible to form free chlorine by vanadium chloride disproportionation based on free energy considerations. Thus, the reactions by which vanadium transfer occurs, and the dual roles of the NaCl and VCl_4, are obscure at present. One may postulate that a complex sodium-vanadium-chloride compound is formed, which is responsible for the transfer of vanadium.

These results adequately demonstrated that target quantities (7 mg/cm^2)$^{(1)}$ of vanadium could be deposited on columbium alloy substrates by the vacuum pack technique without substrate embrittlement or significant pack sintering. The technique described in this section was subsequently employed to vanadize the Cb 752, D-43 C-129Y, C132M and XB88 alloys discussed in subsequent sections (6.1, 6.2 and 7.1) of this report.

5.2 MOLYBDENUM DEPOSITION STUDIES

One of the coating systems proposed by the previous investigators on theoretical grounds as having potential advantages over the Cr-Ti-Si coating was the Ti-Mo-Si system (1). The major deterrent to forming this protective coating was the difficulty in depositing molybdenum on columbium. Various techniques explored by previous investigators (1) were:

1. Pack deposition
2. Slurry spray and sinter
3. Deposition from supercooled liquid metal solutions
4. Oxidation-reduction involving the use of pack activators such as MoO_3, MoS_2 and teflon.
5. Fused salt deposition.

Significant problems were encountered with each of these procedures. Briefly, pack experiments and a thermodynamic calculation showed that the deposition of molybdenum on columbium by a diffusion controlled process was impossible from a practical stand point due to an excessively high temperature requirement. Attempts to codeposit molybdenum with titanium were also unsuccessful, as only titanium was transported. The slurry technique was abandoned because of non-uniform density and inadequate coatings formed by localized and non-uniform sintering of the molybdenum bisque to the substrate surface. Deposition from supercooled liquids (Pb-Mo,Ag-Mo)

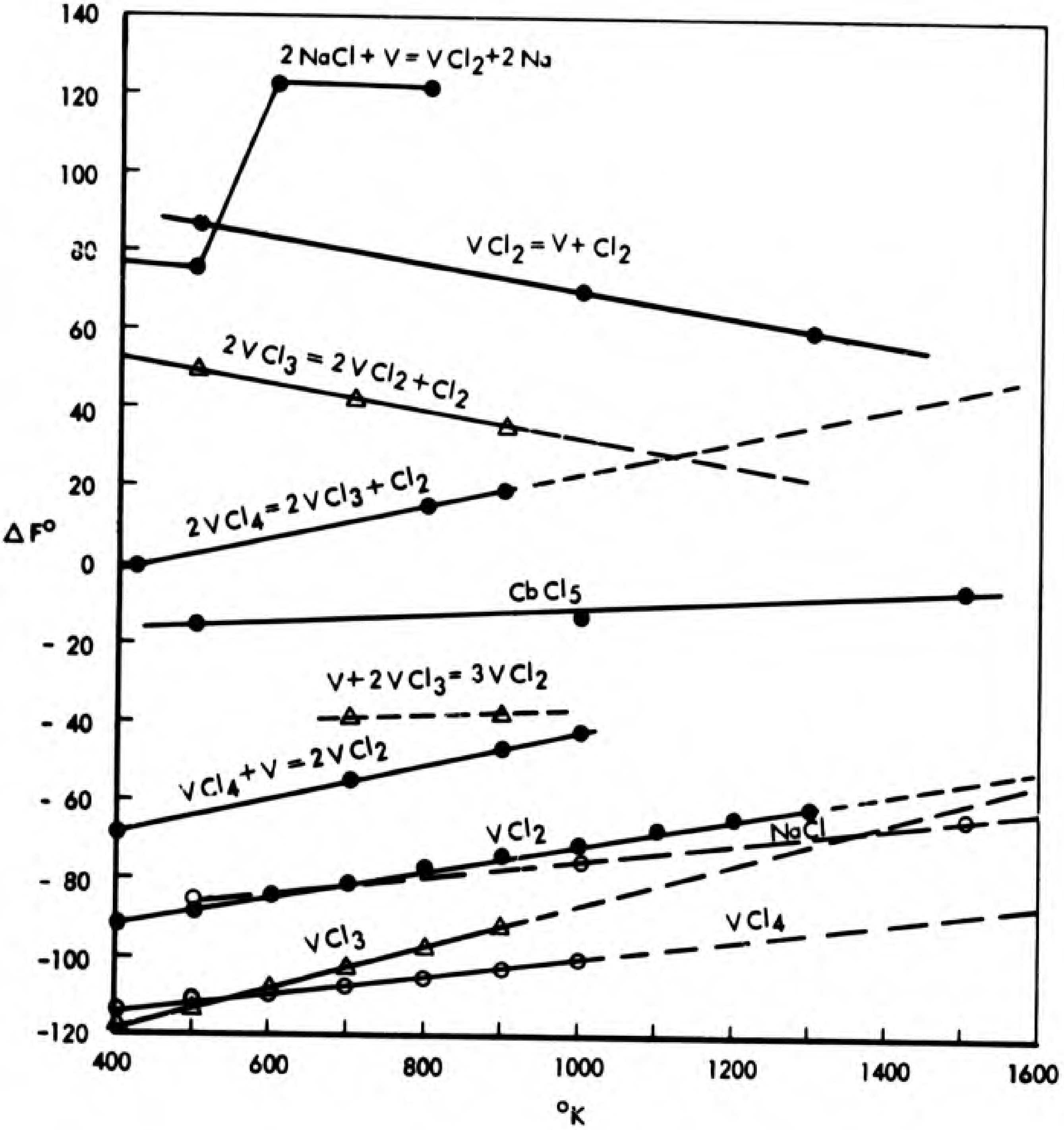


Figure 3 Free Energy of Formation of Chlorides as a Function of Temperature.

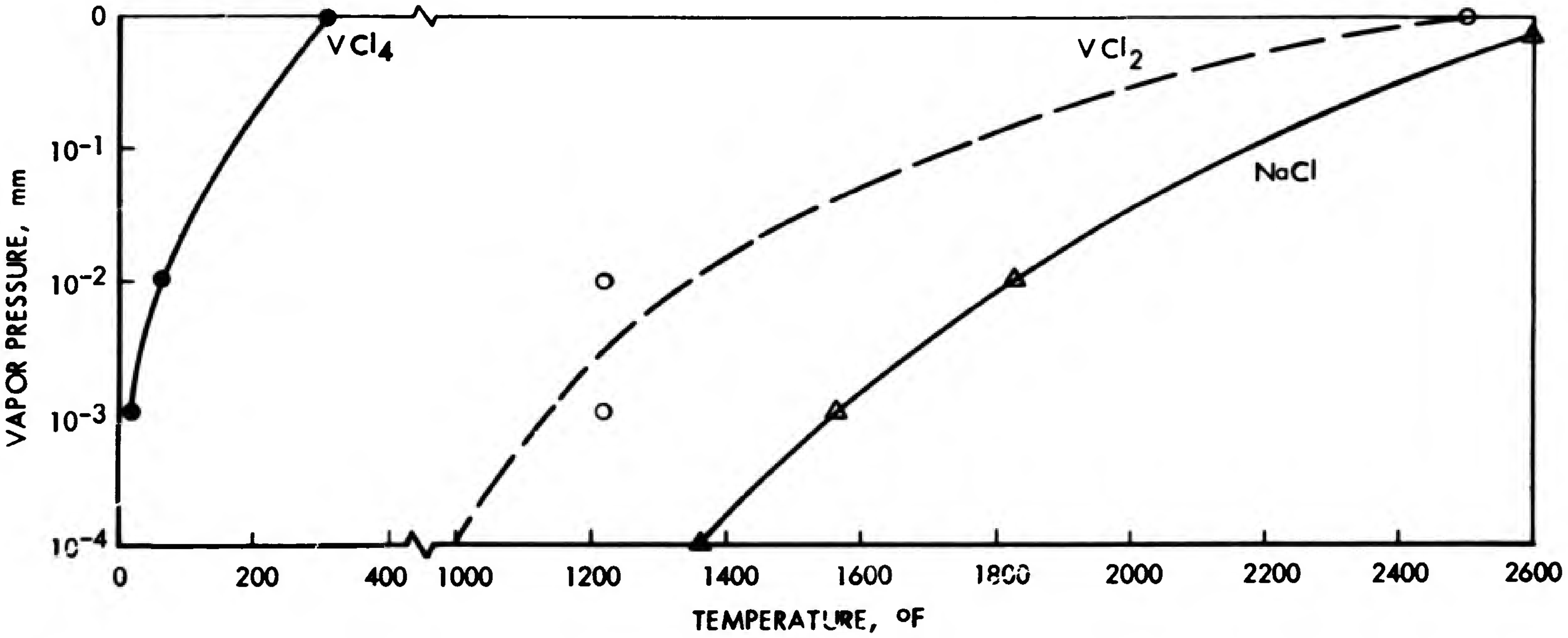


Figure 4 Vapor Pressure of Chlorides as a Function of Temperature.

proved unsuccessful due to the necessity of very high temperatures, the entrapment of the liquid metal constituents and interstitial contamination of the columbium substrate. Extremely low molybdenum deposition rates were obtained by the oxidation-reduction technique, and this idea was also abandoned. Deposition of molybdenum by the fused salt technique resulted in extremely non-uniform depsoits and severe salt corrosion of the columbium material.

Four approaches were pursued in this program in an effort to precoat the surface of a columbium alloy substrate with molybdenum: 1) pack deposition, 2) molybdenum trioxide-hydrogen reaction, 3) slurry spray and sinter, and 4) chemical vapor deposition.

5.2.1 Pack Experiments

Various activators were employed with a pure molybdenum powder pack to evaluate the deposition merits of each activator. The pack deposition results are summarized in Table III. Several pack runs were made at 2200° and 2300°F using pure molybdenum powder (-200 mesh) and 2 w/o NaCl as the halide activator. The largest yield (5.75 mg/cm^2) was obtained at 2200°F under continuous furnace evacuation (10^{-2}mm pressure). No sintering of molybdenum to the coupons was observed; however, the specimens evidenced dark discolored areas, especially on the edges, and were also brittle. Microscopic examination revealed that a diffusion alloy layer was obtained, as shown in Figure 5. An electron microprobe scan verified that this layer was molybdenum. However, a discontinuous oxide layer was formed beneath the molybdenum surface layer, Figure 5. This oxide layer had the characteristic appearance of an oxide formed on columbium at reduced pressures. Solar (1) also observed embrittlement of the columbium substrate during molybdenum pack deposition experiments and, in fact, postulated that volatile molybdenum oxide was the method of transfer in the majority of pack runs.

In an effort to eliminate the oxygen contamination problem, several runs were made in a titanium-gettered double-pack, similar to the technique utilized for vanadium pack deposition studies. No molybdenum weight pickup was experienced with either run. However, the specimens were ductile, as contrasted to the brittle specimens obtained from the ungettered runs. A titanium precoated coupon was also included in Run No. 19 to see if molybdenum would be preferentially deposited on the titanium-columbium alloy surface. A weight loss was observed for this coupon indicating removal of titanium by its reaction with the halide activator. These runs suggested that the method of molybdenum transfer experienced by the previous ungettered runs was the reduction of the gaseous molybdenum oxide by the columbium substrate.

Thermodynamic data (5) show that the temperature of molybdenum halide formation is dependent upon the system halogen pressure. For example, for the chloride, at 2200°F, molybdenum will form a gaseous halide ($MoCl_4$) at one atmosphere of pressure. A reduction in pressure to 10^{-6} atmospheres shifts

TABLE III

PACK DEPOSITION OF MOLYBDENUM ON Cb-752 ALLOY

Run No.	Pack Composition	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Weight Gain mg/cm^2	Remarks
9	Mo Powder[a]	2 NaCl	2300	12	10^{-2}	4.5	Specimens brittle. Gray and black discolored areas.
10	Mo Powder	2 NaCl	2200	6	10^{-2}	5.75	Specimens brittle. Gray and black discolored areas.
18	Mo Powder	2 NaCl	2200	12	1.5	0	Titanium-gettered double pack. Specimens lost weight. Specimens ductile and clean.
19	Mo Powder	2 NaCl	2200	12	10^{-2}	0	Same as Run 18. Titanium precoated coupon also lost weight. Titanium-precoated coupon dark gray with shiny spots of individual grains.
28	Crushed Mo Wire	1 NaCl	2200	4	150 Hydrogen	0.79	Ductile specimens.
29	Crushed Mo Wire	1 NaCl	2200	4	150 Argon	0.00	Ductile specimens.
31	Mo Powder	2 NaCl+ 1 MoCl$_5$	2200	6	150 Argon	-7.2	Coating spalled; black discolored areas.
32	Mo(Crushed Wire)	2 NaCl+ 1 NaCl$_5$	2300	6	150 Argon[b]	-20.6	Coating spalled.
33	Mo(Crushed Wire)	2 NaCl+ 1 NaCl$_5$	2000	6	150 Argon[b]	-44	Coating spalled.
39	Mo Powder	1 NaCl+ 1 MoCl$_5$+ 0.4 Mg	1850	6	150 Argon[b]	-15.9	Specimens brittle. Specimens gray.
40	Mo Powder	1 NaCl+ 1 MoCl$_5$+ 0.4 Mg	2000	6	150 Argon[b]	3.3	Specimens brittle. Specimens gray.

TABLE III

(Continued)

Run No.	Pack Composition	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Weight Gain mg/cm^2	Remarks
41	Mo Powder	1 NaCl+ 1 MoCl$_5$+ 0.4 Mg	2200	6	150 Argon[b]	0.70	Coating spalled off. Specimens brittle.
42	Mo Powder	1 NaCl	2200	6	10^{-2}	0.83	(Same powder used in No. 41);
	Run No. 22 Silicon precoated coupon:					-5.3	Some ductility.
45	Mo Powder	1 NaCl+ 1 MoCl$_5$	2200	6	150 Argon	-3.0	MoCl$_5$ added after pack heated to temperature.
46	75 Mo- 25 Ti	1 NaCl	2250	12	5.0		Specimen bright & ductile.
50	Mo Powder	1KI+ I I	2200	6	150 Argon	-19.5	Specimens black & brittle.
60	Mo Powder	1 NH$_4$Br + 2(NH$_2$)$_2$CO	2200	6	150 Argon	-24	
63	Mo Powder	1 MoCl$_5$ + 2(NH$_2$)2CO	2200	6	150 Argon	-18	
86	Crushed Mo Wire	2 MoO$_3$	1500	1	10^{-2}	-2.2	Specimens brittle. Used Mo pack.
87	Mo Powder	2 MoO$_3$	1500	1	10^{-2}	0.28	Specimens brittle. New powder.

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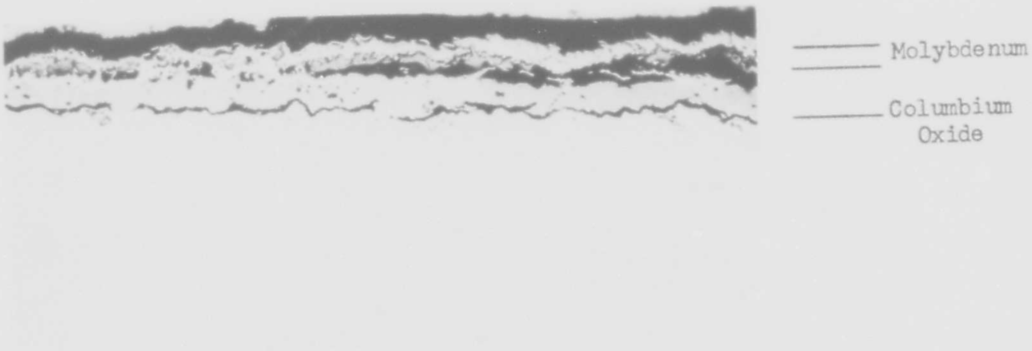
a. -250 mesh powder.
b. Backfilled after 350°F.

Alloy Layer



6 Hours Oxidized Substrate 2200° F

Figure 5 Microstructure of Molybdenum Diffusion Coating on Columbium Alloy Cb-752 at Two Areas Showing Oxidized Substrate. Pure Molybdenum Pack Run No. 10 250X the formation temperature downwards to below 1350°F, which is too low to form a diffusion coating on columbium. Therefore, considering the required temperature and type of facility being used, a pressure on the order of 10-100 mm was necessary to form gaseous molybdenum chlorides. The presence of hydrogen would also enhance molybdenum halide reduction at the specimen surface. These technique modifications were investigated.

Two runs were made using crushed molybdenum wire, NaCl activation and a 150 mm blanket of either argon or hydrogen in the coating furnace. Very little molybdenum transfer to the columbium was achieved, and a photomicrograph of very thin alloy layer formed in Run No. 28 is shown in Figure 6. When molybdenum pentachloride ($MoCl_5$) was added to the molybdenum pack (Runs 31, 32, 33) reasonably thick molybdenum coatings were formed on the columbium substrate. However, these coatings spalled due to chloride corrosion of the columbium substrate, as shown in Figure 6. Reducing the pack temperature from 2300 to 2000°F had no beneficial effect on corrosion.

In an effort to obtain chemical reduction of the molybdenum pentachloride , and possibly lessen chloride corrosion of the columbium substrate, magnesium powder (0.4 w/o) was added to the NaCl-$MoCl_5$ activated molybdenum pack (Runs 39-41). The temperature was varied between 1850 and 2200°F. Non-adherent molybdenum deposits were again formed, and the columbium substrate was embrittled. Urea $(NH_2)CO$ added as a reducing agent (Run 63) to the $MoCl_5$ also proved to be futile.

To see if pack conditioning occurred from previous use of $MoCl_5$, a run was conducted with used pack material and NaCl activation only (Run 42). The specimen weight gain was low, similar to previous results with new packs. A pre-siliconized columbium coupon was included in this latter run to see if molybdenum would deposit preferrentially on the silicide surface. The specimen lost weight, indicating silicon transfer to the molybdenum pack.

Another approach was taken in Run 45, in which case the $MoCl_5$ was added to the NaCl activated pack after the pack had reached the 2200°F diffusion temperature. Again a non-adherent molybdenum deposit was obtained.

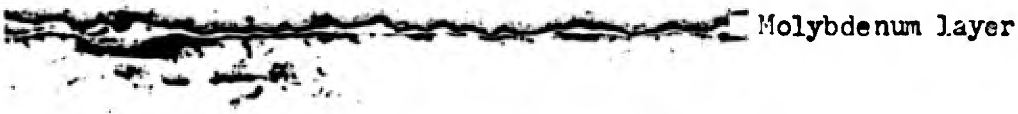
In run No 50, KI and iodine were investigated as molybdenum pack activators (2200°F). Again, corrosion of the columbium substrate was apparent, and molybdenum transfer to the columbium was not achieved. Ammonium bromide and urea (Run 60) also failed to produce molybdenum transfer.

Two runs (Run Nos. 86 and 87) were made with 2 w/o molybdenum trioxide added to a molybdenum pack. The runs were made at 1500°F for one hour under continuous furnace evacuation using both fresh and used molybdenum powder. Only a small weight gain was noted for Cb 752 coupons packed in new molybdenum powder. Specimens placed in the used powder lost weight as a consequence of residual chloride attack.

In the final run in this series, prealloyed 75 Mo-25Ti was employed

2200°F Run No. 28 4 Hours

Activator: 1 w/o NaCl



2200°F Run No. 31 6 Hours

Activators: 1 w/o Nacl + 1 w/o $MoCl_5$

Figure 6 Photomicrographs of Pack Molybdenized Columbium Alloy Cb-752
250 X

as the pack media, and a 6 hour - 2200°F run was made using NaCl activation. The specimens were bright, and a 5 mg/cm^2 weight gain was obtained. However, microprobe analysis showed that only titanium was transferred, and it had diffused approximately 0.12 mils into the columbium alloy surface. It was concluded from these experiments that molybdenum precoating by the pack technique was not feasible.

5.2.2 Molybdenum Trioxide-Hydrogen Reduction

A different approach to molybdenum application was attempted using volatile molybdenum trioxide (MoO_3). With this technique (6) molybdenum trioxide was first deposited on the specimen surface. The oxide was subsequently converted to molybdenum by hydrogen reduction. It was anticipated that oxygen contamination of the substrate could be a problem with this approach.

In the first series of experiments the specimens were exposed directly to molybdenum trioxide vapor. This was accomplished by placing the specimens on a molybdenum screen grid located over the molten molybdenum trioxide bath. A substantial amount (8 mg/cm^2) of molybdenum trioxide was transferred by this technique. However, in all of the runs made using molybdenum trioxide, the Cb 752 specimens were severely embrittled. Preliminary reduction in hydrogen of the coated coupons at 1500° and at 2000°F was unsuccessful because of hydrogen purity. A nitrogen cold trap was added to lower the hydrogen dew point for all subsequent reduction operations.

The next step with the molybdenum trioxide technique was to reduce the exposure time, and hopefully improve the ductility by immersing the coupons directly in molten molybdenum trioxide. A dipping set up was constructed which consisted of a vertical alundum tube furnace heated externally. The molybdenum trioxide was contained in a crucible suspended in the furnace. An argon atmosphere was maintained over the molten bath, which was held at 1470 - 1550°F. Specimens coated by this technique consisted of uncoated and pretitanized columbium alloy Cb 752. The amount of molybdenum trioxide transferred to the coupons was a linear function of immersion time, with a quick dip yielding about 12.8 mg/cm^2 of oxide coating. An immersion of 30 seconds yeilded a weight gain of 36 mg/cm^2. Some of the as-coated specimens were embrittled after immersion (quick dip), whereas others, such as the pretitanized samples, retained ductility. The bath temperature appeared to be a factor, with dipping temperature in excess of 1500°F producing severe embrittlement.

Reduction of the molybdenum trioxide in hydrogen was carried out in two stages (7,8). In the first stage, the MoO_3 was transformed to MoO_2 at 1000°F. The specimens were held for 15 minutes at this temperature. The formation of MoO_2 must be virtually complete before the temperature reaches 1020°F, since the intermediate molybdenum oxide (Mo_4O_{11}) and MoO_3 form a eutectic which melts at about 1020°F. The formation of this liquid eutectic would prevent reduction of the underlying oxide. Furthermore, by using a low first stage reduction temperature, the amount of the trioxide lost by evaporation is restricted. The second stage reduction in hydrogen was performed at 2000°F for 15 minutes, where the MoO_2 was reduced to molybdenum, and the residual oxygen was eliminated.

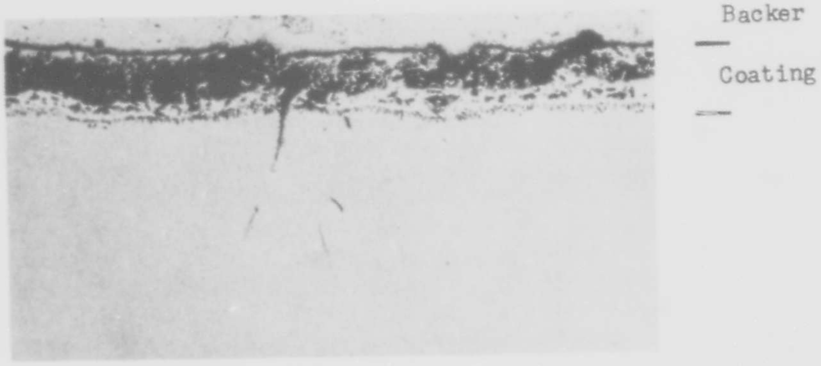
Several hydrogen reduction runs were made before a total conversion of molybdenum oxide to molybdenum metal was visually obtained. The hydrogen flow through the furnace had to be copious enough to remove the water vapor generated during the reduction process.

The coated specimens were brittle after the hydrogen reduction; consequently, some were annealed in vacuum for 5 hours at 2400°F to see if the ductility could be improved by removing residual hydrogen. Ductility after vacuum annealing remained virtually unchanged, indicating that hydrogen was not responsible for embrittlement. Subsequent metallographic examination of coated specimens showed that embrittlement was caused by oxygen ingress into the columbium matrix along preferential paths which produced the cracks shown in Figure 7. The pretitanized material was free of cracking, but contained an oxidized zone visible in Figure 7. That the cracks were caused by molybdenum trioxide corrosion was evidenced by the deposits of molybdenum in the cracks. The cracking appeared to be similar to stress-induced failures observed in other corrosive media.

The molybdenum coating applied over the titanized Cb 752 spalled because of lack of adhesion to the oxidized surface. Reduction of this oxidized zone was not affected during the hydrogen reduction step because of the stable nature of the titanium oxide.

To determine if the embrittlement could be eliminated by prior stress relief and recrystallization, an investigation was conducted on annealed coupons of alloy Cb 752. The specimens were annealed in vacuum at 2400°F for several hours prior to molybdenum trioxide coating. A quick dip in molten molybdenum trioxide resulted in embrittled coupons, as manifested by the reduction in bend ductility.

To see if embrittlement could be eliminated by minimizing the exposure time in MoO_3 vapor, a series of exposures were executed. The specimens were placed over the molten molybdenum trioxide bath, the argon atmosphere was replaced with a vacuum, and the argon atmosphere was then reintroduced after a specified exposure. The MoO_3 weight gain results for Cb 752 alloy are listed in Table IV for two bath temperatures. Specimens of D 43 and C 129Y were also coated with molybdenum trioxide in these experiments.



Cb-752

Pretitanized Cb-752

Figure 7 Molybdenum Coating by Hydrogen Reduction of Molybdenum Trioxide. Coupons Vacuum Annealed for 5 Hours at 2400°F. 250 X

TABLE IV

WEIGHT GAIN DATA FOR COLUMBIUM ALLOY SPECIMENS EXPOSED IN MOLYBDENUM TRIOXIDE VAPOR

Alloy	Exposure Time-Min	Specimen Weight Gain-mg/cm^2 1400-1450°F[a]	Specimen Weight Gain-mg/cm^2 1500-1550°F
Cb 752	5	-	2.8
	10	3.1	3.1
	20	5.7	3.7
	30	5.4	-

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[a] MoO_3 temperature.

All specimens were embrittled after exposure to the molybdenum trioxide vapor. The bath temperature appeared to have an insignificant effect on the amount of molybdenum trioxide transferred. Thus, it was shown that embrittlement occurred rapidly for exposures of five minutes or more in the MoO_3 vapor. Reduction of the molybdenum trioxide in dry hydrogen failed to improve specimen ductility, and yielded severely embrittled specimens which disintegrated when handled. Furthermore, investigations (9, 10) recently conducted on the effect of water-hydrogen environments on columbium alloys generally show adverse effects of this environment on alloy ductility.

Based on the above results, the molybdenum trioxide-hydrogen reduction method was not considered to be suitable for application of molybdenum to columbium alloys.

5.2.3 Slurry Coating Experiments

The procedure consisted of spraying the columbium alloy specimens with a slurry containing molybdenum powder, a binder and a volatile liquid vehicle (lacquer). The material to be coated was thereby enveloped in a continuously evacuated furnace. The specimens were placed in a columbium retort and supported on a molybdenum wire frame during the diffusion treatment.

The sintering studies included the use of additives such as titanium and nickel to enhance the solid-state sintering rate, and the use of low-melting metals such as aluminum, copper and silver to facilitate sintering in the presence of a liquid phase.

Initial experiments were conducted with molybdenum powder (-325 mesh) which contained no additives to promote sintering. The bisques were vacuum (0.3 micron) sintered at 2700°F in a coating furnace, Table V. Although

TABLE V

RESULTS OF MOLYBDENUM SLURRY-SPRAY AND SINTER EXPERIMENTS FOR COATING COLUMBIUM ALLOY Cb-752

Run No.	Slurry Composition w/o	Bisque Thickness Mils	Temp. °F	Time Hrs.	Pressure mm	Average Specimen Weight Gain mg/cm^2	
1	Mo$^{(a)}$	10	2700	8	10^{-2}	-	Coating sintered to coupons. Specimens black and brittle.
2	Mo	1	2700	8	10^{-2}	84	Same as No. 1.
3	Mo + 1/2 Ni	10	2050	20	10^{-2}	-	Coating sintered to coupons. Coupons gray and brittle.
4	Mo + 1/2 Ni	1	2300	20	10^{-2}	42	Coating sintered to coupons. Specimens blackish and ductile.
23	Mo$^{(b)}$ + 1/4 Al	3	2050	20	10^{-2}	0	No sintering of coating to coupons.
	Mo + 1/2 Al	3				0	Specimens light to dark gray and ductile.
	Mo + 1/4 Ni	3				0	
	Mo + 1/2 Ni	3				0	
	Mo + 1 Ti	3				0	
25	Mo + 5 TiH	3	2600	15	10^{-2}	4.85	Bisque partially adherent.
	Mo + 1 Ti					2.3	Some sintered spots. Coupons gray and brittle.

TABLE V

(Continued)

Run No.	Slurry Composition w/o	Thickness mils	Temperature °F	Time Hrs.	Pressure mm	Average Weight Gain-mg/cm^2	Remarks
30	Mo$^{(b)}$+5 TiH	4	2750	25	10^{-2}	-	Coating sintered. T. C. broke.
34	Mo$^{(b)}$+5 TiH	2	2400	15	10^{-2}	2.2	Bisque scrapped off.
35	Mo$^{(b)}$+5 Al	2	2200	12	150 Argon	1.1	Bisque easily removed.
43a	Mo$^{(b)}$+1 Ag	4	2400	10	10^{-2}	2.8	Bisque scrapped off. Specimens ductile.
43b	Mo$^{(b)}$+0.6 Ni	4	2400	10	10^{-2}	2.2	Bisque scrapped off. Nickel nitrate used to coat Mo. Specimens ductile.
44	Mo$^{(b)}$+4Cu-Al$^{(c)}$	4	2300	2	10^{-2}	2.4	Bisque removed. Dark spots penetrated Cb. Specimens brittle.

(a) Mo: 4-6 microns particle size.
(b) Mo:-325 mesh.
(c) Ratio of 3 Cu to 1 Al.

they sintered adherently to the specimens, the columbium alloy substrate was embrittled.

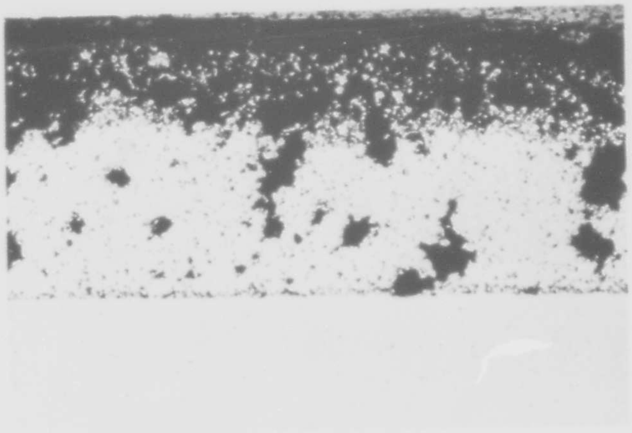
Microscopic examination indicated that thicker bisques produced a uniform molybdenum-columbium diffusion layer, as show in Figure 8 However, the sintered molybdenum coating was porous and excessively thick. A thin bisque, on the other hand, produced a discontinuous interdiffusion layer in addition to a non-uniform, porous coating.

Sintering of metal powders can be enhanced (11) by small additions of group VIII metals such as nickel. A second experiment was conducted using a molybdenum slurry containing 0.5 w/o nickel powder. Two sintering temperatures - 2050 and 2300°F - were employed. The nickel-columbium system displays a eutectic at 2140°F and this reaction might also enhance the bonding process. Microscopic examination showed that the nickel definitely improved the sintering characteristics of the molybdenum bisque, as demonstrated by the improved appearance of the bisque surface and the reduction in porosity, Figure 8. In addition to the interfacial diffusion zone,deep intergranular penetration of the columbium substrate by the nickel was also evident.

To reduce the nickel penetration, smaller nickel additions were tried using molybdenum powder of 4 to 6 microns particle size. Diffusion annealing at 2050°F under continuous furnace evacuation failed to produce an adherently sintered coating. In all cases, the bisques were easily removed and no sintering was noted. All specimens were ductile following this sintering treatment. When similar nickel coated specimens were sintered at 2400°F, (Table VI), the adherency of the coating was improved and yielded the densification shown in Figure 9.

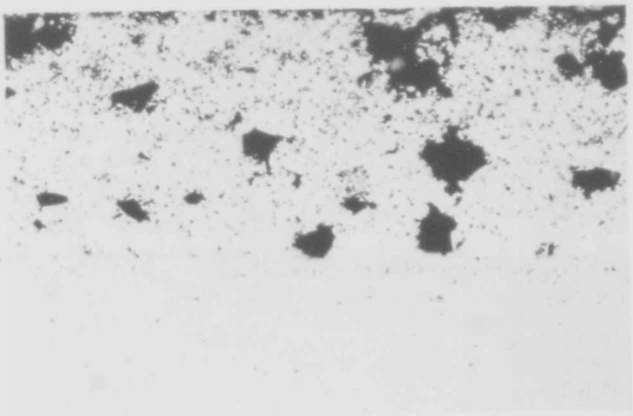
Solar (1) investigated the use of molybdenum powder containing 5 w/o titanium hydride, and found that a diffusion treatment at 2760°F produced a relatively dense coating. A similar experiment was also conducted in this program using a molybdenum powder (4 to 6 microns) slurry containing 5 w/o titanium hydride applied to columbium Cb 752. Specimens sprayed with a 3 mil thick bisque were diffusion annealed at 2600°F under continuous evacuation (0.3 micron)in the coating furnace. The bisque was partially sintered to the substrate surface, but could be removed with difficulty. Some sintering of molybdenum to the columbium substrate was observed.The specimens were brittle after the coating run.

The titanium and titanium hydride additions to the molybdenum powder produced the coating layers shown in Figure 10. Sintering at higher temperature (2750°F) yielded bisques sintered to the columbium substrate. Sintering at lower temperatures produced very thin diffusion coatings, which became progressively thinner as the diffusion temperature was reduced. At these lower sintering temperatures, the bisque was only partially adherent and could be removed by scraping.



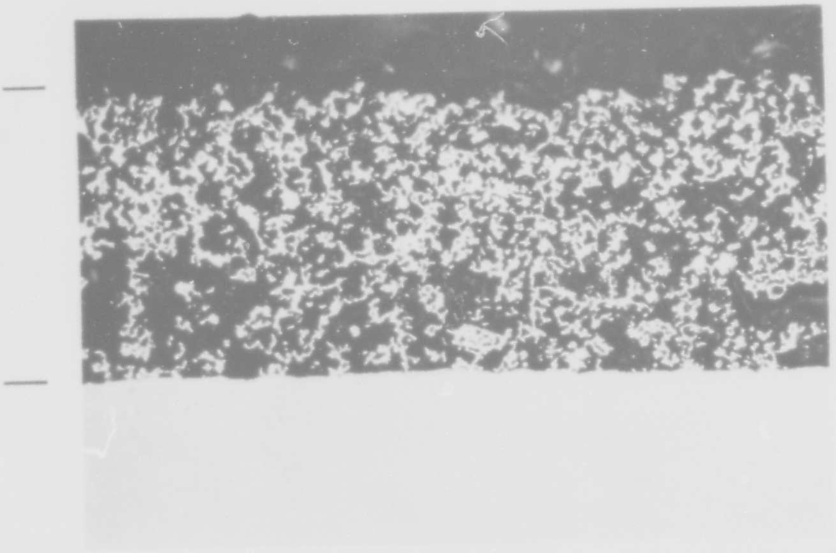
8 Hours Run No. 1 2700°F

(a)

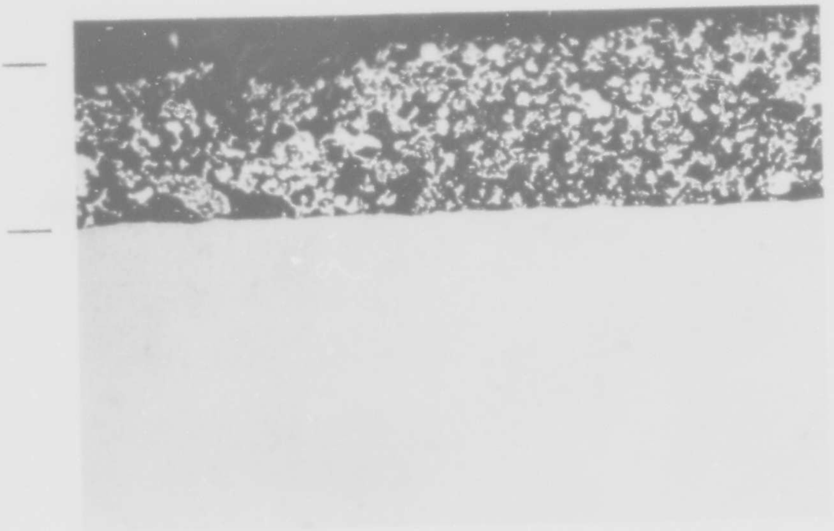


20 Hours Run No. 3 2050°F

Figure 8 Microstructure of Molybdenum Coatings on Columbium Alloy: a) Molybdenum with no additive; b) Molybdenum powder Coated with 1/2 w/o Nickel. 250X

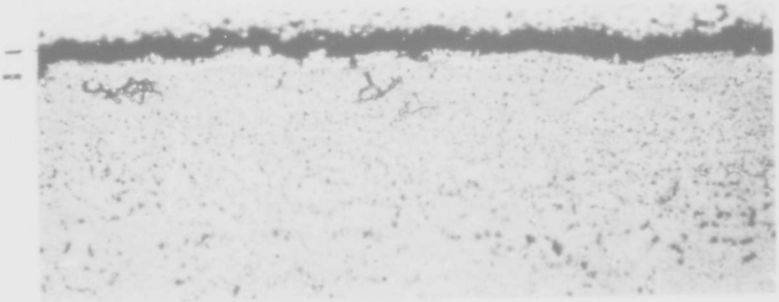


10 Hours Molybdenum-Nickel Coated (0.6 w/o Ni) 2400 °F



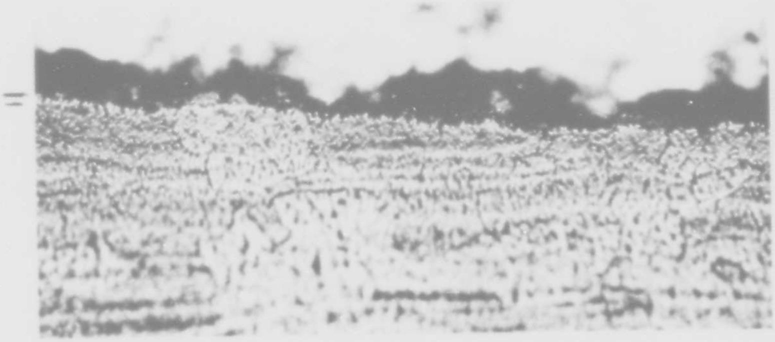
10 Hours 10w/o Ag + Mo 2400 °F

Figure 9 Molybdenum Slurries on Cb-752 Fired at 2400°F in Vacuum. 250 X

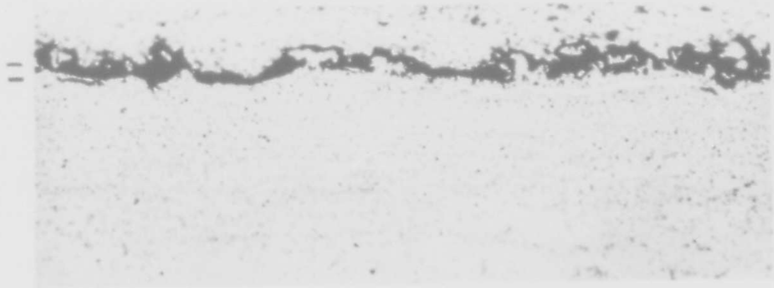


2600°F
Mo + 1 w/o Ti
Run No. 25

500 X

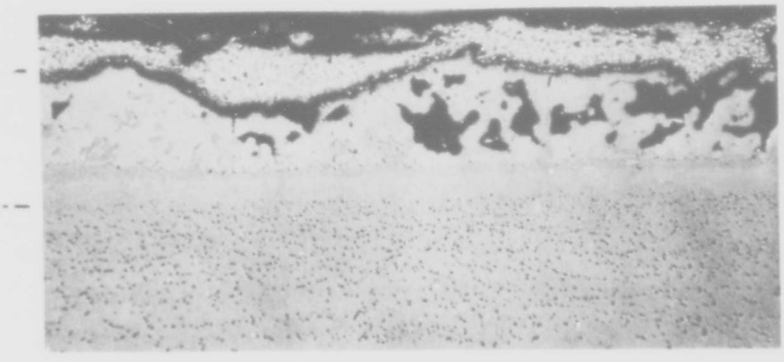


2400°F
Mo + 5 w/o TiH
Run No. 34
1000 X



2600°F
Mo + 5 w/o TiH
Run No. 25

500 X



2750°F

Mo + 5 w/o TiH
Run No. 30

250 X

Figure 10 Photomicrographs of Slurry Applied Molybdenum on Columbium Alloy Cb-752.

TABLE VI

SLURRY DEPOSITION OF MOLYBDENUM ON Cb-752

Slurry Composition	Firing Temperature, °F	Time	Remarks
Mo[a] + 5 w/o TiH_2	2800	2	Visually sintered and bonded
Mo + 5 w/o TiH_2	3000		Visually sintered and bonded
Mo + 5 w/o TiH_2	3200	2	Visually sintered and bonded
10 w/o Cu + Mo	2400	10	Bonding not good; porosity
20 w/o Cu + Mo	2400	10	Bonding not good; porosity
30 w/o Cu + Mo	2400	10	Bonding not good; porosity
10 w/o Cu + 4 w/o Al + Mo	2400	10	Bonding not good; coating smooth
20 w/o Cu + 8 w/o Al + Mo	2400	10	Bonding not good; coating smooth
1 w/o Ni coated Mo[b]	2400	10	Bonding questionable
0.6 w/o Ni coated Mo[b]	2400	10	Bonding questionable
5 w/o Ag + Mo	2400	10	Bonding good; coating smooth
10 w/o Ag + Mo	2400	10	Bonding good; coating smooth
20 w/o Ag + Mo	2400	10	Bonding good; coating smooth
5 w/o Ag + Mo	2550	4	Bonding good; coating smooth
10 w/o Ag + Mo	2550	4	Bonding good; coating smooth
20 w/o Ag + Mo	2550	4	Bonding good; coating smooth
Mo[c] + 5 w/o TiH_2	2700	10	Bonding questionable; coating with craze cracks.
Mo[c] + 10 w/o Ag	2400	10	Bonding questionable; coating smooth - C129Y alloy substrate

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[a] Mo-4-6 microns particle size

[b] Mo powder mixed with aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, dried and fired in vacuum for 1 hour at 900°F prior to application.

[c] Mo - 0.2 microns particle size.

In further experimentation with the TiH_2 additive sintering was performed in the Brew furnace at higher vacuum (0.05 microns) and in a cleaner environment. The amount of slurry applied to each specimen was 15-20 mg/cm^2 as tablulated below in Table VII. The spray-coated specimens were dried and then fired for 2 hours at 2800, 3000 and 3200°F in vacuum (0.05 microns). The temperature was controlled to ± 25°F during sintering.

TABLE VII

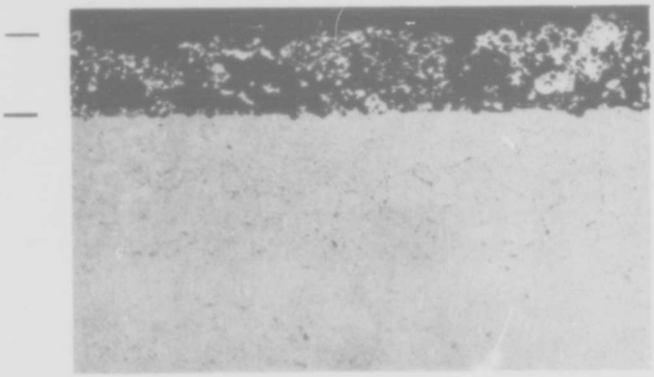
WEIGHT GAIN DATA FOR PARTICULATE MOLYBDENUM SINTERED ON Cb-752

Weight after Spraying mg/cm^2	Firing Temp. °F	Weight after Firing mg/cm^2
14.6	2800	13.7
15.4	2800	14.3
18.8	2800	18.0
16.0	3000	15.4
17.7	3000	16.8
19.1	3000	18.6
19.1	3200	18.8
19.1	3200	18.8
18.8	3200	18.3
17.1	3200	16.8

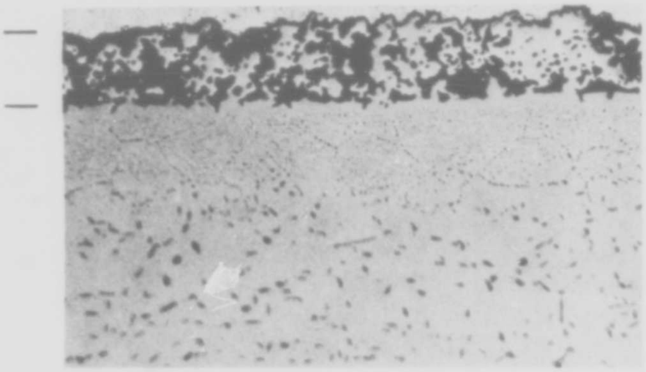
The bisques were bonded to the specimen surfaces and, visually, sintering appeared satisfactory in all cases.

Metallography for the specimens coated with the 5 w/o TiH_2-Mo slurry (Table VI) showed that sintering was achieved, however, the molybdenum coating was porous, Figure 11. Some titanium (and molybdenum) diffusion into the columbium substrate was also evident. When molybdenum powder with a particle size of 0.2 micron was used with the titanium additive in place of the 4-6 micron powder, the densification was improved, Figure 12. These specimens were sintered in vacuum (0.05 microns) for 10 hours at 2700°F in the Brew furnace. The fine molybdenum powder produced a crazed surface as a result of shrinkage, and bonding to the substrate was poor.

To catalyze sintering of the molybdenum by the presence of a liquid phase, additions of low-melting elements such as aluminum, silver, copper and aluminum-copper were made, Table VI, to the molybdenum slurry which was sprayed on Cb 752 alloy specimens. These coated specimens were subsequently fired in vacuum (0.3 microns) in the coating furnace. In this process the "fugitive" metallic vehicle aids solid-state sintering, and ideally is removed by evaporation because of its high vapor pressure at the sintering temperature. The mechanism of sintering in fugitive vehicle slurries is not established. However, it is related to the liquid-solid surface energy and the extent of solubility of the solid in the liquid.

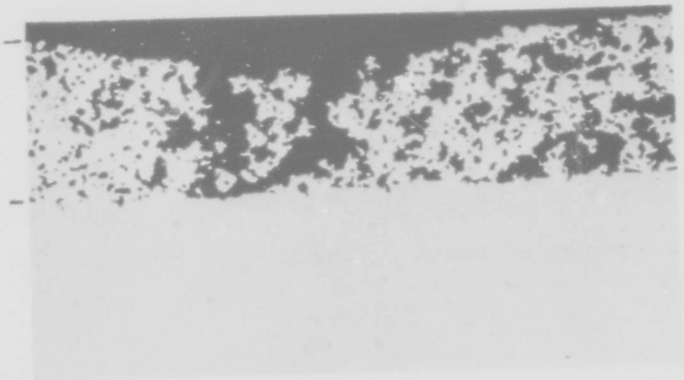


2800°F



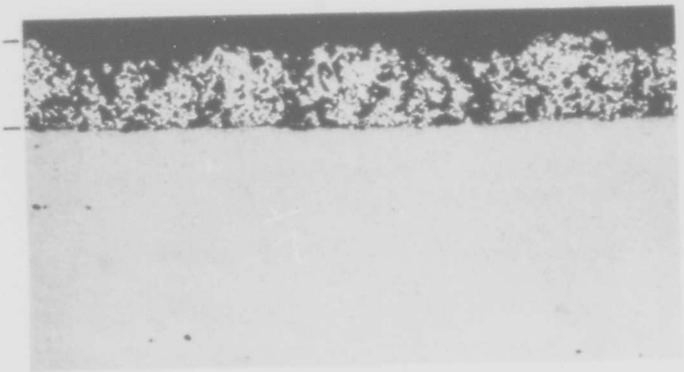
3200°F

Figure 11 Molybdenum (4 to 6 Microns) - 5w/o TiH_2 Slurry Sintered on Columbium Alloy Cb-752 in Vacuum at the Indicated Temperatures for Two Hours. 250 X



10 Hours Mo + 5 w/o TiH_2 2700 °F

Cb 752



10 Hours Mo + 10 w/o Ag 2400 °F

C129Y

Figure 12 Photomicrographs of 0.2 Micron Slurry Applied Molybdenum with Titanium Hydride and Silver Additives. 250X

The initial experiments with the fugitive vehicle additions of Al, Ag and Cu-Al to the molybdenum powder produced non-adherent bisques on the columbium substrate, Table V. Particle bonding was not achieved at sintering temperatures of 2200-2400°F, and the bisques were easily scraped from the specimen surfaces. Microscopic examinations showed extremely thin surface deposits of unknown composition.

When the sintering temperature was increased, Table VI, bonding was improved. The silver additions produced the most densification, Figures 9 and 13. Severe copper penetration into the columbium substrate was evident for the copper-containing slurries, Figure 13, and the densification generally increased with copper content.

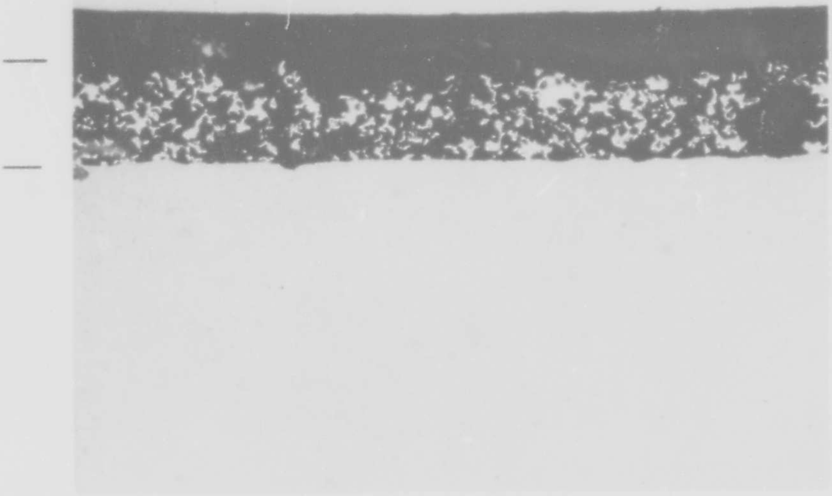
The sintering experiments using 10 w/o Ag as the fugitive vehicle were repeated using molybdenum powder with a particle size of 0.2 microns. Samples of Cb 752 and Cb 132M were sprayed with the powder mixture suspended in a nitrocellulose lacquer, dried and fired in vacuum at 2400°F for 10 hours. The coating appeared to be adherent, and microscopic examination, Figure 12, showed a dense molybdenum coating containing some voids. Microprobe analysis indicated that no silver was present in the coating. The utilization of the fine molybdenum powder did enhance the overall consolidation. However, in subsequent coating steps (CrTi and Si), the molybdenum coating spalled, suggesting that the bonding of the molybdenum to the columbium substrate was poor.

Thus, the use of fine molybdenum powder with both silver and titanium additives improved the overall densification of the slurry applied molybdenum precoating. However, the adherence of the coating to the substrate was not as good as with the coarser (4 to 6 microns or -325 mesh) powders.

In summary, the use of nickel, titanium and silver additives enhanced the densification of the particulate molybdenum. The densification was also improved as the particle size of the molybdenum powder decreased. However, because of the larger amount of shrinkage associated with use of the finer powder and the probable increase in residual tensile stress in the coating, the adherence of the coating with the fine particle molybdenum was impaired. Furthermore, uniformity of coating and the ability to form a thin, continuous and impervious coating appeared to be difficult to accomplish by the slurry technique.

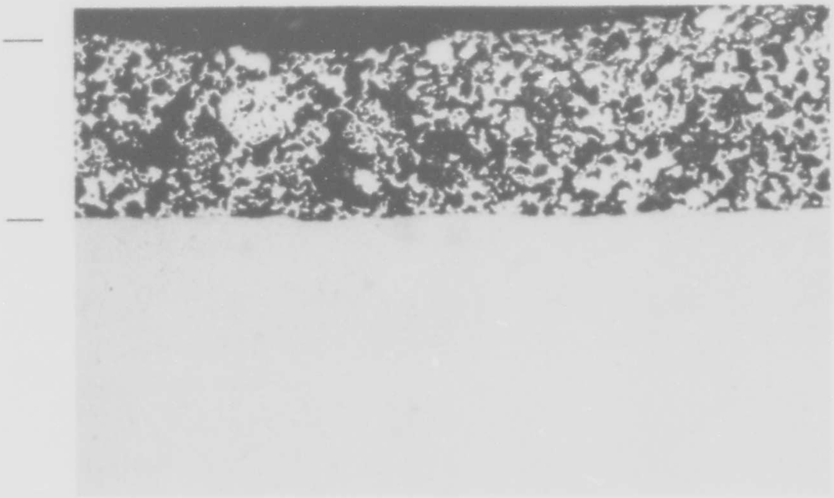
5.2.4 Chemical Vapor Deposition

The application of molybdenum to columbium alloys by chemical vapor deposition (CVD) consisted of passing molybdenum pentachloride ($MoCl_5$) vapor as the plating agent, and hydrogen as the reducing agent, over the heated specimens. The specimens were heated in a revolving barrel reactor to produce a tumbling action. The problems associated with directional flow of the plating gases were eliminated by the random movement of the coupons in rotating barrel. This random motion exposed all specimen surfaces equally to the plating gases, leading to a very uniform coating. The reactant gases



10 Hours 2400 °F

10 w/o Cu + 4 w/o Al + Mo



10 Hours 2400 °F

10 w/o Cu + Mo

Figure 13 Molybdenum Slurries on Cb-752 Fired at 2400°F in Vacuum. 250 X entered one end of the plating chamber and the by-product gases were removed from the opposite end. The system was evacuated at completion of the coating cycle to eliminate the chance of hydrogen embrittlement during the cool-down period.

The coating parameters used in the CVD experiments were:

1) deposition temperature: 1800-1900°F
2) system pressure: 10-20 torr
3) coating time: 1-2 hours
4) molar ratio of hydrogen to $MoCl_5$: 10 to 1

Typical molybdenum coatings produced on Cb 752 alloy are shown in Figure 14. The deposited molybdenum thickness varied between 0.25 and 1.2 mils, and showed a nodular growth pattern common with vapor deposits. The coatings were generally adherent and the coated specimens were ductile.

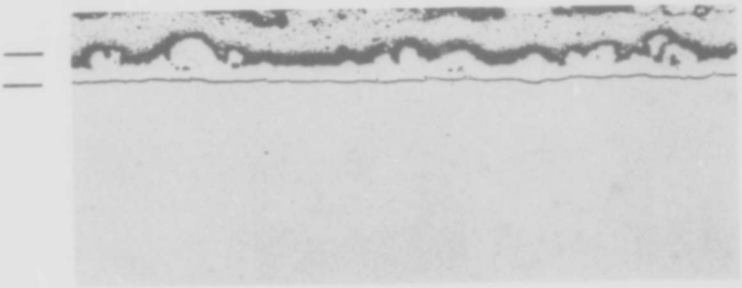
This method of forming molybdenum coatings on columbium was considered to be the most expedient means of producing the many molybdenum containing silicide coating systems designed for study in this program. However, large specimens such as erosion bars could not be coated by this technique because of equipment limitations.

To determine the effect of the method of molybdenum application method (CVD vs slurry) on cyclic oxidation life, 5w/o TiH_2-Mo slurry coated (15-20 mg/cm^2) Cb 752 specimens and CVD molybdenum (1.3 and 13.7 mg/cm^2) coated specimens were Cr-Ti and Si coated in Runs 138 and 145. The Cr-Ti run involved 2300°F for 8 hours at 10^{-2}mm, and the silicon run 2050°F for5 hours at 10^{-2}mm pressure. Both pack runs contained 1 w/o KF as activator. The weight gains and oxidation life for each are tabulated below in Table VIII.

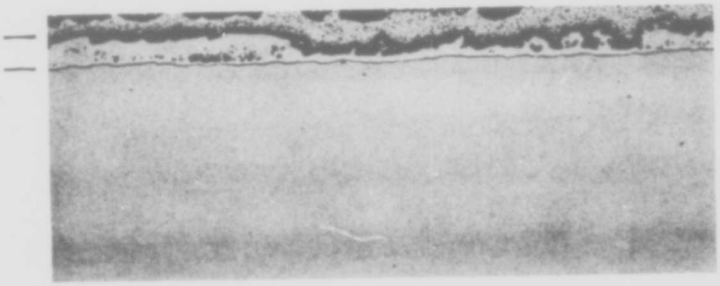
TABLE VIII

OXIDATION TEST RESULTS-Mo-(CrTi)-Si COATINGS ON Cb 752 ALLOY

mg/cm^2			Oxidation Life, hr	
Molybdenum	Cr,Ti	Si	2400°F	Remarks
14	29	12	177	Slurry applied Mo-Run 135
17.7	30	12	177	Slurry applied Mo-Run 136
18	29	11.7	177	Slurry applied Mo-Run 137
13.7	27	8.3	130	CVD applied Mo-CVD 117
1.3	29	9.6	177	CVD applied Mo-CVD 122,123



CVD Run No. 99



CVD Run No. 98

Figure 14 Photomicrographs showing Chemically Vapor Deposited Molybdenum on Columbium Alloy Cb-752 250 X

These results suggested that the coating systems containing molybdenum slurry precoatings were as oxidation resistant as systems containing the CVD applied molybdenum coatings. Metallography showed that the slurry coated coupons contained a high degree of porosity as compared to the CVD coated coupons, Figure 15. However, the application of Cr-Ti and silicon reduced the original porosity noted previously in the as-fired samples, compare Figures 11 and 15. In subsequent experiments, however, slurry-applied molybdenum precoatings showed pronounced coating spalling in erosion-oxidation rig tests (section 6.10.3).

5.3 SILICIDE COATING SYSTEMS

Based on previous work (1) the only elements which offered significant promise as coating constituents for columbium alloys were Cr,Ti,Si,Mo,V and Al.

An extensive look was therefore taken at many coating compositions possible from these element combinations. Since only certain sequences of element deposition were possible, all combinations were not included. The basic idea was to form the systems, and evaluate them in cyclic oxidation tests as a means of selecting a number of the promising compositions for a more comprehensive study in Phase II.

The following silicide coating systems were selected and formed on columbium alloy Cb 752 for oxidation screeening:

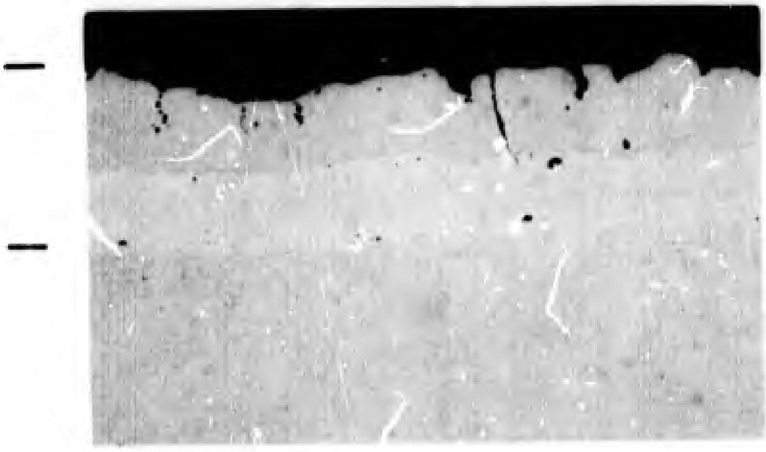
Ti-Mo-Si
Ti-Mo-V-Si
Ti-Mo-Cr-Si
Ti-Mo-CrTi-Si
Ti-Mo-V-Cr-Si
Ti-V-Cr-Si
Ti-V-Si
Ti-Ta-Si

V-Cr-Si
V-CrTi-Si
V-Ti-Si
V-Mo-Ti-Si
V-Mo-CrTi-Si
V-Ai-CrTi-Si

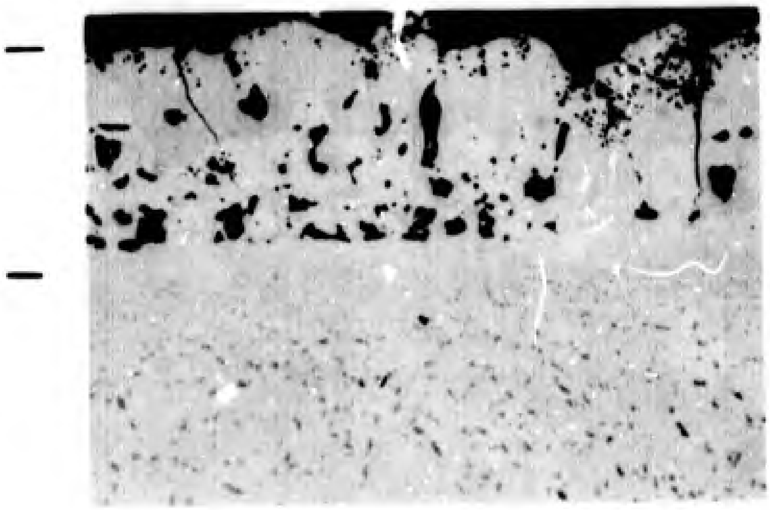
Mo-Ti-Si
Mo-CrTi-Si
Mo-V-Si
Mo-V-Ti-Si
Mo-V-CrTi-Si

The above systems were formed by vacuum pack and CVD techniques according to the flow diagram shown in Figure 16. The average specimen weight gains are also indicated in the flow chart. The pack coating parameters are summarized in Table IX, and the CVD molybdenum coating parameters used were identical to those described in Section 5.2.4. Difficulties were encountered in forming several of the silicide systems, as noted in Figure 16 and Tables IX and X. The difficulties were manifested as: 1) an inability to deposit certain elements sequentially after others, and 2) the formation of rough, blistered or spalled coatings after the introduction of certain elements. The coating runs are described in more detail below.

Titanizing of columbium alloy Cb 752 resulted in a shiny surface with some rough or raised areas as a result of pack particle sintering to the coupon surface. Titanizing was performed in a pure titanium pack (-8 +30 mesh) at 2000°F using 1 w/o KF as the activator. A prealloyed 75 w/o Ti-25 w/o



CVD Mo: 13.7 mg/cm^2
(a)



Slurry Mo: 18 mg/cm^2
(b)

Figure 15 Microstructure of Mo-CrTi-Si Coatings on Columbium Alloy Cb-752: a) CVD applied Molybdenum and b) Slurry (Mo-5 w/o TiH_2) applied Molybdenum. 250 X

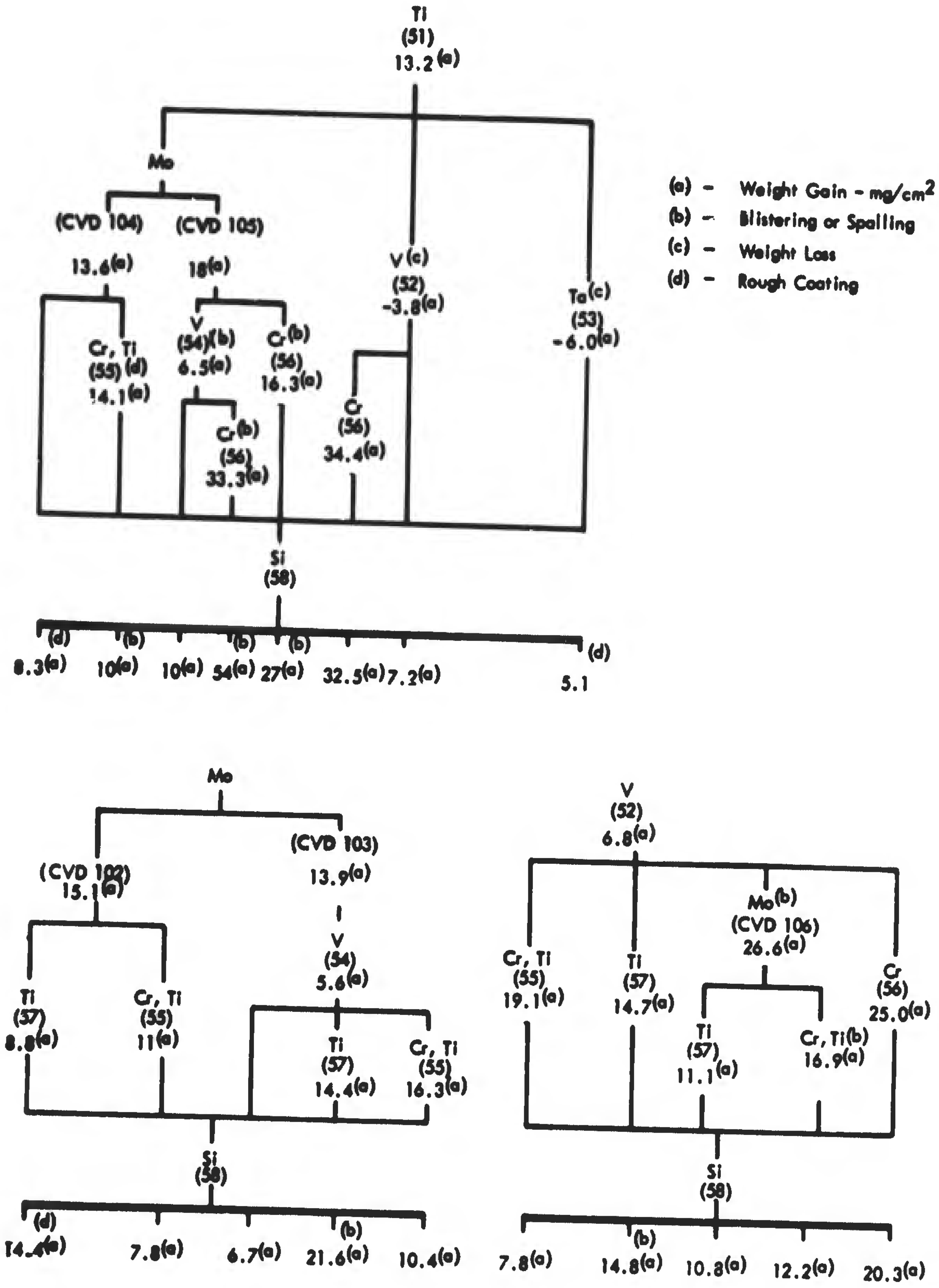


Figure 16 Flow Diagram Showing Oxidation Specimen Preparation Sequence, Run Numbers (In Parenthesis) and Average Weight Gains.

TABLE IX

RESULTS OF PACK DEPOSITION ON COLUMBIUM ALLOY Cb-752

Run No.	Pack Material	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Weight Gain mg/cm^2	Remarks
51	Ti	1KF	2000	6	10^{-2}	-	a	Shiny specimens Some sintering.
52	V	2 NaCl+ 0.2 VCl$_4$	2200	12	150 Argon	-	a	Slight Sintering
53	Ta	1 NaCl	2200	6	10^{-2}	-	a	c
54	V	2 NaCl+ 0.2VCl$_4$	2200	12	150 Argon	a	a	c
55	60Cr-40Ti	1KF	2300	8	10^{-2}	a	a	c
56	Cr	0	2350	15	10^{-2}	a	a	c
57	Ti	1KF	2000	6	10-2	a	a	c
58	Si	1/2KF	2000	4	10^{-2}	a	a	c
37	Ti	1KF	2000	2	150 Argon	-	13.9	Mo precoated (11 mg/cm^2)
38	Si	1KF	1800	8	150 Argon	-	12.8 25.0	Mo precoated Mo+Ti (37) precoated.
47	75Ti-25 Mo^b	1NaCl	2250	12	10^{-2}	-	-	Specimens rough & spalling. Sintered pack.
361^d	60Cr-40Ti	1KF	2340	8	1.5	-	13.0 18.0	Mo precoated.
359^d	Si	1KF	2100	5	0.2	-	14.7 21.3	(Cr,Ti)Precoated(361) Mo and (Cr,Ti) precoated (361). Gray and gold; cracks.
59	Ta	1NaCl	2200	6	10^{-2}	-	0	Clean specimens

TABLE IX

(Continued)

Run No.	Pack Material	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Weight Gain mg/cm^2	Remarks
61	56Cr-44Al	1KF	1900	16	150Ar	51,52	10.6	Ti-V precoat
						51	5.8	Ti-V precoat
						51,53	6.3	Ti-Ta precoat
62	Si	1KF	2000	4	10^{-2}	51,52,61	2.5	Rough and flaking coatings.
						51,61	3.4	
						51,53	5.5	
64	V	$0.2VCl_4$	2200	6	150Ar	-	1.6	NaCl left out
366[d]	60Cr-40Ti	1KF	2340	8	1.5	-	15.4	Cb-752,C129Y and D-43 specimens.
367[d]	Si	1KF	2100	5	0.02	366	13.4	
370[d]	56Cr-44Al	1KF	2100	10	150Ar	49,64	11.5	V precoated
373 [d]	Si	1KF	2100	5	0.2	67	12	Ti precoated D-43
						69	15	Adherent coatings.
376[d]	60Cr-40Ti	1KF	2340	8	1.5	49,370	19.4	V-Al precoated.
						64,370	11.2	
377[d]	Si	1KF	2100	5	0.2	49,64 370,376	17	V-Al-Cr,Ti precoated.
						13	12	Ti precoated Cb-752.
						69	16.4	Ti precoated D-43 Adherent coatings.
73	Ti	1KF	2000	2	150Ar	-	7.2	To be Mo coated.
74	V	2NaCl+ $0.2VCl_4$	2200	12	150Ar	-	7.2	To be Mo coated.
82	Cr	-	2350	10	10^{-2}	73,CVD108	7.1	Ti-Mo precoat. Mottled and some spalled areas.
83	Cr	1NaF	2350	10	10^{-2}	73,CVD108	2.0	Ti-Mo precoat.

TABLE IX

(Continued)

Run No.	Pack Material	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Weight Gain mg/cm^2	Remarks
84	Cr	-	2350	12	10^{-2}	73,CVD108	-	Thermocouple broke. Coating spalled.
85	-	-	2400	15	10^{-2}	73,CVD108	-	Diffusion anneal. Specimens clean but some embrittlement.
92	Cr	-	2350	10	10^{-2}	73,CVD 108,85	16.0	Ti-Mo precoat. Mottled surface. Some blistered areas. Specimens embrittled.
100	Si	1NaF	2225	5	0.2	73,CVD109 +112	19.2	Ti-Mo precoat. Adherent coating. Specimens ductile.

---

a. See Figure 16,
b. Prealloyed.
c. See Table X.
d. Large retort 7-1/2" dia. X 20", otherwise 3" dia. X 10".

Mo powder was utilized in a preliminary run (No. 47) to see if sintering during titanizing could be reduced, Table IX. This pack was run at 2250°F for 12 hours at a pressure of 10^{-2}, using NaCl as the activator. The pack was severely sintered and weight change data were not obtainable.

Titanizing of molybdenized Cb752 alloy resulted in smaller weight gains than for uncoated material (c.f. runs 51 and 57 in Figure 16). These specimens had a purplish hue after titanizing, and there was negligible sintering. Prevanadizing, on the other hand, enhanced titanium pick-up, although the effect was not pronounced, Figure 16. No sintering was in evidence and the specimens were clean.

Application of the (Cr,Ti) coating to precoated Cb 752 alloy resulted in the lowest weight gains for premolybdenized material and the greatest (Cr,Ti) pick-up for the prevanadized substrate. The quantity of (Cr,Ti) transferred to the molybdenized samples increased when titanium or vanadium was present in the coating, with the largest weight gains occurring with coupons containing vanadium. The (Cr,Ti) coating (Run No.55) on the Ti-Mo coated samples resulted in a rough textured coating. On the other hand, (Cr,Ti) coating of molybdenized only Cb 752 coupons resulted in smooth coatings for a range of (Cr,Ti) contents. This latter observation was made with specimens coated in other runs in addition to No. 55.

Vanadizing of titanized Cb 752 resulted in a weight loss in pack run No. 52. On the other hand, titanizing of vanadized coupons was feasible, as discussed above. Thus, the sequence of Ti and V application was important; moreover, the vanadizing application must preceed the titanizing step. Thermodynamically the titanium halide is more stable than the vanadium halide (greater negative free energy of formation), thus titanium on the substrate surface reacts with the pack activator.

Vanadium was successfully applied on molybdenized material in Run No. 54, however, vanadium application on Ti-Mo coated material resulted in blistered coatings. Blistering was presumabley due to the vaporization of titanium halides by reaction of the activator with the titanium precoat.

The application of tantalum on titanized material also resulted in a weight loss. A tantalum run (No. 59) was therefore made to see if tantalum could be applied to uncoated Cb 752, Table IX. The run was made at 2200°F for 6 hours with NaCl activation. Weight gain data indicated that tantalum was not transferred. Tantalum transfer to columbium is thermodynamically not feasible because columbium halide is more stable than the tantalum halide.

The chemical vapor deposition of molybdenum on uncoated columbium alloys and on titanized material (CVD runs 104 and 105) yielded adherent molybdenum coatings. On the other hand, molybdenum coating (CVD run 106) of vanadized material produced coupons with some coating spalling, Figure 17. Conversely, vanadium was successfully applied on molybdenized material. Thus, again the sequence of element application was important in obtaining adherent coatings in these systems.

Chromizing (Run No. 56) resulted in spalled coatings when applied on Ti-Mo and Ti-Mo-V coated specimens. Adherent chromized coatings were obtained on the vanadized specimens and on the Ti-V coated specimens. The amount of vanadium present in the coating was questionable in the latter coating system, since the coupons lost weight during vanadizing. The titanized specimens showed the greatest affinity for the chromium, with the vanadized coupons next, and the Ti-Mo coated coupons showing the smallest chromium weight gains. Material lost because of coating spalling may have accounted for the lower weight gains noted for the latter system.

In a few preliminary runs, siliconizing of molybdenized and Mo-Ti coated coupons at 1800°F for 8 hours (150 mm pressure of argon) using KF activation (Run No. 38) resulted in rough and blistered coatings. In contrast, siliconizing (Run No.359) of (Cr,Ti) coated and Mo-(Cr,Ti) coated coupons resulted in adherent coatings that were mottled gray and gold in color, with areas of grain boundary etching. Thus, siliconizing over precoats containing appreciable titanium in the absence of chromium resulted in spalled coatings.

Siliconizing of the various coating systems outlined in Figure 16, was performed in Run No. 58. This run was made at 2000°F for 4 hours with 0.5 w/o KF activation and continuous furnace evacuation (10^{-2}mm pressure). Rough silicide coatings were obtained on the Ti-Mo,Ti-Ta, and Mo-Ti coated coupons. Spalled silicide coatings were obtained on the Ti-Mo-(Cr,Ti), Mo-V-Ti and the V-Ti precoated coupons, in addition to other systems which had showed spalling after various intermediate runs.

Since the siliconizing was performed in a single run, the weight gains obtained for the various systems can be compared. The siliconizing results showed that various elements influenced the silicon weight gain in decreasing order: Cr,T,V, (Cr,Ti) and Mo. Chromium had the most pronounced effect on silicon weight gain, although it is recognized chromium was present in great abundance. The chromium containing specimens generally picked up 3 to 8 times as much silicon as the chromium-free coupons.

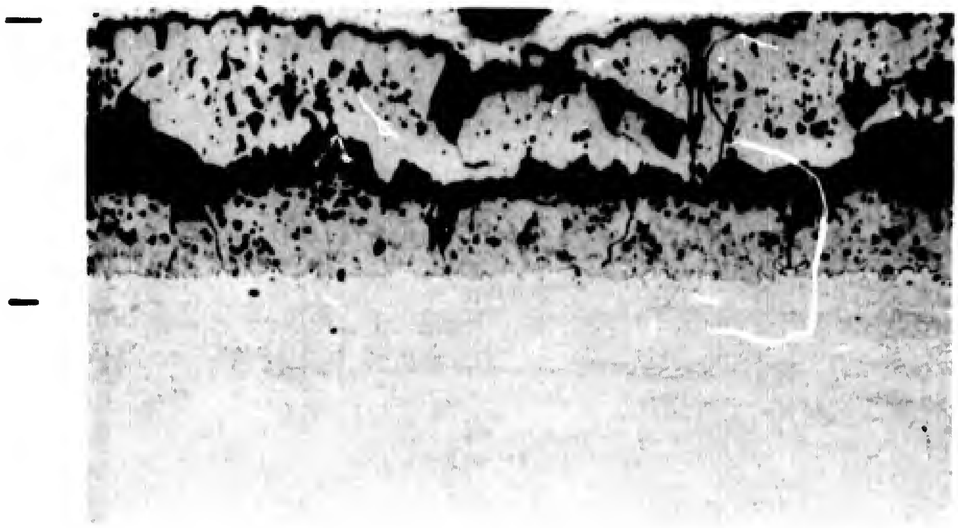
A general summary concerning the influence of elements previously deposited upon sequential element deposition is given in Table X. The prior elements are listed in order of decreasing effect on weight gain for each deposited element.

Typical microstructures of some of the silicide systems formed for oxidation screening are shown in Figures 17 through 19. Cracking or spalling was observed for the V-Cr-Si, V-Mo-CrTi-Si and Ti-V-Cr-Si systems. The V-Cr-Si system cracking was lateral in the silicide; however, the cracking was not evident on visual inspection prior to sectioning. The spalling in the V-Mo-CrTi-Si system was at the vanadized-molybdenum interface, although some molybdenum diffusion and bonding to the vanadized layer was apparent. The spalling with this system was visually evident after molybdenum deposition on the prevanadized substrate, as discussed previously.

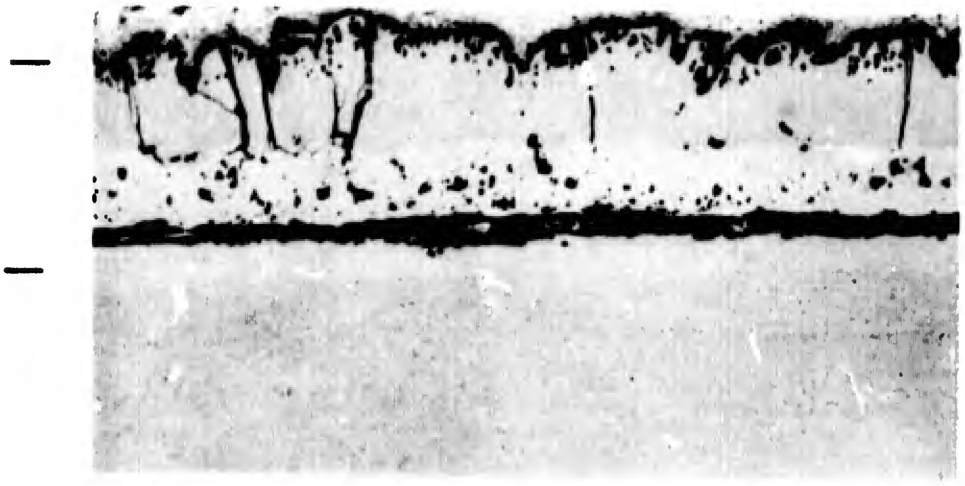
TABLE X

GENERAL SUMMARY LISTING EFFECT OF PRIOR ELEMENTS ON SUBSEQUENTIAL ELEMENT WEIGHT GAIN AND COATING APPEARANCE. PRIOR ELEMENTS LISTED IN DECREASING ORDER OF EFFECT-LARGEST WEIGHT PICK-UP FIRST.

Element Deposited	Prior Elements (Decreasing Effect)	Coating Appearance
Ti	1. V	Satisfactory
	2. Mo-V	Satisfactory
	3. V-Mo	Satisfactory
	4. Mo	Satisfactory
(Cr,Ti)	1. V	Satisfactory
	2. V-Mo	Rough and Spalling
	3. Mo-V	Satisfactory
	4. Ti-Mo	Rough
	5. Mo	Satisfactory
Cr	1. Ti-V	Satisfactory
	2. Ti-Mo-V	Spalling
	3. V	Satisfactory
	4. Ti-Mo	Spalling
Si	1. Ti-Mo-V-Cr	Spalling
	2. Ti-V-Cr	Satisfactory
	3. Ti-Mo-Cr	Spalling
	4. Mo-V-Ti	Rough and Spalling
	V-Cr	Satisfactory
	5. V-Ti	Spalling
	Mo-Ti	Rough
	6. V-Mo-CrTi	Satisfactory
	V-Mo-Ti	Satisfactory
	Mo-V-CrTi	Satisfactory
	Ti-Mo-CrTi	Spalling
	Ti-Mo-V	Satisfactory
	7. Ti-Mo	Rough
	Mo-CrTi	Satisfactory
	V-CrTi	Satisfactory
	8. Ti-V	Satisfactory
	Mo-V	Satisfactory
	9. Ti-Ta	Rough
	V	Satisfactory



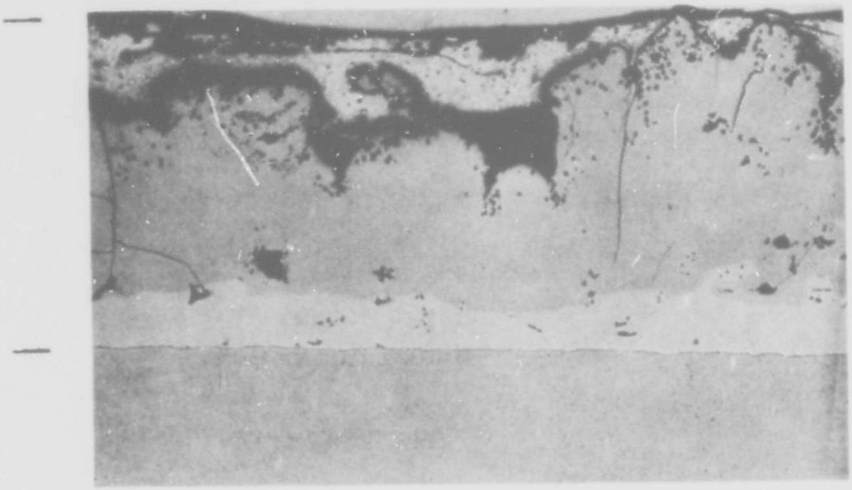
V-Cr-Si
(52 + 56 + 58)



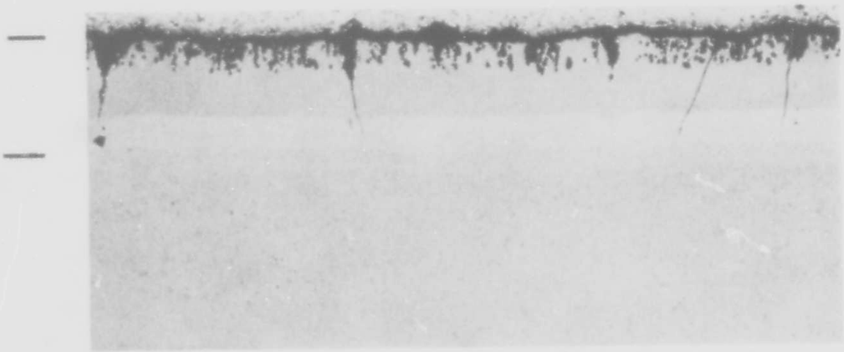
V-Mo- Cr Ti -Si
(52 + CVD106 + 55 + 58)

V- Cr Ti -Si
(52 + 55 + 58)

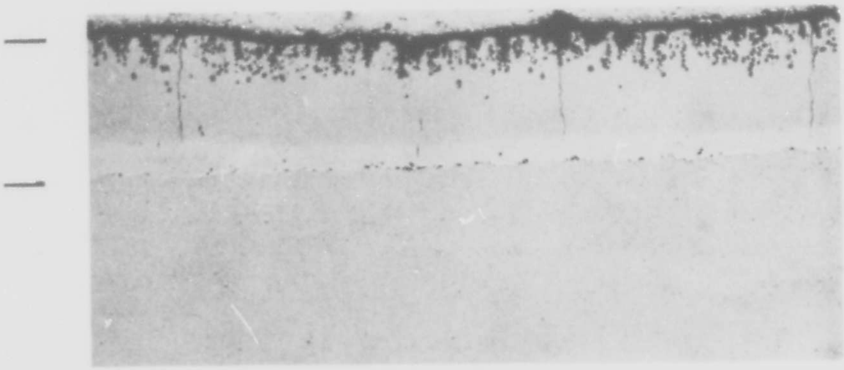
Figure 17 Microstructures of Silicide Coating Systems on Cb-752 Alloy. Run Numbers in Parenthesis. 250 X



Mo- Cr Ti -Si
(CVD100 + 361 + 359)



Mo Cr Ti -Si
(CVD102 + 55 + 58)

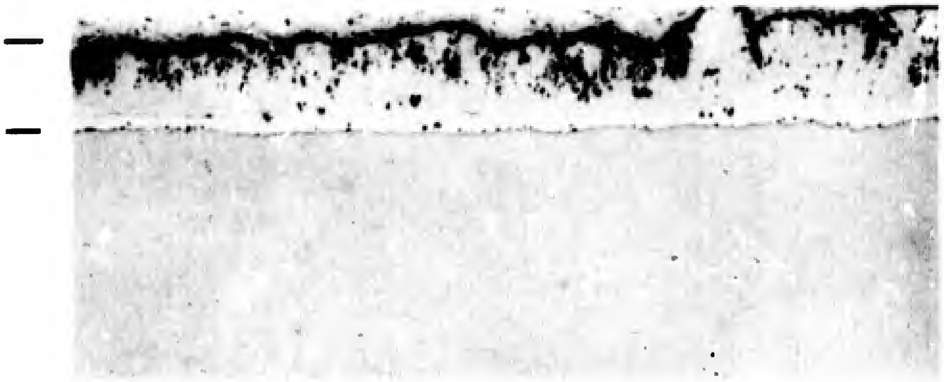


Mo-V- Cr Ti -Si
(CVD103 + 54 + 55 + 58)

Figure 18 Microstructures of Silicide Coating Systems on Cb-752 Alloy. Run Numbers in Parenthesis. 250 X

Ti-V-Cr-Si

(51 + 52 + 56 + 58)



Mo-V-Si

(CVD103 + 54 + 58)

Ti-V-Si

(51 + 52 + 58)

Figure 19 Microstructures of Silicide Coating Systems on Cb-752 Alloy. Run Numbers in Parenthesis 250 X

Another system which showed evidence of spalling upon microscopic examination but not externally was the Ti-V-Cr-Si system. In this system cracks appeared to propogate from the very thick silicide layer into relatively brittle sublayers.

The systems involving a chromizing step showed apparent chromium penetration into the columbium alloy matrix as evidenced by the grain boundary precipitate, Figures 17 and 19. The effect of larger (Cr,Ti) and Si contents on the silicide layer thickness for the Mo-CrTi-Si system is shown in Figure 18. These systems were produced in different runs.

The Ti-V-Al-Si and V-Al-CrTi-Si systems were formed in runs also listed in Table IX. The application of vanadium over the titanized columbium alloy substrate was not feasible as previously noted. Siliconizing of this system (Ti-V-Al-Si) resulted in a rough and flaky coating. The V-Al-CrTi-Si coating was visually satisfactory, and two levels of vanadium were applied - 1.4 and 5.5 mg/cm^2.

In addition to the above silicides, the CrTi-Si coating system was formed on several columbium alloys to serve as an oxidation standard. The average weight gain for the (Cr,Ti) was 13 mg/cm^2, and for the silicon-12 mg/cm^2. The (Cr,Ti)was deposited from a 60Cr-40Ti alloy pack in an 8-hour run at 2340°F (with 1 w/o KF activator) at a nominal pressure of 1.5 mm. The silicon was deposited from a silicon pack in a 5-hour run at 2100°F (with 1 w/o KF activator) at a pressure of 10^{-2}mm.

A number of the silicide systems formed for oxidation screening developed blistered or spalled coatings at various stages of the coating cycles. A preponderance of these systems contained titanium applied in an independent coating cycle. Before eliminating these systems from further consideration in Phase II, it was deemed desirable to determine the feasibility of forming some of these systems using different coating parameters. The systems were: Ti-Mo-Cr-Si, Ti-Mo-CrTi-Si, V-MoCrTi-Si, Mo-Ti-Si and V-Ti-Si.

To determine if the Ti-Mo-Cr-Si system could be formed without spalling after chromizing, Cb 752 coupons were molybdenized and titanized in Run 73. Several chromium runs were made in an attempt to deposit chromium on the Ti-Mo precoated coupons. The chromium runs (82 through 84) were made with NaF activation and without activator at 2350°F, on the as CVD molybdenum coated-pretitanized Cb 752 coupons Spalled and flaking coatings of chromium were obtained in each of these runs. To improve the adhesion of the molybdenum which was deposited by chemical vapor deposition, the Ti-Mo coated samples were diffusion annealed at 2400°F for 15 hours. Chromium coating of the diffusion annealed samples in a chromium metal powder pack without activator also produced blistered coatings, although there was considerable improvement over the previous chromized samples. The amount of chromium transferred varied from 2 to 16 mg/cm^2 in these runs. Thus, this series of experiments confirmed the difficulties experienced previously in forming the Ti-Mo-Cr containing system. Furthermore, the specimens were embrittled during the chromium deposition step.

Microscopic examination of the chromium coatings on the Ti-Mo precoated coupons showed that the spalling occurred at and below the chromium-molybdenum interface, Figure 20. Diffusion annealing of the molybdenum and titanium coated coupons before chromizing resulted in some porosity at the molybdenum-titanium coating interface. This porosity may have been the result of a Kirkendall effect.

Siliconizing of pretitanized columbium alloys without spalling was accomplished by raising the siliconizing temperature to over 2000°F and using large retorts. Two duplicate runs (373 and 377) were made, with adherent silicide coatings formed in each run, Figure 21. The silicon weight gain was generally a function of the titanium content as indicated below:

Run No.	Alloy	Mg/Cm^2 Titanium	Mg/Cm^2 Silicon
373	D-43	14	12
373	D-43	27	15
377	D-43	27	16.4
377	Cb-752	8.6	12

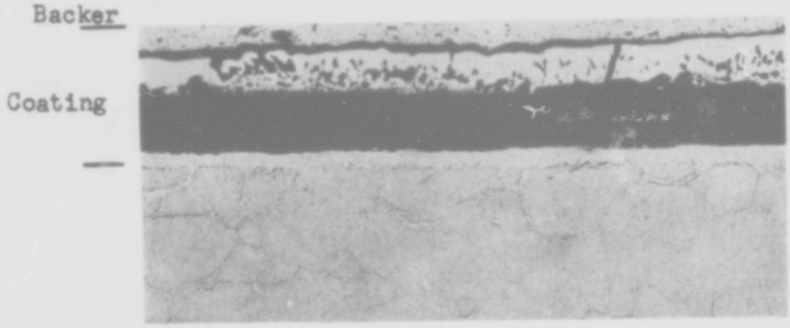
Other systems which spalled after siliciding were the Mo-Ti-Si and V-Ti-Si systems. To determine the feasibility of forming these systems and to obtain oxidation data on sound coatings, additional coating trials were conducted to reform these two coatings.

The Mo-Ti-Si and V-Ti-Si coating systems were prepared from coupons which were molybdenum and vanadium coated in Runs CVD 100, 49 and 64. The molybdenized and vanadized coupons were then titanized in Run 99 under conditions similar to previous titanizing runs. Since one silicon run (No. 100) made on pretitanized (7.2 mg/cm^2) and molybdenized (2.2 mg/cm^2) Cb-752 at 2225°F in a large retort produced an adherent silicide coating, siliconizing of the Mo-Ti and V-Ti precoated coupons was performed in a large retort in Run 102. The parameters for this latter run were 5 hours at 2225°F in a pure silicon powder (-8 + 30 mesh) pack containing 1 w/o NaF as the activator. The silicide coatings obtained on the Mo-Ti and V-Ti precoated Cb-752 coupons were adherent and metallic, Figure 22.

In summary, visual and microscopic examination show that only 9 silicide systems of the original 19 systems selected forstudy were readily formed without gross cracking and/or spalling. These were:

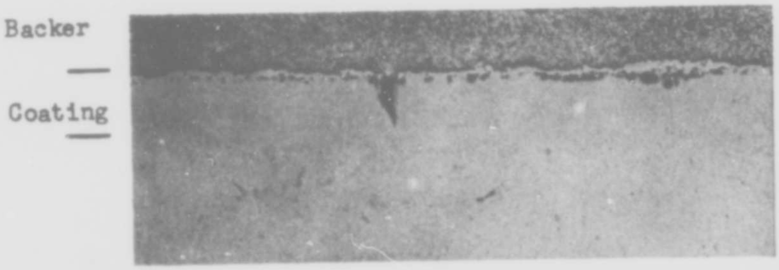
Ti-V-Si
Mo-CrTi-Si
Mo-V-CrTi-Si
Mo-V-Si
V-CrTi-Si
Mo-Ti-Si
V-Ti-Si
V-Al-CrTi-Si
V-Si

The remaining systems could not be formed without coating defects and were thus eliminated from further consideration.

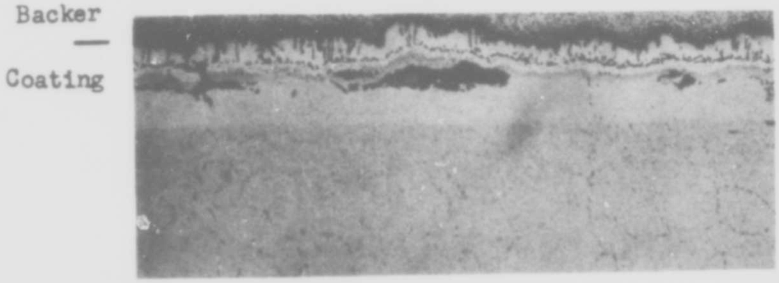


Chromizing Run 83
1 w/o NaF

Chromizing Run 82
No Activator

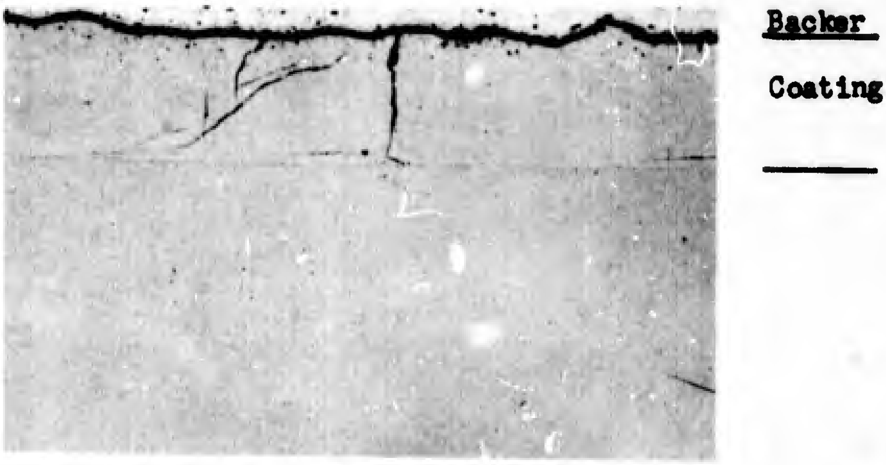


Ti-Mo
Diffusion Annealed
15 hours at 2400°F



Chromizing Run 92
After Diffusion Anneal

Figure 20 Chromizing Microstructures of Ti-Mo Precoated Cb-752, 250X.



Cb-752:
Ti Run 13 (8.6 mg/cm^2)

Si Run 377 (12mg/cm^2)

D-43:
Ti Run 69 (27 mg/cm^2)

Si Run 377 (16.4 mg/cm^2)

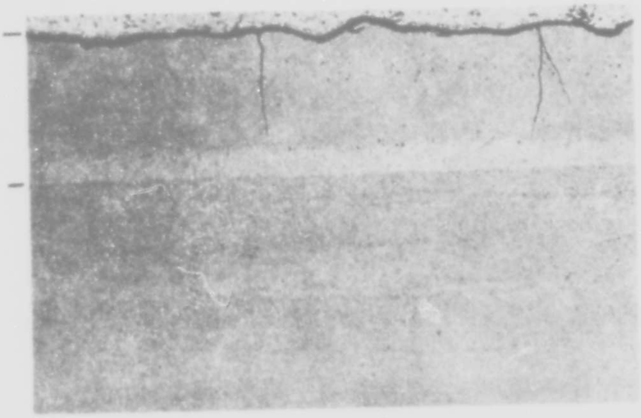
Figure 21 Columbium Alloys Cb-752 and D-43 After Titanizing and Siliciding.

Mo Run CVD 100 (10 mg/cm^2)

Ti Run 99 (6.6 mg/cm^2)

Si Run 102 (17.6 mg/cm^2)

Mo-Ti-Si



V Run 49 (6.1 mg/cm^2)

Ti Run 99 (9.7 mg/cm^2)

Si Run 102 (15.1 mg/cm^2)

V-Ti-Si

Figure 22 Microstructures of Silcide Coating Systems on Columbium Alloy Cb-752.

5.3.1 Cyclic Oxidation Tests at 1600 and 2400°F.

Cyclic oxidation test results on the various silicide coating systems evaluated in Phase I are listed in Table XI. The oxidation data for the standard CrTi-Si coating system are summarized in Table XII for comparison purposes. The systems with cyclic oxidation lives equivalent to or exceeding lifetimes shown by the CrTi-Si system at 1600°F are listed below:

Ti-Ta-Si
Mo-CrTi-Si
Mo-V-CrTi-Si
V-CrTi-Si
V-Mo-CrTi-Si
V-Al-CrTi-Si
V-Ti-Si

Of these systems the V-CrTi-Si and Mo-V-CrTi-Si systems showed protective capabilities at 1600°F well over 1000 hours of exposure with no coupon failures. The standard CrTi-Si coating protectiveness was variable on the various columbium alloys, with the best performance shown on the columbium alloy D-43 coupons. These data were not representative of the CrTi-Si system in that sufficient Cr-Ti and Si were not deposited to yield the optimum composition of 18-22 mg/cm^2 Cr-Ti and 14-16 mg/cm^2 Si. The Ti-Ta-Si (actually the Ti-Si system since no Ta was deposited) showed good potential for low temperature protectiveness with an oxidation life in excess of 1000 hours.

Of the above systems only those listed below showed potential protective capabilities at both 1600 and 2400°F comparable to or exceeding the capabilities of the CrTi-Si system:

Mo-CrTi-Si
Mo-V-CrTi-Si
V-Al-CrTi-Si
V-CrTi-Si

The fact that all of the oxidation resistant silicon systems contained titanium and chromium was not surprising, since Solar (1) found that the (Ti,Cr)-$_5$Si$_3$ silicide possessed both excellent oxidation resistance and tolerance for columbium. The V-Al-CrTi-Si system looked especially promising at 2400°F, with a protective life well in excess of any of the systems tested, including the CrTi-Si system. Microstructures after oxidation testing of the more resistant Phase I coating systems are presented in Figures 23 through 26. Metallographic examination was performed to determine the imperviousness of the initially formed coatings to oxygen transport. Substrate hardness is also listed for each system. The hardnesses were obtained with a Tukon hardness tester and a Knoop indentor using a 100 gram load.

Metallographic examination of the specimens after test revealed localized oxidation in coating cracks in the silicide layer. The substrate was protected by the coating, however, since the cracks did not penetrate the entire coating. No increase in substrate hardness from oxidation exposure was noted for any of the coating systems. Substrate hardness of the as-received sheet was KHN 201.

TABLE XI

CYCLIC OXIDATION DATA FOR VARIOUS SILICIDE COATING SYSTEMS ON COLUMBIUM ALLOY Cb-752

Code	System	Weight Gains - mg/cm^{2}								Oxidation Life - Hrs.	
		Ti	Mo	V	Cr,Ti	Cr	Ta	Al	Si	1600°F	2400°F
A	Ti-Mo-Si	13.2	13.6	-	-	-	-	-	8.3^{a}	4,4^{b}	2,7^{c}
21	Ti-Mo-Si	7.2	2.2	-	-	-	-	-	19.2	24,24^{b}	24^{b},79
B	Ti-Mo-CrTi-Si	13.2	13.6	-	14.1^{a}	-	-	-	10.0^{d}	4,13^{b}	1,54^{b}
C	Ti-Mo-V-Si	13.2	18.0	6.5^{d}	-	-	-	-	10.0	4,8^{b}	1,2^{b}
D	Ti-Mo-V-Cr-Si	13.2	18.0	6.5^{d}	-	33.3^{d}	-	-	54.0^{d}	4,32^{b}	4^{b},2
E	Ti-Mo-Cr-Si	13.2	18.0	-	-	16.3^{d}	-	-	27.6^{d}	4,4	11,2^{b}
F	Ti-V-Cr-Si	13.2	-	-3.8^{e}	-	34.4	-	-	32.5	8,4	5,8^{b}
G	Ti-V Si	13.2	-	-3.8^{e}	-	-	-	-	7.2	24,28	6,8
L	Ti-Ta-Si	13.2	-	-	-	-	-6.0^{e}	-	5.1^{a}	76	6
LI	Ti-Ta-Si	14.1	-	-	-	-	-5.4^{e}	-	5.5^{a}	564,1337	9,16
M	Mo-Ti-Si	8.8	15.1	-	-	-	-	-	14.4^{a}	8,32^{b}	6,4^{b}
22	Mo-Ti-Si	6.6	10	-	-	-	-	-	17.6	24,48^{b}	72,72^{c}
N	Mo-CrTi-Si	-	15.1	-	11.1	-	-	-	7.8	16,452	374,379
O	Mo-V-Ti-Si	14.5	13.9	5.6	-	-	-	-	21.6^{d}	4,8	4,1
P	Mo-V-CrTi-Si	-	13.9	5.6	16.3	-	-	-	10.4	1465,1421	209,355^{c}
R	Mo-V-Si	-	13.9	5.6	-	-	-	-	6.7	20^{c},8	9,9
S	V-CrTi-Si	-	-	6.8	19.1	-	-	-	7.8	1465,1421	78^{c},180
T	V-Ti-Si	14.7	-	6.8	-	-	-	-	14.8^{d}	36,8^{b}	2,1
23	V-Ti-Si	8.1	-	1.6	-	-	-	-	16.9	600,840	72,72^{b}
24	V-Ti-Si	9.7	-	6.1	-	-	-	-	15.1	984,1032	48^{b},175

TABLE XI

(Continued)

Code	System	Weight Gains - mg/cm^2 Ti	Mo	V	Cr,Ti	Cr	Ta	Al	Si	Oxidation Life-Hrs. 1600°F	2400°F
U	V-Mo-Ti-Si	11.1	26.6^d	6.8	-	-	-	-	10.8	4,4^c	7,4
W	V-Mo-CrTi-Si	-	26.6^d	6.8	16.9^d	-	-	-	12.2	8,500	5,13
X	V-Cr-Si	-	-	6.8	-	25	-	-	20.3	4,4^c	25,24
I	Mo-CrTi-Si	-	11	-	17.8	-	-	-	21.3	128^b ,136	49,32
14	V-Al-CrTi-Si	-	-	5.5	19.4	-	-	12.5	17.2	567,670	787,636
15	V-Al-CrTi-Si	-	-	1.4	11.2	-	-	10.5	16.5	144,567	286,334

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a. Rough Coating
b. Surface failures-otherwise edge failures
c. Surface and edge failure
d. Spalling or blistering
e. Weight loss-no element deposition

TABLE XII

CYCLIC OXIDATION DATA FOR THE Cr Ti -Si COATING SYSTEM

No.	Alloy	Weight Gains-Mg/cm^2		Coating Runs-No.		Oxidation Life - Hrs.	
		Cr,Ti	Si	(Cr,Ti)	Si	1600°F	2400°F
3	Cb-752	12.7	14.7	361	359	16,>1397	54,131 (a)
13	Cb-752	14.8	12.2	366	367	96,96	218,266
11	C129Y	15.2	13.5	366	367	24,120	218,218
12	D-43	16.2	11.1	366	367	>1157, >1157	218,218

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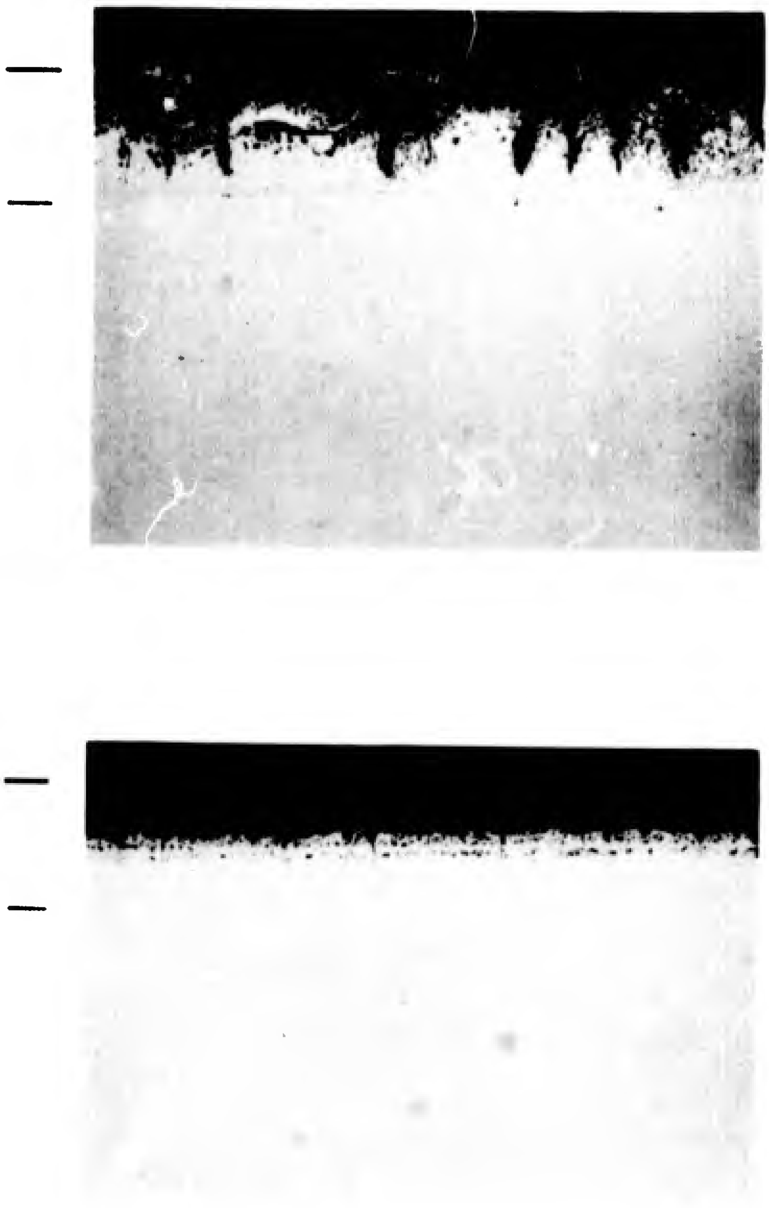
a. Surface failures-otherwise edge failures.
b. Surface and edge failure.



5.5V-12.5 Al-19Cr Ti-17Si

>787 Hr at 2400°F

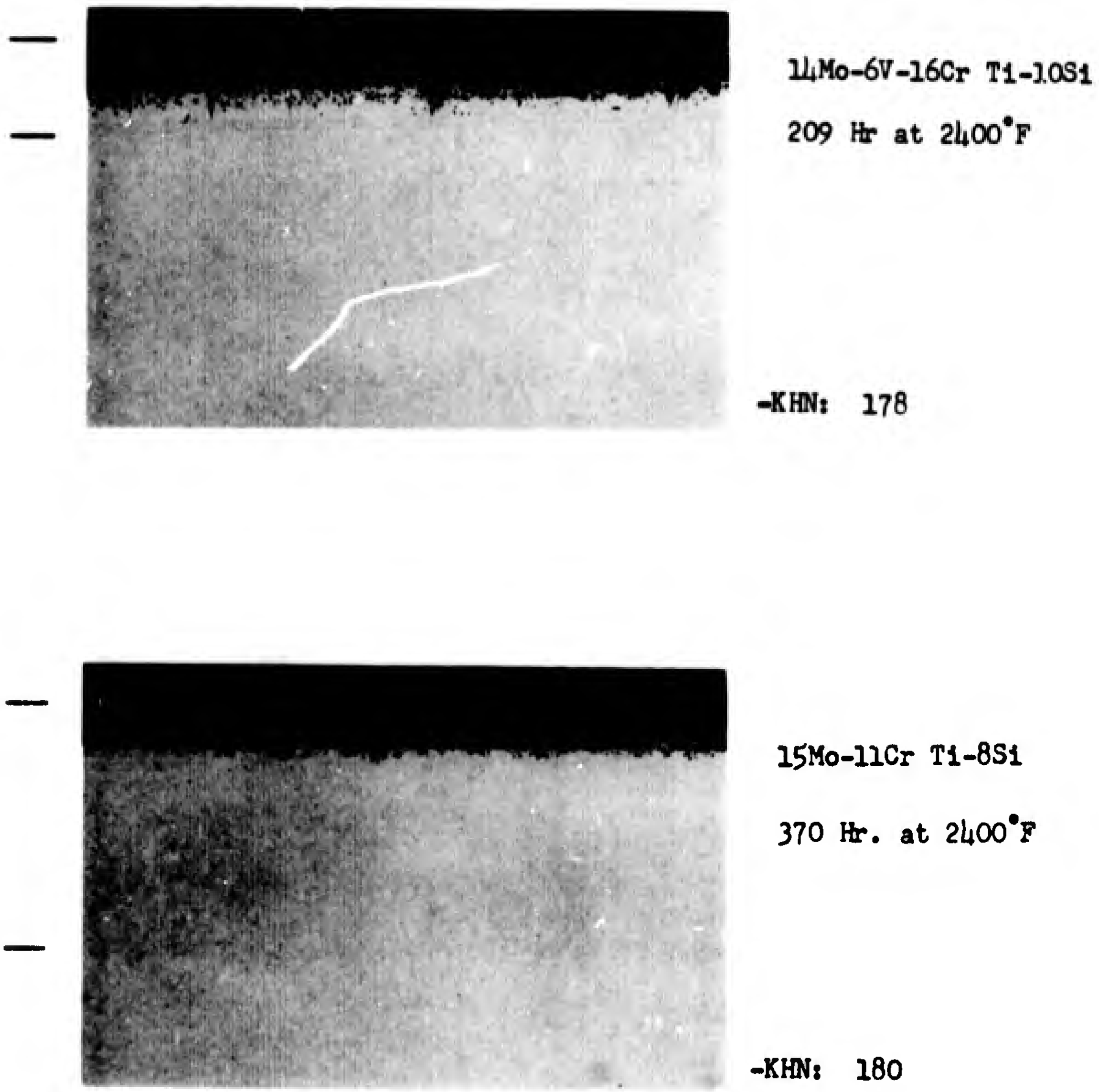
-KHN: 181

7V-19Cr Ti-8Si

180 Hr at 2400°F

-KHN: 185

Figure 23 Photomicrographs of Exposed Phase I Coatings on Cb-752. 100 X



14Mo-6V-16Cr Ti-10Si

209 Hr at 2400°F

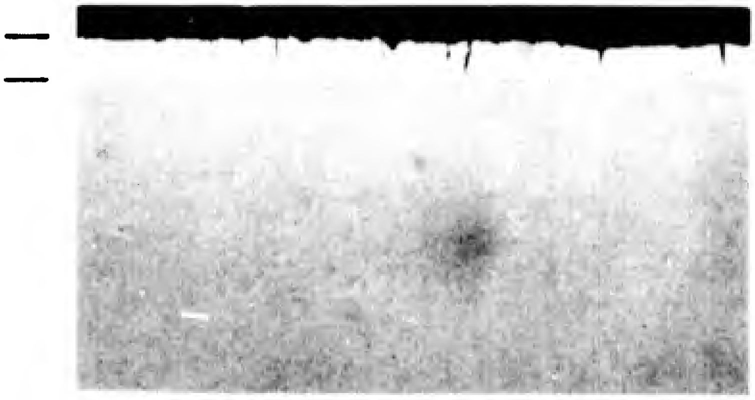
-KHN: 178

15Mo-11Cr Ti-8Si

370 Hr. at 2400°F

-KHN: 180

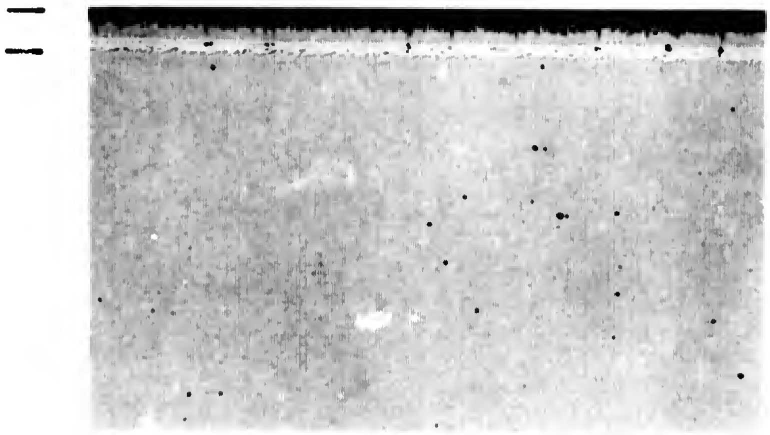
Figure 24 Photomicrographs of Exposed Phase I Coatings on Cb-752. 100 X



14Mo-6V-16Cr Ti-10Si

$>$ 1465 Hr at 1600°F

-KHN: 184



7V-19Cr Ti-8Si

$>$ 1465 Hr at 1600°F

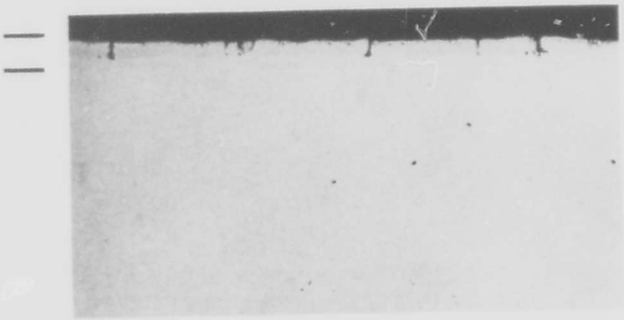
-KHN: 195

Figure 25 Photomicrographs of Exposed Phase I Coatings on Cb-752. 100 X

27Ti-7Al

➤ 998 Hr at 1600°F
(D-43 Alloy)

-KHN: 168



14Ti-5.5Si

➤ 1337 Hr at 1600°F

-KHN: 185

27Ti-7Al-20Si

583 Hr at 1600°F

-KHN: 165

Figure 26 Photomicrographs of Exposed Phase I Coatings on Cb-752 and D-43. 100 X

5.4 ALUMINIDE COATING SYSTEMS

Based on work performed under contract AF33(615)-1598(1), several aluminide coating systems were considered to be potentially useful as intermediate, ductile coating layers. These included Ti-Al, Ti-Al-Si and Cb-(50-60) Ti-10 Al. Preliminary aluminide system coating studies were therefore initiated, and the titanizing, aluminizing and siliconizing pack run data and results are given in Table XIII. Representative microstructures of several coatings are presented in Figures 27 through 30.

Titanizing of columbium alloy Cb-752 resulted in a shiny surface with rough or raised areas as a result of pack particle sintering to the coupon surface. Titanizing was performed in a pure titanium (-8+30) mesh pack using 1 w/o KF as the activator at 2000°F. The argon backfilled pack runs produced greater titanium deposition (16.8 mg/cm^2) as opposed to the continuously evacuated pack runs (4.6 mg/cm^2), c.f. run Nos. 5 and 6, Table XIII. The titanium also diffused to a greater depth for the larger weight gain, as evidenced by the polished microstructure, Figure 27.

The titanized coupons were then aluminized using a 56 w/o Cr-44 w/o Al prealloyed powder (-8 +30 mesh) pack and 1 w/o KF as the activator. Two temperatures were used to perform the aluminizing - 1600 and 1900°F. The pack and coupons were evacuated and then backfilled with argon (150 mm nominal pressure). The aluminum weight gains were on the order of 4 to 6 mg/cm^2 regardless of temperature. The aluminum weight gains in aluminizing run No. 7 appeared to be slightly dependent upon the initial titanium content of the columbium substrate. The coupons with low titanium (4.6 mg/cm^2) picked up 4.4 mg/cm^2. The aluminized coupons were light gray with dark spots at sinter points with the pack material. The aluminized microstructures are shown in Figure 28 for the pre-titanized columbium alloy Cb-752 coupons. The low-titanium content coupon formed an aluminide which penetrated the entire depth of the titamium alloy layer. The aluminide layer contained cracks running to the columbium alloy substrate. The high-titanium content coupons formed an aluminide layer which contained porosity and cracks. The cracks terminated near the aluminide - (titanium-columbium) layer interface.

Some of the titanized plus aluminized coupons were subsequently siliconized. The silicon runs were conducted at 1800°F for 8 hours with an argon backfill utilizing a pure silicon pack (-8 +30 mesh) and 1 w/o KF as the activator. Silicon weight gains again appeared to be dependent upon the initial titanium content - the coupons with low-titanium content (4.6 mg/cm^2) showed weight gains of 4.9 mg/cm^2 and the coupons with high-titanium content (16.8 mg/cm^2) showed weight gains of 13.9 mg/cm^2. The coupons were a mottled light gray

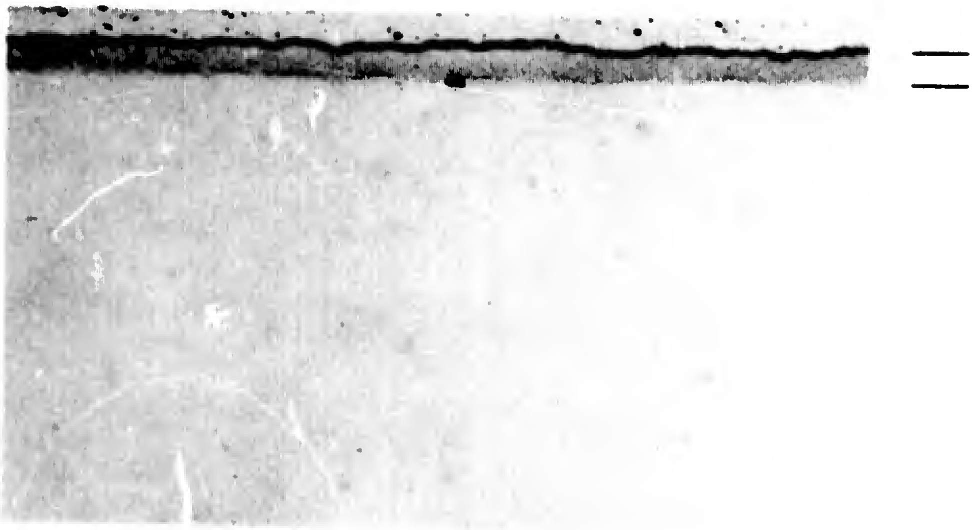
TABLE XIII

RESULTS OF TITANIUM, ALUMINUM AND SILICON PACK DEPOSITION ON COLUMBIUM ALLOY Cb-752

Run No.	Pack Composition	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Average Weight Gain mg/cm^2	Remarks
5	Titanium	1KF	2000	4	10^{-2}	-	4.6	Shiny surface, sintered raised areas.
6	Titanium	1KF	2000	4	150Ar	-	16.8	Shiny surface-rough sintered areas.
13	Titanium	1KF	2000	1.25	150Ar	-	8.6	Shiny surface-rough sintered areas.
7	56 w/o Cr- 44 w/o Al	1KF	1600	10	150Ar	5	5.6	Dark sintered specs on light gray coupons.
						6	4.4	Dark sintered specs on mottled gray-black coupons.
8	Silicon	1KF	1800	8	150Ar	5 + 7	4.9	Coupons brown and gray with some rough areas of sintering.
						6 + 7	13.9	Rough and bubbled coating mottled gray and dark brown.
20	56 w/o Cr- 44 w/o Al	1KF	1900	10	150Ar	13	4.7	Coupons light gray with dark sintered spots.
22	Silicon	1KF	1800	8	150Ar	13 + 20	12.5	Mottled light and dark gray coupons with dark sintered spots.
						No precoat	9.1	Dark gray coupons.

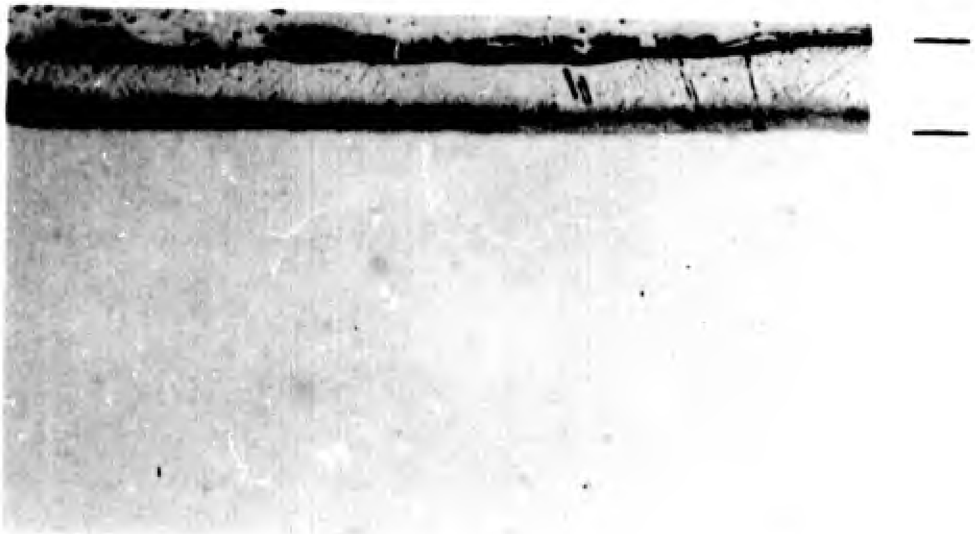
TABLE XIII
(Continued)

Run No.	Pack Composition	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Average Weight Gain mg/cm^2	Remarks
36	56Cr-44Al	1KF	1900	10	150Ar	-	5.0	
37	Ti	1KF	2000	2	150Ar	36	7.8	
38	Si	1KF	1800	8	150Ar	36 + 37	30.0	Specimens rough and spalling.



4 Hours Run No. 5 2000°F

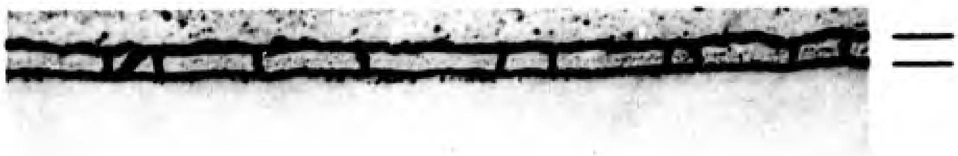
4.6 mg/cm^2 Titanium



4 Hours Run No. 6 2000°F

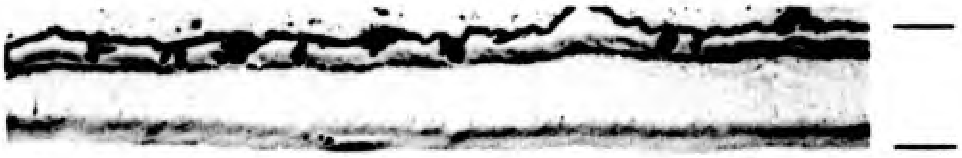
16.8 mg/cm^2 Titanium

Figure 27 Microstructure of Titanium Diffusion Coatings on Columbium Alloy Cb-752 as a Function of Pack Deposition Pressure - Pure Titanium Pack 250X



Run Nos. 5 + 7

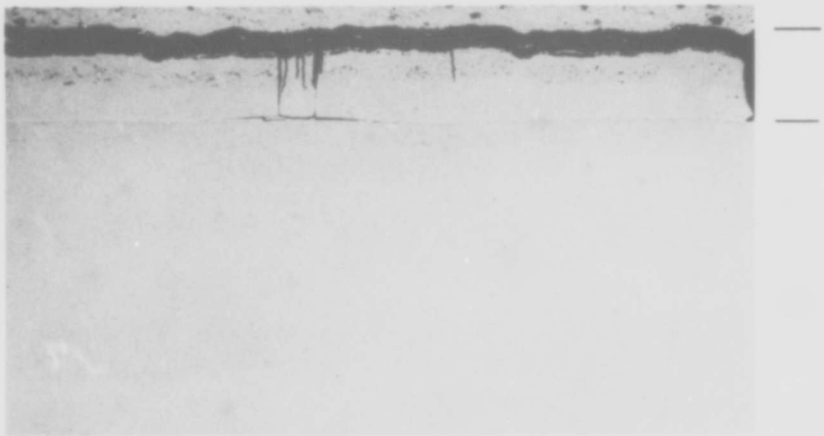
4.6 mg/cm^2 Titanium
5.6 mg/cm^2 Aluminum



Run Nos. 6 + 7

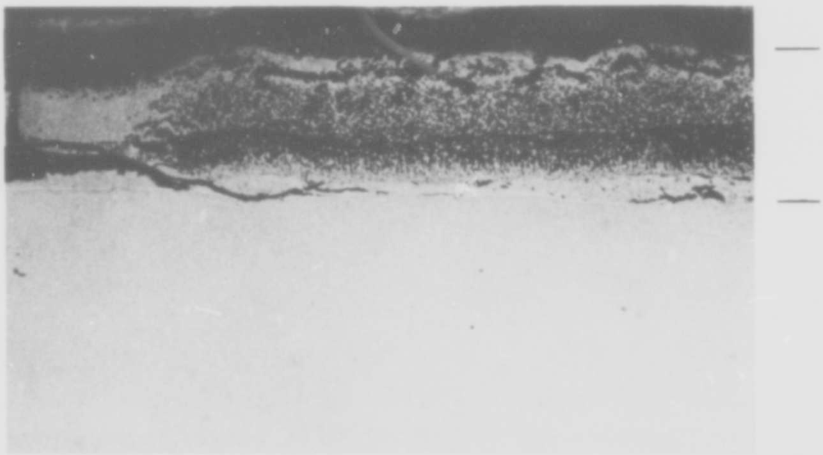
16.8 mg/cm^2 Titanium
4.4 mg/cm^2 Aluminum

Figure 28 Microstructure of Titanium-Aluminum Diffusion Coatings on Columbium Alloy Cb-752 as a Function of Prior Titanium Content 250X



Run Nos. 5 + 7 + 8

4.6 mg/cm^2 Titanium
5.6 mg/cm^2 Aluminum
4.9 mg/cm^2 Silicon



Run Nos. 6 + 7 + 8

16.8 mg/cm^2 Titanium
4.4 mg/cm^2 Aluminum
13.8 mg/cm^2 Silicon

Figure 29 Microstructure of Ti-Al-Si Diffusion Coatings on Columbium Alloy Cb-752 as a Function of Prior Titanium and Aluminum Contents 250X

Run Nos. 13 + 20 + 22

8.6 mg/cm^2 Titanium
4.7 mg/cm^2 Aluminum
12.5 mg/cm^2 Silicon

Figure 30 Microstructure of Silicon Diffusion Coatings on Columbium Alloy Cb-752 as a Function of Prior Titanium and Aluminum Contents 250X and dark gray or brown, with some areas where the pack material sintered to the coupons. The large silicon weight gains (13.9 mg/cm^2) and large initial titanium content (16.8 mg/cm^2) were associated with rough, bubbled coatings whereas the other coupons evidenced smooth coatings which were quite adherent. The siliconized microstructures are shown in Figures 29 and 30. The siliconizing produced cracking in the diffusion layer with definite lateral cracking or spalling of the heavily titanized coupon.

Several oxidation test specimens were prepared with aluminide coatings using the vacuum pack coating technique. The sequence of coating for these latter systems was reversed as opposed to those prepared earlier to see if more aluminum could be deposited. The specimens were first aluminized and then titanized, Table XIII. The amount of aluminum deposited (5.0 mg/cm^2) on the uncoated columbium substrate was similar to the weight gains observed previously for titanized material. Titanizing of the aluminized material also resulted in a weight gain (8 mg/cm^2) comparable to that normally obtained for uncoated material, c.f. runs 37 and 13, Table XIII. Thus the sequence of application of aluminum and titanium did not appear to have a marked effect on the transfer of these elements to the columbium alloy substrate. However, siliconizing (Run No. 38) of the Al-Ti precoated coupons at 1800°F for 8 hours using 1 w/o KF activation resulted in a weight gain of 30 mg/cm^2 as contrasted to 12.5 mg/cm^2 for siliconizing Ti-Al material under identical conditions (Run No. 22). Thus, the sequence of Al and Ti application did have an appreciable effect on the rate of silicon deposition. Also, the Al-Ti-Si system was rough and spalling, as contrasted to the adherent Ti-Al-Si coating obtained in Run No. 22. This exfoliation was apparently due to the rapid growth of the titanium rich silicide layer, and the inability of the phase to accommodate the volume increase and attendant growth stresses.

To conduct a more comprehensive evaluation survey of the Ti-Al system, a series of pack runs were made to define deposition parameters for the following nominal compositions:

	mg/cm^2		
System	Ti	Al	Si
Ti-Al	10	1.5	
Ti-Al-Si	10	1.5	1.5
Ti-Al	20	3.2	
Ti-Al-Si	20	3.2	3.2
Ti-Al	30	5.0	
Ti-Al-Si	30	5.0	5.0

The coating parameters developed for alloy D-43 are summarized in Table XIV. The titanizing parameters were developed in Runs 65 through 69 at a coating temperature of 2000°F. The titanized D-43 structure shown in Figure 31 shows a single-phase diffusion zone. The surface roughness was a function of titanium deposition, with the surface roughness increasing with increasing titanium content.

TABLE XIV

TITANIUM, ALUMINUM AND SILICON PACK DEPOSITION ON D-43 COLUMBIUM ALLOY

Run No.	Pack Material	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Weight Gain mg/cm^2	Remarks
65	Ti	1KF	2000	1-1/2	150Ar	-	10.6	Rough surface.
66	Ti	1KF	2000	6	150Ar	-	21.6	Rough surface.
67	Ti	1KF	2000	13	1.5	-	14.0	
68	Ti	1KF	2000	13	150Ar	-	-	Control stuck-temp overshot.
69	Ti	1KF	2000	13	150Ar	-	27.2	
70	56Cr-44Al	1KF	1900	4	150Ar	65,66,69	5.2	Ti precoated.
71	56Cr-44Al	1KF	1900	4	10^{-2}	65,66,69	4.2	Ti precoated.
72	56Cr-44Al	1KF	1900	1	10^{-2}	65,66,69	3.3	Ti precoated.
75	56Cr-44Al	1KF	1600	1	10^{-2}	65,66,69	0.8	Ti precoated.
76	56Cr-44Al	1KF	1600	2	150Ar	65,66,69	1.8	Ti precoated.
77	56Cr-44Al	1KF	1600	2	150Ar	65	1.9	Ti precoated.
373[a]	Si	1KF	2100	5	0.2	67 69	12.0 15.0	Ti precoated D-43 Adherent coatings.
78	56Cr-44Al	1KF	1900	1	10^{-2}	66	3.9	Ti precoated
79	56Cr-44Al	1KF	1900	4	150Ar	69	7.2	Ti precoated
80	Si	1KF	2100	1	10^{-2}	65,67; 66,78	6.0	Ti-Al precoat. Coating flaking.
101[a]	Si	1NaF	2250	5	10^{-2}	69,79	10.5	Ti-Al precoat. Adherent coating.
81	W and Si	1KF	2200	1/2	10^{-2}	67,77; 66,78; 69,70	-4.1	Ti-Al precoat. Specimens in W over Si+ Activator.

TABLE XIV

(Continued)

Run No.	Pack Material	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Precoating Runs	Weight Gain mg/cm^2	Remarks
89	Si	1KF	2250	1/2	10^{-2}	65,66; 77,78	10.4	Ti-Al precoat. Coatings rough and flaking.
90	Si	1KF	2250	1/4	10^{-2}	65,77; 66,78; 69,79	9.9	1/2 hr.hold 1500°F. Coatings rough and flaking. Specimens brittle.
91	Si	1KF	1500	1	10^{-2}	65,77; 66,78; 69,79	6.8	Ti-Al precoat. Powdery coatings. Specimens brittle.
94	Si	-	1500	1	10^{-2}	65,77; 66,78; 69,79		Ti-Al precoat. Powdery coatings.
100[a]	Si	2NaF	2225	5	0.2	65,77 66,78 69,79	19.6	Ti-Al precoat. Adherent coatings.
97	10Si+ 90Al_2O_3	1/2 NaF	2250	1.5	1.5	65,77 66,78 69,79	2.2 6.4 4.2	Ti-Al precoats Coating Adherent.

---

a. Large retort - 7-1/2" dia X 20", otherwise 3" dia X 10".

Figure 31 Titanized Microstructure of Columbium Alloy D-43.
Titanium Run 67. 250 X

The aluminizing parameters were developed in runs 70 through 77 using prealloyed 56 w/o Cr-44 w/o Al powder and two temperatures - 1600 and 1900°F. The Ti-Al coated microstructures are shown in Figure 32. The aluminized zone was manifested as a band, the thickness of which depended upon the amount of titanium deposited prior to aluminizing. The thickness of this zone varied from 0.02 to 2 mils, with generally a thinner aluminum zone formed as the titanium content increased.

Siliconizing of the Ti-Al coated coupons without coating flaking or embrittlement proved to be a formidable task and consumed most of the effort. Besides silicide coating spalling, another problem was to reduce the silicon content to the desired levels.

Siliconizing runs of Ti-Al precoated columbium alloy D-43 were conducted at 1500, 2100, 2225 and 2250°F in pure and refractory diluted silicon packs, with and without activator, and under different pressure conditions. When siliconizing was performed in a large retort at 2225 to 2250°F, an adherent, metallic silicide layer was obtained. See Run Nos. 100 and 101, Table XIV. However, when these runs were repeated in a smaller retort, flaking coatings were obtained, c.f. runs 80, 89 and 90 with 100 and 101, Table XIV. The diffusion times in the small retorts were kept short, and continuous evacuation was used (10^{-2}mm) to reduce the amount of silicon transferred. However, even with these measures, larger amounts of silicon were deposited than desired. The microstructures after siliconizing for the above runs are shown in Figures 33 and 34.

To reduce the silicon deposition, one run (81) was made with Ti-Al precoated specimens placed in tungsten powder, over a layer of silicon powder which contained the activator. The run was conducted at 2200°F for 1/2 hour. The specimens lost weight, indicating loss of titanium and/or aluminum from the precoated columbium. Several siliciding runs (91 and 94) were made at 1500°F using pure silicon packs, with and without activator. The silicon coatings produced at this temperature were powdery and non-adherent. Microscopic examination showed that a porous silicon layer was formed at this low temperature, Figure 35.

The final siliciding run (97) made in this series consisted of siliconizing the Ti-Al precoated specimens for 1-1/2 hours at 2250°F in a silicon pack diluted with 90 w/o bubbled alumina and 1/2 w/o NaF activator. The furnace was blanked-off after reaching heat (1.5mm). Adherent, metallic silicon coatings were obtained in this run, and the silicon weight gains varied from 2.2 to 6.4 mg/cm^2, depending upon the titanium and aluminum precoat weights. The microstructures produced in this run are shown in Figure 36.

The reasons for the differences noted between the siliconizing runs conducted in the small and large retorts are not clear, although the diluted pack results suggested that the differences were somehow connected with the silicon halide vapor pressure. The rate of silicon

Ti Run 65 (10 mg/cm^2)

Al Run 71 (4 mg/cm^2)

Ti Run 69 (27 mg/cm^2)

Al Run 71 (4 mg/cm^2)

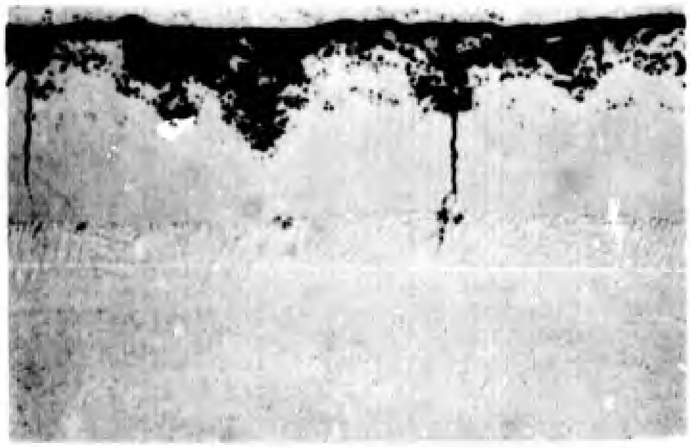
Ti Run 65 (10 mg/cm^2)

Al Run 76 (1.8 mg/cm^2)

Ti Run 69 (27 mg/cm^2)

Al Run 79 (1.8 mg/cm^2)

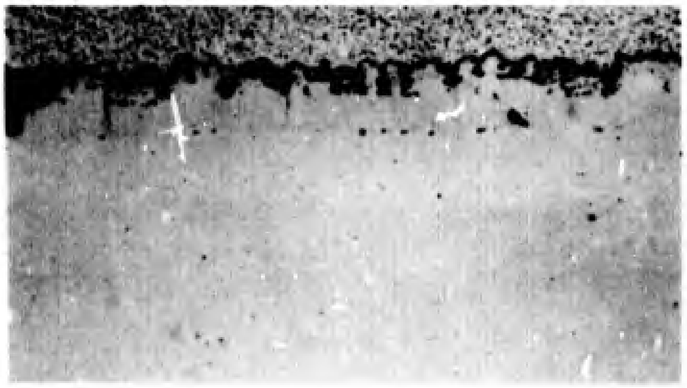
Figure 32 Microstructure of Ti-Al Coated Columbium Alloy D-43. 250X.



Ti Run 69 (27 mg/cm^2)

Al Run 79 (7 mg/cm^2)

Si Run 101 (11 mg/cm^2)



Ti Run 65 (10 mg/cm^2)

Al Run 77 (1.9 mg/cm^2)

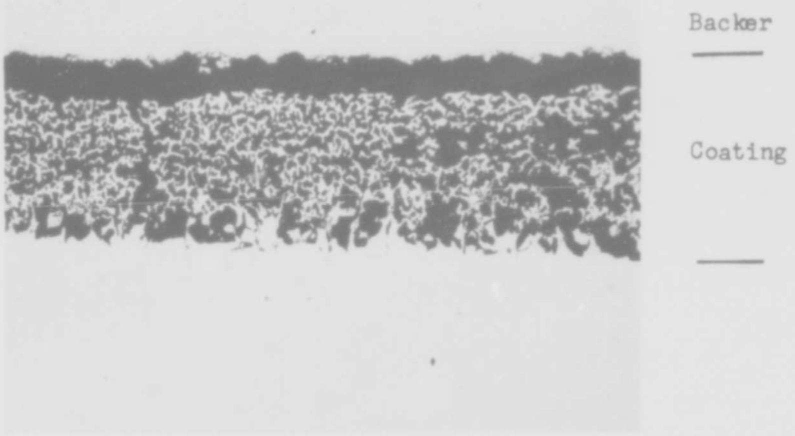
Si Run 80 (6 mg/cm^2)

Ti Run 66 (20 mg/cm^2)

Al Run 78 (4 mg/cm^2)

Si Run 80 (6 mg/cm^2)

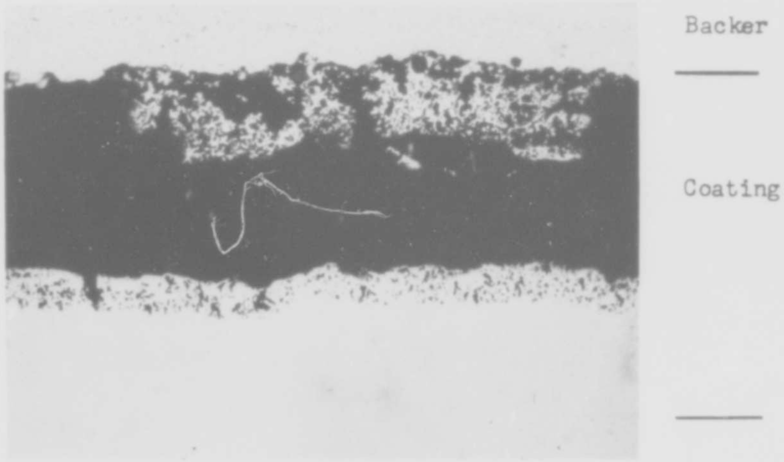
Figure 33 Microsturcture After Siliciding of Ti-Al Coated D-43. 250X.



Ti Run 65 (10 mg/cm^2)

Al Run 77 (1.9 mg/cm^2)

Si Run 90 (10 mg/cm^2)



Ti Run 69 (27 mg/cm^2)

Al Run 79 (7 mg/cm^2)

Si Run 90 (10 mg/cm^2)

Figure 34 Microstructure After Siliciding of Ti-Al Coated D-43. 250 X.

Ti Run 65 (10 mg/cm^2)

Al Run 77 (1.9 mg/cm^2)

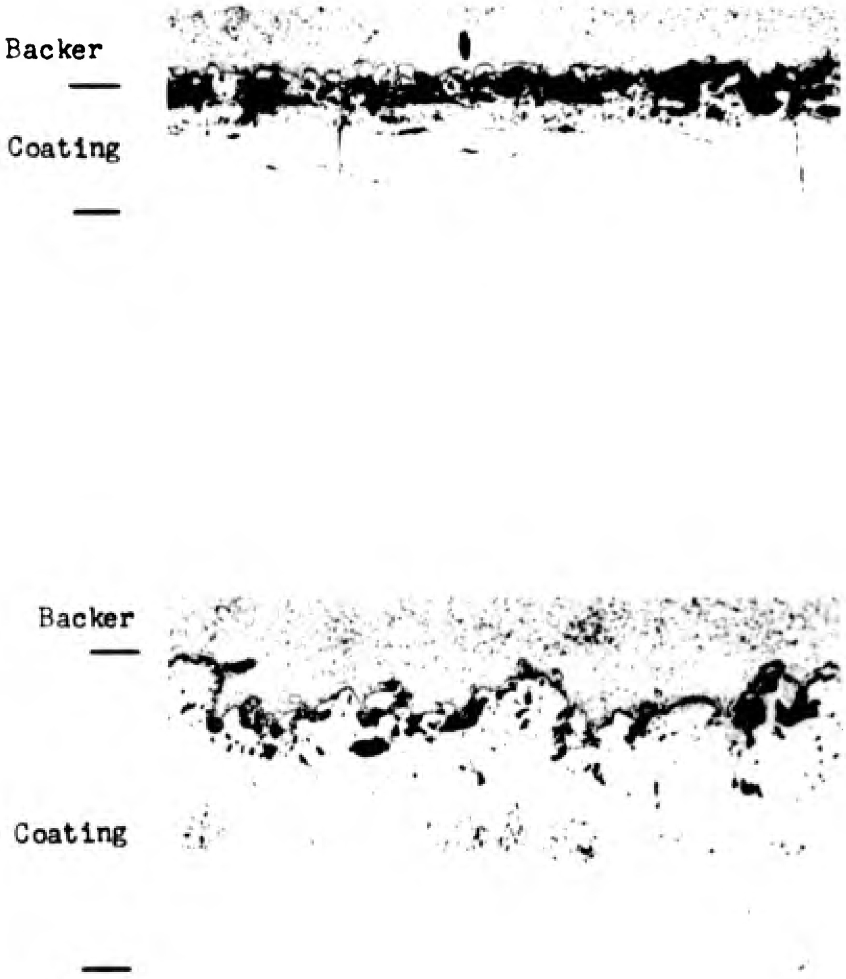
Si Run 91 (7 mg/cm^2)

Ti Run 69 (27 mg/cm^2)

Al Run 79 (7 mg/cm^2)

Si Run 91 (7 mg/cm^2)

Figure 35 Microstructure After Siliciding of Ti-Al Coated D-43, 250 X.



Ti Run 65 (10 mg/cm^2)
Al Run 77 (1.9 mg/cm^2)
Si Run 97 (2 mg/cm^2)

Ti Run 69 (27 mg/cm^2)
Al Run 79 (7 mg/cm^2)
Si Run 97 (4 mg/cm^2)

Figure 36 Microstructure After Siliciding of Ti-Al Coated D-43. 250X transfer can be reduced by diluting the silicon pack with inert material, and adherent coatings can be obtained at high temperatures. The high siliconizing temperatures yielded metallic coatings, whereas low temperatures produced powdery silicide coatings.

5.4.1 Cyclic Oxidation Tests at 1600 and 2400°F

The Ti-Al and Ti-Al-Si aluminide systems were screened for oxidation resistance at 1600 and 2400°F. Coupons were oxidized in Globar element heated box furnaces with the temperatures controlled to ± 10°F. The individual coupons were placed on silica blocks which were supported on a pure alumina fire brick. The coupons were exposed at 1600 and 2400°F according to standard MAB-201-M test procedures (11), and examined after each cycle for evidence of coating failure.

The oxidation results at 1600°F, Table XV, showed the Ti-Al and Ti-Al-Si systems with the largest amounts of titanium (25 mg/cm^2 or more) and with a titanium-aluminum ratio of about 4 to 1 provided the longest lives. Introduction of relatively large amounts of silicon (19.6 mg/cm^2) into the Ti-Al system impaired oxidation life at 1600°F. Specimens with flaky coatings failed early. The coupons coated with titanium only failed after one cycle at 1600°F; while the coupons coated with silicon only showed a life of 64 cyclic hours. These results show that the Ti-Al-Si and Ti-Al coating systems within the compositional limits tested did not possess the necessary resistance to high temperature (2400°F) oxidation. However, these systems showed potential for use at lower temperatures(1600°f) for up to about 1000 hours.

5.5 IMPACT TESTS

To determine the effect of coating application upon the Cb-752 alloy ductility, impact tests were performed on several of the Phase 1 coated specimens. The impact tests were conducted at room temperature with a 6-ounce hammer. Each specimen (1/2 in. x 1/2 in. x 0.03 in.), held in a vice, was struck with about the same force on a flat surface. The specimens either failed under impact, indicating substrate embrittlement, or bent, indicating substrate ductility. The results of impact testing are summarized in Table XVI.

The following coating-substrate systems showed room temperature embrittlement:

Ti-Mo-Si
Ti-V-Cr-Si
Ti-V-Al-Si
V-Cr-Si

It was not possible to correlate a certain coating sequence with embrittlement, since no bend tests were conducted at intermediate steps during coating application. However, for systems containing chromium, the adverse effect on ductility may be associated with the chromizing cycle. Previously, as noted in Section 5 for the Ti-Mo-Cr system, the chromium

TABLE XV

CYCLIC OXIDATION DATA FOR TITANIUM-ALUMINUM SYSTEMS ON COLUMBIUM ALLOYS Cb-752 AND D-43

			mg/cm^2						Oxidation Life, Hrs.	
Code	Alloy	Coating System	Ti	V	Al	Ta	Si	Run No.1	1600°F	2400°F
C1	Cb-752	Ti-Al	4.6	-	5.6	-	-	5 + 7	20 [a]	4,4 [a]
C2	Cb-752	Ti-Al	16.8	-	4.4	-	-	6 + 7	64	3,3
C3	Cb-752	Si	-	-	-	-	9.1	22	64	6,20
C4	Cb-752	Ti	8.6	-	-	-	-	13	8	1,1
C5	Cb-752	Ti-Al-Si	4.6	-	5.6	-	4.9	5+7+8	24	9,15
C6	Cb-752	Ti-Al-Si	16.8	-	4.4	-	13.9 [a]	6+7+8	8	3,8
C7	Cb-752	Al	-	-	5.0	-	-	36	36,20,20	2,2
C8	Cb-752	Al-Ti	7.8	-	5.0	-	-	37+36	4,4	1,1
C9	Cb-752	Al-Ti-Si	7.8	-	10.6	-	30.0 [a]	36+37+38	8	1
CH	Cb-752	Ti-V-Al-Si	13.2	-3.8 [b]	5.8	-	2.5 [a]	51+52+61+62	8,8[d]	2,2[c]
CI	Cb-752	Ti-Al-Si	13.2	-	5.8	-	3.4 [a]	51+61+62	28,52	50,146
CJ	Cb-752	Ti-Al	13.2	-	6.3	-	-	51+61	124,564	6,9[c]
CK	Cb-752	Ti-Ta-Al	13.2	-	1.9	-5.4 [b]	-	51+53+61	76,180	12,12[c]
D1	D-43	Ti-Al	10.6	-	3.9	-	-	65+77	24	-
D2	D-43	Ti-Al	21.6	-	7.2	-	-	66+78	374	-
D3	D-43	Ti-Al	27.2	-	7.2	-	-	69+79	998	-
D4	D-43	Ti-Al-Si	10.6	-	1.9	-	19.6	65+77+100	24	-
D5	D-43	Ti-Al-Si	21.6	-	3.9	-	19.6	66+78+100	247	-
D6	D-43	Ti-Al-Si	27.2	-	7.2	-	19.6	69+79+100	583	-

---

a. Rough or flaky coatings.
b. Weight loss.
c. Surface failure-otherwise edge failure.
d. Both surface and edge failures.

TABLE XVI

IMPACT TEST RESULTS ON VARIOUS COATING SYSTEMS

Code	System	Impact Test
A	Ti-Mo-Si	F[a]
B	Ti-MoCrTi-Si	B
C	Ti-Mo-V-Si	B
D	Ti-Mo-V-Cr-Si	B
E	Ti-Mo-Cr-Si	B
F	Ti-V-Cr-Si	F
G	Ti-V-Si	B
CH	Ti-V-Al-Si	F
CI	Ti-Al-Si	B
CJ	Ti-Al	F
CK	Ti-Ta-Al	F
L	Ti-Ta-Si	B
M	Mo-Ti-Si	B
N	Mo-CrTi-Si	B
O	Mo-V-Ti-Si	B
P	Mo-V-CrTi-Si	B
R	Mo-V-Si	B
S	V-CrTi-Si	B
T	V-Ti-Si	B
U	V-Mo-Ti-Si	B
W	V-Mo-CrTi-Si	B
X	V-Cr-Si	F
I	Mo-CrTi-Si	B
15	V-Al-CrTi-Si	B
3	CrTi-Si	B
11	CrTi-Si	B
12	CrTi-Si	B
13	CrTi-Si	F
69/72	Ti-Al	B
69/71	Ti-Al	B
D-1	Ti-Al	B
	Mo-Ti-Si	B
	V-Ti-Si	B

---

a. B - bent
F - fractured

deposition step from a pure chromium pack resulted in embrittlement. The adverse effect of chromium upon ductility was also observed by other investigators.(1) The embrittlement appears to be associated with oxidation of the columbium substrate, with the chromium pack media serving as the source of oxygen.

5.6 SELECTION OF PHASE II COATING SYSTEMS

The coating systems screened in Phase I are listed below:

Ti-Mo-Si
Ti-Mo-V-Si
Ti-Mo-Cr-Si
Ti-Mo-CrTi-Si
Ti-Mo-V-Cr-Si
Ti-V-Cr-Si
Ti-V-Si
Ti-Ta-Si
Ti-Al
Ti-Al-Si
Ti-Ta-Al

V-Cr-Si
V-CrTi-Si
V-Ti-Si
V-Mo-Ti-Si
V-Mo-CrTi-Si
V-Al-CrTi-Si

Mo-Ti-Si
Mo-CrTi-Si
Mo-V-Si
Mo-V-Ti-Si
Mo-V-CrTi-Si

The Systems were selected from the above list for the Phase II effort on the basis of the following criteria:

1) A number of systems were eliminated from further evaluation because of the impossibility of depositing or depositing sequentially the elements Ti-V, Ti-Ta and Ta. The systems therefore eliminated were: Ti-V-Cr-Si, Ti-V-Si, Ti-Ta-Si, Ti-Ta-Al, Ti-Mo-V-Si and Ti-Mo-V-Cr-Si.

2) Sound coating systems formed but exhibiting poor oxidation performance were the V-Cr-Si, Mo-V-Si, Ti-Mo-Si and Mo-Ti-Si systems.

3) A system excluded because of coating spalling and poor coating integrity owing to the chromizing cycle was the Ti-Mo-Cr-Si system.

4) Systems showing promise for both low-and high-temperature applications based on cyclic oxidation screening tests were: Mo-CrTi-Si, Mo-V-CrTi-Si, V-CrTi-Si and V-Al-CrTi-Si.

5) Systems showing promise for low-temperature applications only based on cyclic oxidation tests were: Ti-Al, Ti-Si, and Ti-Al-Si.

6) Systems eliminated because of duplication included Ti-Mo-CrTi-Si V-Mo-Ti-Si, V-Mo-CrTi-Si and V-Ti-Si.

Based on the above considerations, the following systems were chosen for Phase II optimization:

For both low-and high-temperature evaluation:

Mo-V-CrTi-Si
Mo-V-CrTi-Si
V-CrTi-Si
V-Al-CrTi-Si

For low-temperature evaluation only:

Ti-Al
Ti-Si
Ti-Al-Si

SECTION VI

PHASE II: ADVANCEMENT OF CANDIDATE COATING SYSTEMS

Candidate coating systems were selected from the Phase I preliminary cyclic oxidation screening effort for further investigation. Each system was formed within a broader range of coating compositions for evaluation and coating improvement. In addition, a parametric study was conducted to establish reproducible processing parameters for deposition of appropriate elements.

6.1 THE V-Al-CrTi-Si SYSTEM

The nominal compositions which were selected for coating system variations were:

Element Weight - mg/cm^2			
V	Al	Cr,Ti	Si
3	5	12	15
3	5	18	15
3	10	12	15
3	10	18	15
7	5	12	15
7	5	18	15
7	10	12	15
7	10	18	15

The pack coating runs by which the above systems were formed on columbium alloy Cb-752 are summarized in Table XVII. Both sample runs and oxidation coupon coating runs are included. The coupons were vanadized in Runs 106 and 107; chromium-titanium (Cr,Ti) coated in Runs 114, 115, 117 and 119; and siliconized in Run 124 Little pack particle sintering was encountered during vanadizing, and the weight gains were similar to those previously obtained under identical processing conditions, Figure 37. Weight gains were parabolically dependent upon diffusion time up to 6 hours. Beyond 6 hours, the caducous behavior of the curve shows that the activators were depleted from the pack.

The aluminum weight gains were dependent upon the prior vanadium content, with greater aluminum weight gains being experienced for the coupons containing the larger amounts of vanadium, Figure 38.

The chromium-titanium (Cr,Ti) weight gains obtained at 2340°F (1.5mm pressure) were dependent upon the prior vanadium content, with negligible effect of prior aluminum content, Figure 39. However, the aluminum reduced the amount of Cr,Ti transferred as compared to vanadized only coupons. The weight gains appeared to be parabolically dependent upon diffusion time, even for those coupons that were coated in two runs On the other hand,

TABLE XVII

COATING DATA FOR V-Al-CrTi-Si, V-CrTi-Si AND CrTi-Si SYSTEMS FORMED ON COLUMBIUM ALLOY Cb-752

Run No.	Pack Composition		Pack Conditions			Precoating		Average Weight Gain mg/cm^2	Remarks
	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.		
103	V	2NaCl+ 0.2VCl$_4$	2200	1	150mm Ar	-	-	2.4	
104	V	2NaCl+ 0.2VCl$_4$	2200	6	150mm Ar	-	-	6.0	Slight sintering.
105	V	2NaCl+ 0.2VCl$_4$	2200	10	150mm Ar	-	-	6.7	Slight sintering.
						6V	104	10.0	Slight sintering.
106	56Cr-44Al	1KF	1900	16	150mm Ar	2.4V	103	7.0	
						6V	104	9.5	
107	56Cr-44Al	1KF	1900	7	150mm Ar	2.4V	103	5.3	
						6V	104	7.8	
108	60Cr-40Ti	1KF	2300	6	10^{-2}	2.4V+ 5Al	103+ 107	8.3	
						2.4V+ 7Al	103+ 106		
						6V+5Al	104+ 107	11.3	
						6V+9.5Al	104+ 106		
						6.7V	105	15.3	
109	60Cr-40Ti	1KF	2300	9	10^{-2}	6.7V	105	15.8	
						9.5V	104+ 105		
						2.4V+ 5.3Al	103+ 107	8.4	
						2.4V+7V	103+ 106		

TABLE XVII

(Continued)

	Pack Composition		Pack Conditions			Precoating		Average Weight Gain mg/cm^2	
Run No.	Pack	Activator w/o	Temp °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.		Remarks
109	60Cr-40Ti	1KF	2300	9	10^{-2}	6.7V 9.5V	105 104+ 105	15.8	
						2.4V+ 5.3Al 2.4V+7V	103+ 107 103+ 106	8.4	
						6V+7.8Al 6V+9.5Al	104+ 107 104+ 106	11.3	
						2.4V	103	13.7	
110	60Cr-40Ti	1KF	2300	5	10^{-2}	Same as 109	Same as 109	21.3	Total Wt.Pick up of Runs 109+110
						+CrTi	+109	12.4 12.4 16.6 16.6 18.9	
						-	-	7.9	
112	60Cr-40Ti	1KF	2300	8	1.5	2.4V+5.3Al 2.4V+7Al	103+ 107 103+ 106	9.7	
						6V+7.8V 6V+9.5Al	104+ 107 104+ 106	13.6	

TABLE XVII

(Continued)

	Pack Composition		Pack Conditions			Precoating		Average	
Run No.	Pack	Activator w/o	Temp °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.	Weight Gain mg/cm^2	Remarks
112						2.4V	103	13.9	
						-	-	11.1	
113	60Cr-40Ti	1KF	2340	10	1.5	2.4V+5.3Al	103+ 107	13.7	
						2.4V+9Al	103+ 106		
						6V+7.8V	104+ 107	19.4	
						6V+9.5Al	104+ 106		
						2.4V	103	17.3	
						-	-	14.7	
114	60Cr-40Ti	1KF	2340	6-1/2	1.5	2.4V+5.3Al	103+ 107	9.1	Power failed.
						2.4V+7Al	103+ 106		
						-	-	7.1	
115	60Cr-40Ti	1KF	2340	12	1.5	Same as 114	Same as 114	19.6	Total Wt. pick up from Runs 114+115
						+Cr,Ti	+114		
						-	-	18	
117	60Cr-40Ti	1KF	2340	9	1.5	2.4V+5.3Al	103+ 107	8.1	
						2.4V+7Al	103+ 106		
						6V+9.5Al	104+ 106	12.7	
						6V+7.8Al	104+ 107		
						2.4V	103	14.1	
						-	-	11.1	

TABLE XVII
(Continued)

Run No.	Pack Composition Pack	Pack Composition Activator w/o	Pack Conditions Temp °F	Pack Conditions Time Hrs.	Pack Conditions Pressure mm	Precoating Elements mg/cm2	Precoating Run Nos.	Average Weight Gain mg/cm2	Remarks
118	60Cr-40Ti	1KF	2340	11	1.5	2.4V	103	20.7	
						6V+7.8Al	104+ 107	23.0	
						6V+9.5Al	104+ 106		
						-	-	17.2	
119	60Cr-40Ti	1KF	2340	7	1.5	6V+7.8Al	104+ 107	16.1	
						6V+9.5Al	104+ 106		
						-	-	14	
121	Si	1/2KF	2100	4	10^{-2}	All V-Al-Cr,Ti	-	10.1	
						All V-Cr,Ti	-	8.4	
123	Si	1/2KF	2100	15	10^{-2}	All V-Al-Cr,Ti	-	16.4	
						2.4V+21Cr,Ti	103+ 118	11.5	14.9 av. for All V-Cr,Ti.
						6.7V15Cr,Ti	105+ 108	13.1	
						6.7V+21 Cr,Ti	105+ 109+110	19.4	
						9.5V+21 Cr,Ti	104+105 +109+110	15.8	
124	Si	1/2KF	2100	11	10^{-2}	All V-Al-Cr,Ti	-	15.8	
						V-Cr,Ti	Same as 123	12.7 13.7	14.1 Av.
						Same as 123		18.9 16.0	
126	Si	1/2KF	2100	13	10^{-2}	V-Cr,Ti	Same as 123	13.5 16.0	16.7 Av.
						Same as 123		19.0 18.0	

TABLE XVII

(Continued)

Run No.	Pack Composition		Pack Condition			Precoating		Average Weight Gain mg/cm^2	Remarks
	Pack	Activator w/o	Temp °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.		
129	Si	1/2KF	2100	6	10^{-2}	Cr,Ti	114+115	16	
131	Si	1/2KF	2100	12	1.5	2.4V+21 Cr,Ti	103+118	22.7	
						6.7V+15 Cr,Ti	105+108	26	
132	Si	1/2KF	2100	6	10^{-2}	6.7V+21	105+(109+110)	14	
						9.5V+21 Cr,Ti	(104+105)+(109+110)	15	

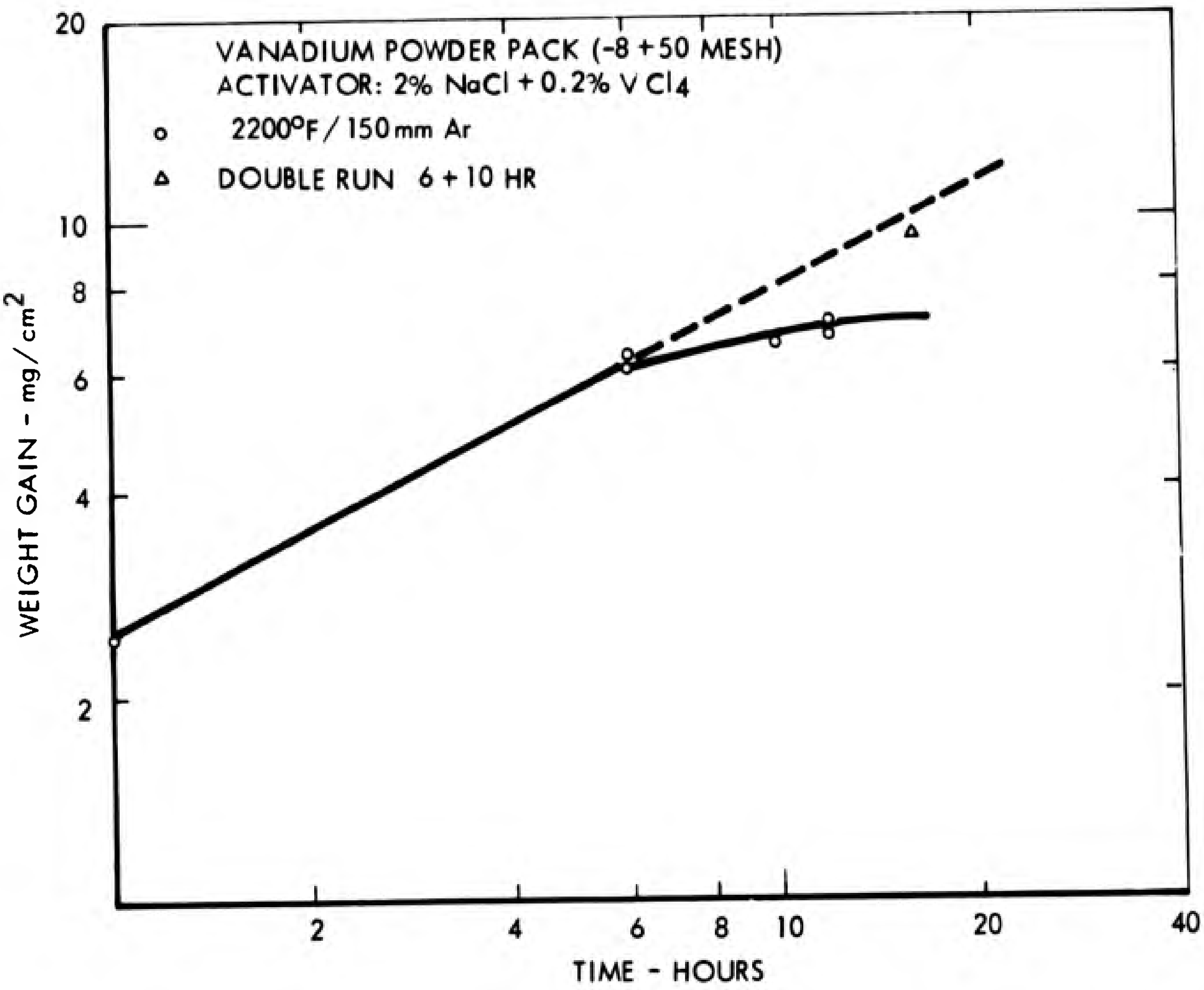


Figure 37 WEIGHT GAIN DATA FOR VACUUM PACK VANADIZING OF COLUMBIUM ALLOY Cb-752 AT 2200°F.

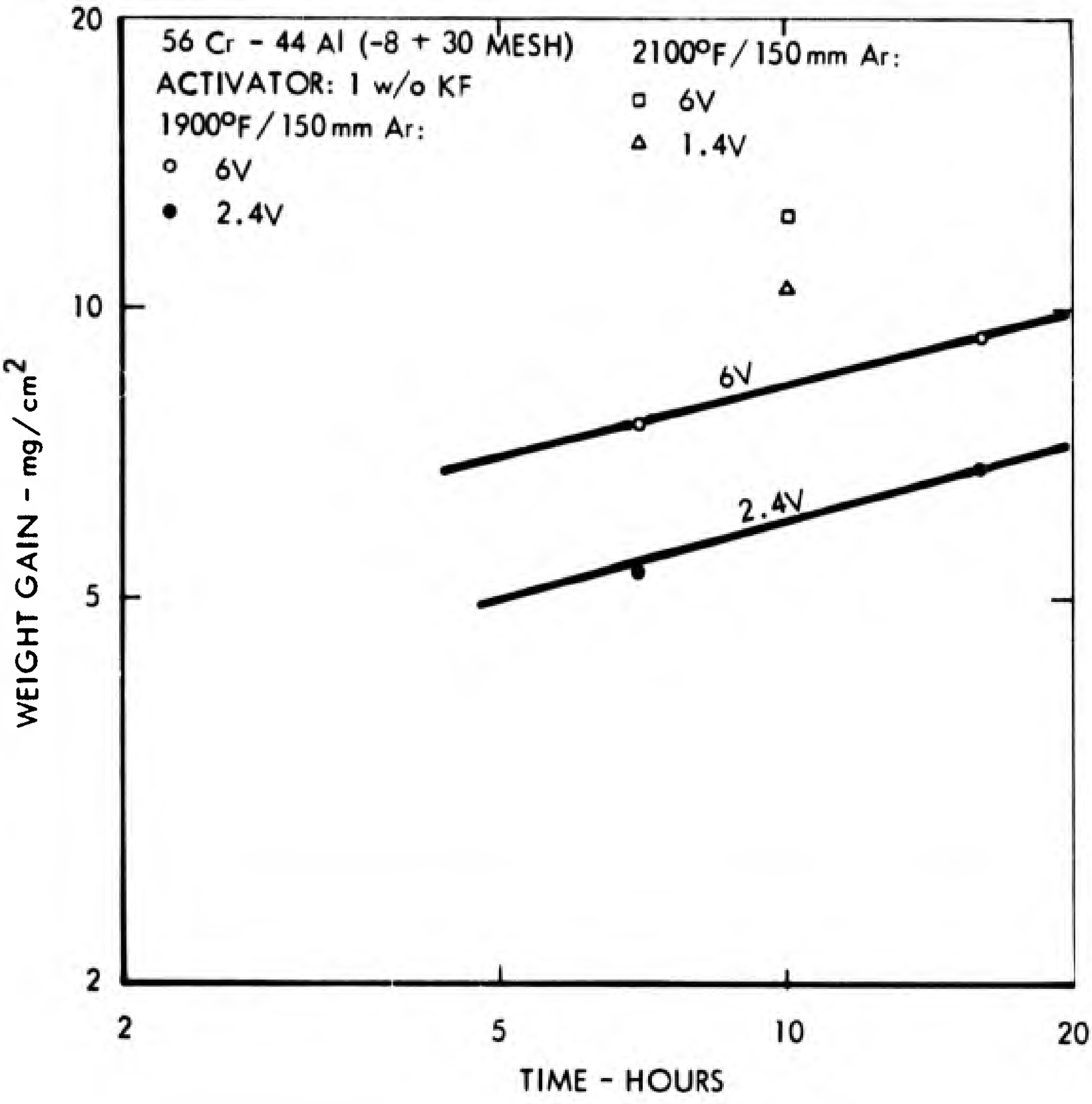


Figure 38 WEIGHT GAIN DATA FOR ALUMINIZING OF VANADIZED COLUMBIUM ALLOY Cb-752.

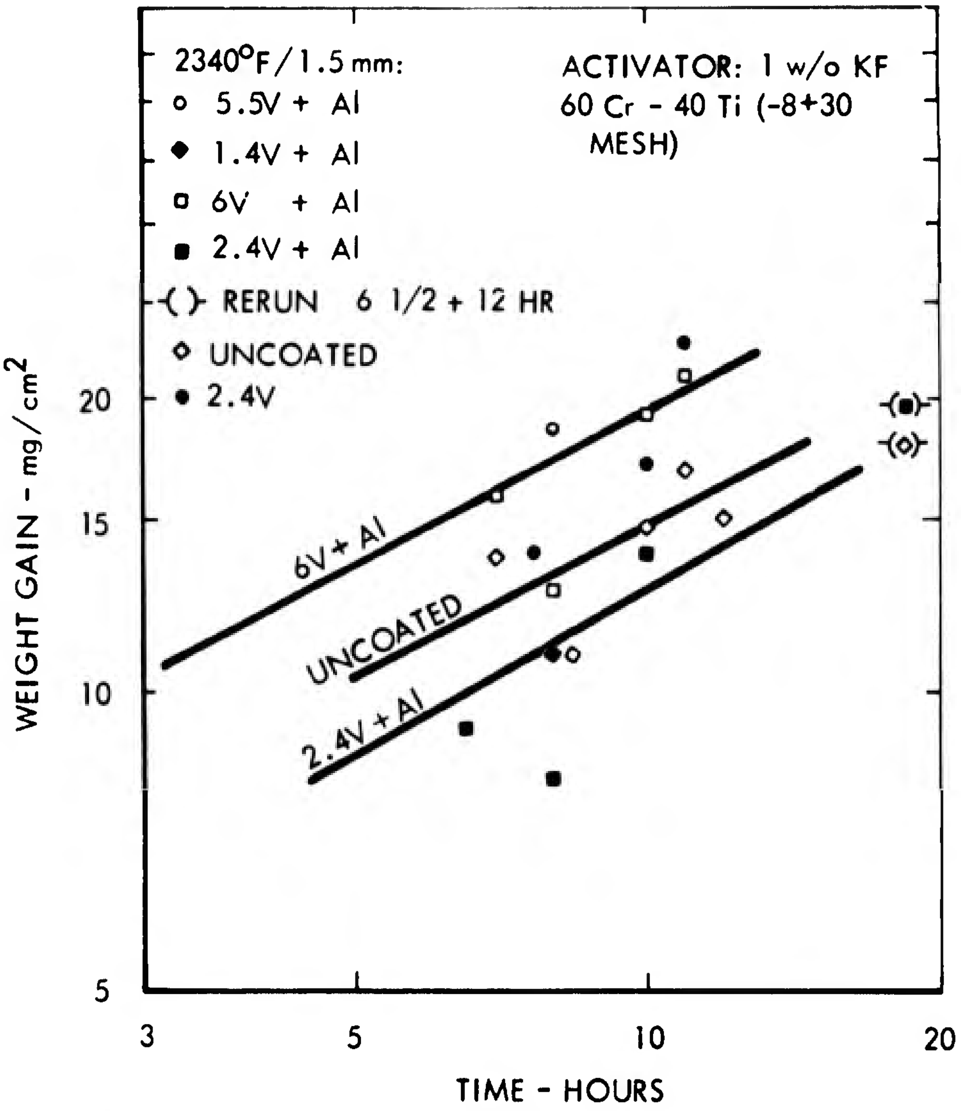


Figure 39 WEIGHT GAIN DATA FOR Cr-Ti COATING OF VANADIUM AND ALUMINUM PRECOATED COLUMBIUM ALLOY Cb 752.

weight gains (Runs 108 and 109) obtained at 2300°F (10^{-2} mm pressure) appeared not to follow parabolic control. Double runs (Runs 109 + 110), however, yielded weight gains that appeared to be parabolically dependent upon time.

Siliconizing of the V-Al-CrTi precoated coupons at 2100°F yielded similar weight gains for all of the combinations, thus indicating a negligible effect of the prior coating element quantities on silicon transfer. The silicon transfer appeared to be diffusion controlled as indicated in Figure 40.

Typical microstructures after each coating step are presented in Figures 41 and 42. Hardness traverses are also given for each completed coating system. The coating hardness varied from 1380 Knoop hardness number at the surface to 360 KHN at the coating matrix interface. Porosity noted after the Cr-Ti coating step, Figure 41, was probably caused by loss of aluminum through evaporation or volatile halide formation.

Cyclic oxidation test results for this system are summarized in Table XVIII. Electron probe analyses of as coated and oxidized coupons are presented in Section 6.8. Representative photomicrographs and substrate hardness after testing are presented in Figure 43. Similar to Phase I results, these data show no oxygen contamination of the columbium alloy Cb-752 substrate. Again, the hardness of the as-received substrate (KHN 216) was lowered by the coating processing.

The oxidation results at 1600° and 2400°F indicate that coating life is dependent upon the V,Al and Cr-Ti contents at one silicon level, the coating life being extended with increasing quantities of these elements, Oxidation lives in excess of 600 hours at 1600°F and 200 hours at temperatures over 2000°F to 2400°F were obtained. Taking into consideration the performance of Phase I and II composition variations, the preferred composition is

7V-10Al-18CrTi-17Si

where the numerical prefix [2] before each element symbol denotes weight of coating deposited, expressed in mg/cm^2. The Cr-Ti: Si ratio which yielded longest oxidation li [illegible] was in the range 0.9 - 1.1.

6.2 THE V-(Cr,Ti)-Si SYSTEM

The nominal compositions selected for coating system investigation were:

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[2] This nomenclature will be used throughout this report.

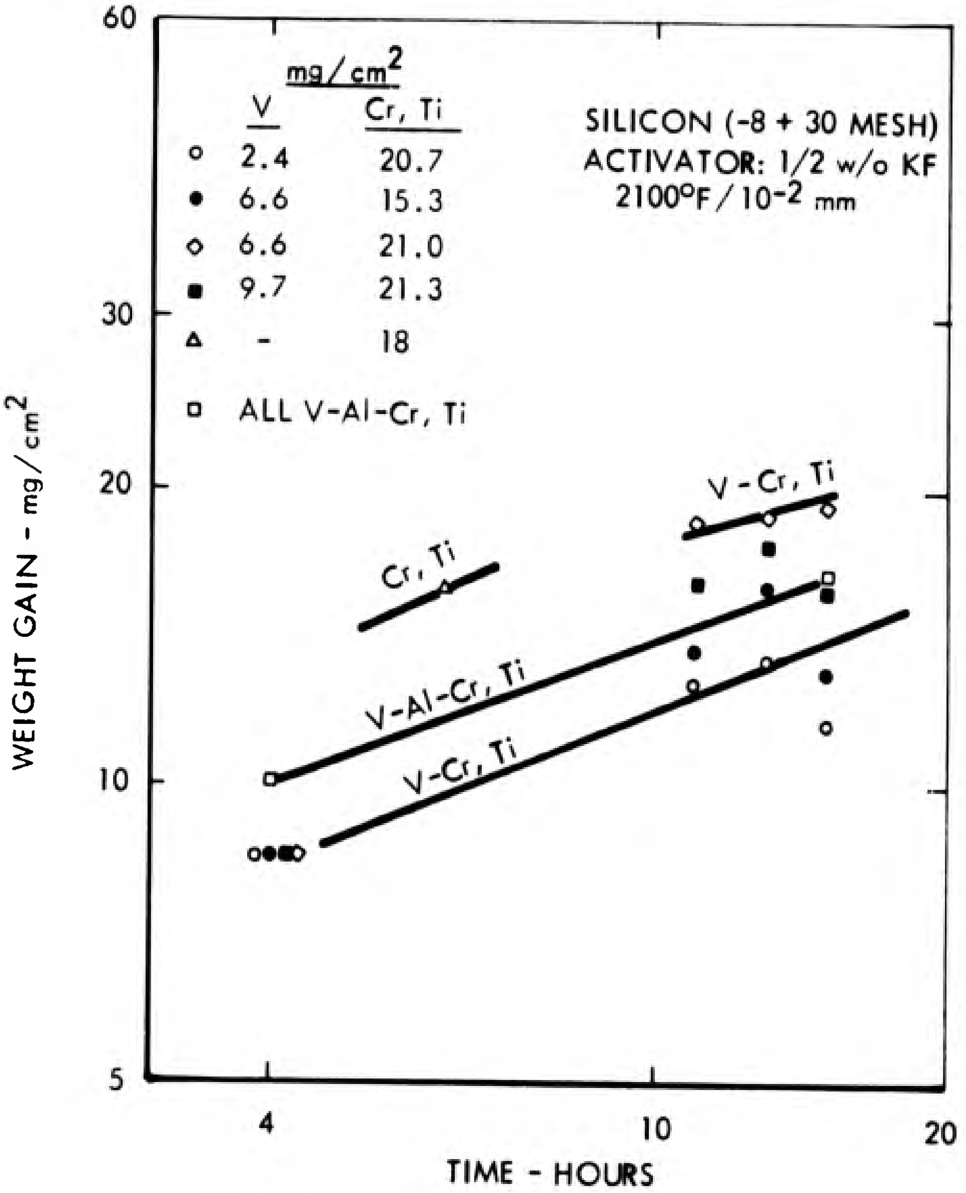
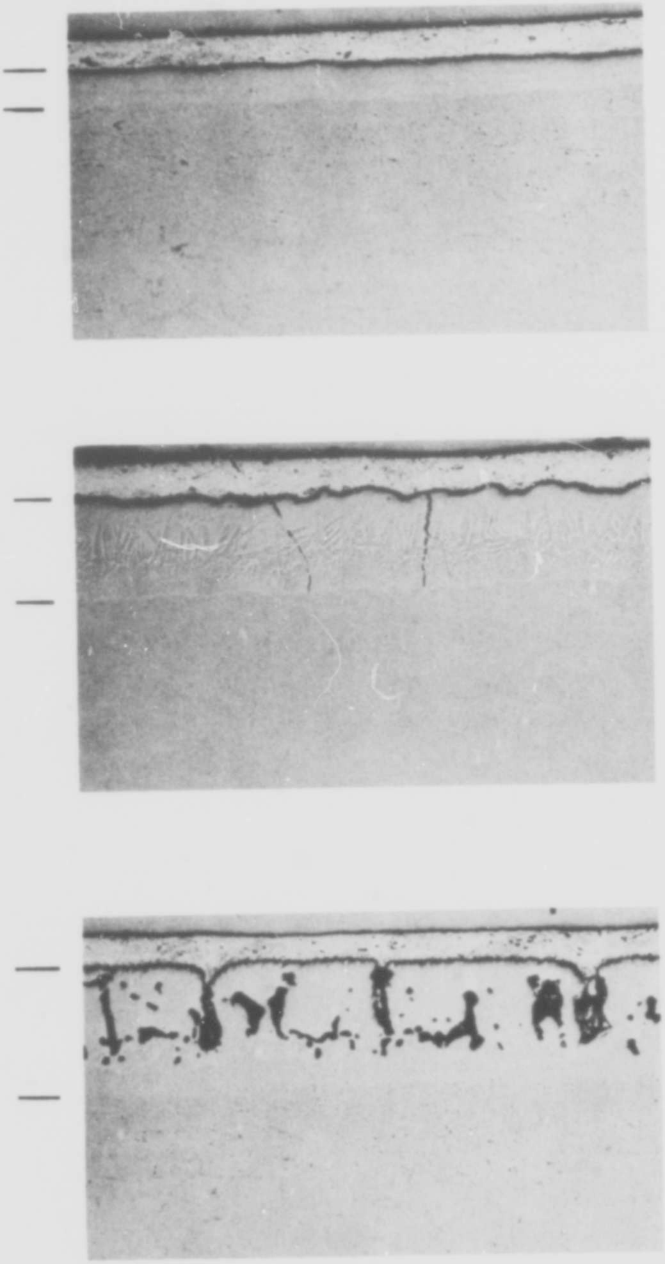


FIGURE 40 WEIGHT GAIN DATA FOR SILICONIZING OF V-Al-CrTi AND V-CrTi SYSTEMS ON COLUMBIUM ALLOY Cb-752.



V Run 104, 105

V Run 104

Al Run 106

V Run 104

Al Run 106

CrTi Run 119

Figure 41 Microstructures of Columbium Alloy Cb-752 after V, Al and Cr-Ti Coating. 100 X

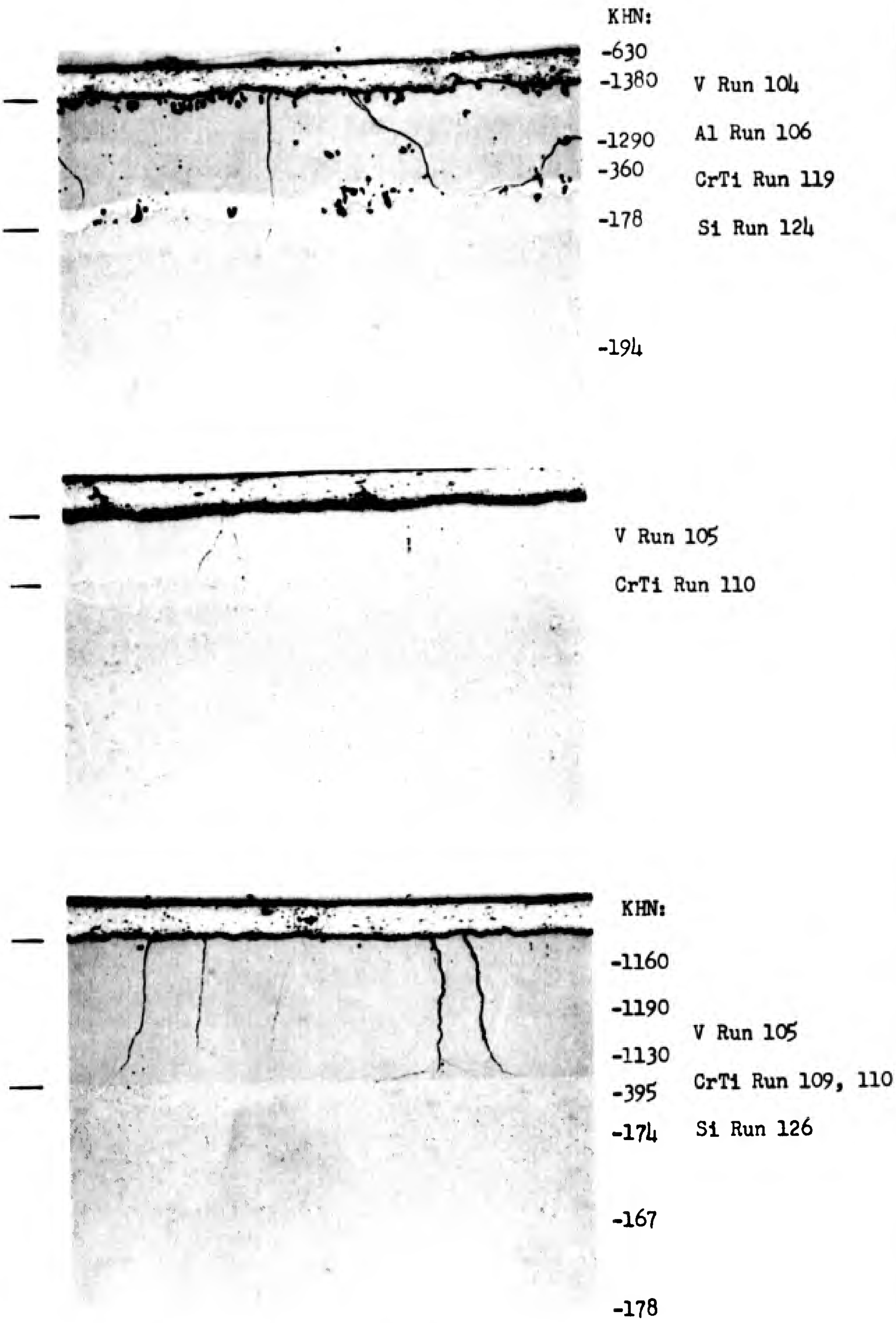
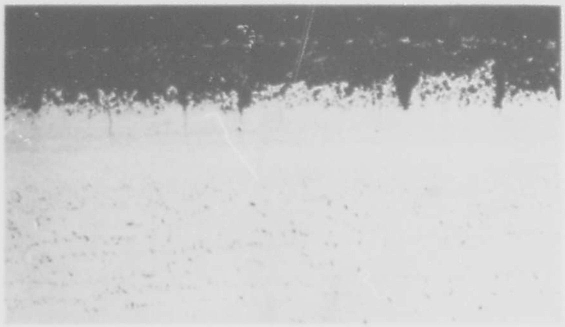


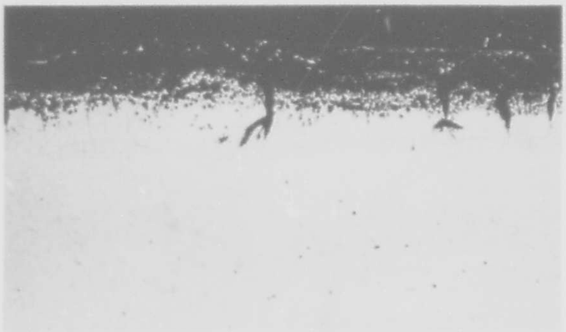
Figure 42 Microstructures of Columbium Alloy Cb-752 after V, Al, Cr-Ti and Si Coating.



6V-8Al-17CrTi-16Si

$>$ 224 Hr at 2400°F

-KHN: 187



2V-7Al-20CrTi-16Si

$>$ 224 Hr at 2400°F

-KHN: 200

6V10Al-15CrTi-16Si

$>$ 238 Hr at 2400°F

-KHN: 187

Figure 43 Photomicrographs of Phase II Exposed V-Al-CrTi-Si System Coatings on Cb-752. 100 X

TABLE XVIII

PHASE II OXIDATION RESULTS FOR THE V-Al-CrTi-Si SYSTEM ON Cb-752

	mg/cm^2				Oxidation Life^a, Hrs.			
Code	V	Al	Cr,Ti	Si	1600°F	2000°F	2200°F	2400°F
E1	2.4	5.3	9.4	15.8	$688^{(2)}$	275, >283	150,150	134,169^b,168^b
F1	2.4	5.3	19.6	15.8	$>688^{(2)}$	$>283^{(2)}$	249, >329	214,200,244
G1	2.4	7.0	7.0	15.8	120,688	275, >283	150,169	110,168^b,176
H1	2.4	7.0	19.6	15.8	120, >688	>283	273,273	262,248, >224
I1	6.0	7.8	11.5	15.8	$>688^{(2)}$	208,208	-	200,262,248
J1	6.0	7.8	17.0	15.8	120,120,224	$>283^{(2)}$	$>329^{(2)}$	280, >280, >224
K1	6.0	9.5	14.0	15.8	$>688^{(2)}$	208, >208	-	182,280^s, >280
L1	6.0	9.5	15.0	15.8	$>688^{(2)}$	208^s,208	-	280,272^b, >238

---

a. Failures: s-surface; b-surface and edge; unmarked-edge.
b. ( ) Indicates number of specimens with same exposure time.

Element Weight - mg/cm2

V	Cr,Ti	Si
3	18	12
3	18	18
7	12	12
7	12	18
7	18	12
7	18	18
12	18	12
12	18	18

The coupons were vanadized in Runs 103, 105 and 104 + 105; chromium-titanized (Cr,Ti) in Runs 108, 118 and 109 + 110; and siliconized in Runs 126, 131 and 132. The coating data are summarized in Table XVII. Representative photomicrographs of coated specimens are presented in Figures 41 and 42.

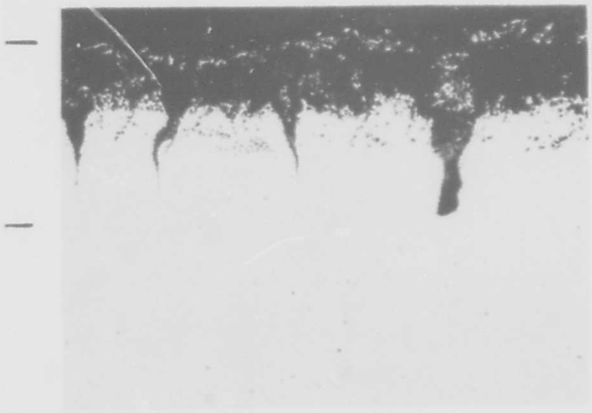
The relatively large amounts of vanadium were deposited on the Cb-752 coupons in two runs, since pack activator depletion did not permit the achievement of the desired amount in a single run. The double run yielded vanadium weight gains that were in agreement with diffusion controlled transfer, Figure 37.

The chromium-titanium (Cr,Ti) weight gains were dependent upon the prior vanadium content, with the larger weight gains being experienced for the coupons containing the larger amounts of vanadium, up to about 7 mg/cm^2. For example, the vanadized coupons which contained about 7 mg/cm^2 of vanadium picked up about 14% more (Cr-Ti) than the coupons which contained about 2 mg/cm^2 of vanadium. Beyond 7 mg/cm^2, the vanadium content did not appear to have any additional effect on (Cr-Ti) transfer.

The amount of silicon transferred to the V-CrTi precoated coupons appeared to be a function of both the vanadium and chromium titanium content. The silicon weight gains generally increased with increasing V or Cr-Ti contents. For an equal Cr-Ti content, the silicon transfer increased as the vanadium content increased from about 2 to 7 mg/cm^2, and then decreased when the vanadium content went up to about 10 mg/cm^2.

Cyclic oxidation test results are summarized in Table XIX, and representative photomicrographs and substrate hardnesses after exposure are presented in Figure 44. Electron probe analyses of as-coated and oxidized samples are shown in Section 6.8.

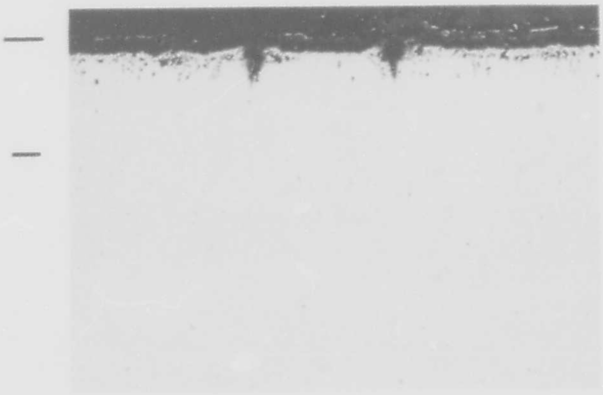
Cyclic oxidation results indicated that the intermediate vanadium content was best. Oxidation life in excess of 600 hours at 1600° and 200 hours at temperature over 2000°F was obtained. Both a high Cr-Ti and Si content appeared to prolong system life, as long as the Cr-Ti: Si ratio was greater than 1.1



2V-21CrTi-23Si

$>$238 Hr at 2400°F

-KHN: 196



7V-21CrTi-14Si

$>$238 Hr at 2400°F

-KHN: 196

Figure 44 Photomicrographs of Phase II Exposed V-CrTi-Si System Coatings on Cb-752. 100 X

TABLE XIX

PHASE II OXIDATION RESULTS FOR THE V-CrTi-Si SYSTEM ON Cb-752

	mg/cm^2			Oxidation Life^a, Hr.			
Code	V	Cr,Ti	Si	1600°F	2000°F	2200°F	2400°F
E2	2.4	20.7	14.4	$>688^{(2)b}$	275,>283	225,249	168,190,176
F2	2.4	20.7	22.7	88,88,>632	67,251	150,193	88^s,294,>238
G2	6.7	15.3	16.2	$>688^{(2)}$	275,275	145,145	142,168,200
H2	6.7	15.3	26	56^s,56^s,160	171,283	145,145	88^s,214,214
I2	6.7	21.3	14	$>632^{(2)}$	>208,>208	-	>238,>294,>294
J2	6.7	21.3	18.6	$>688^{(2)}$	208^s,208	-	214,224,248
K2	9.5	21.3	15	$>632^{(2)}$	$>283^{(2)}$	193,>329	190,214,>294
L2	9.5	21.3	17.9	$>688^{(2)}$	275,275	169,193	182,176,280

---

a. Failures: s-surface; b-surface and edge; unmarked-edge.
b. ( ) Indicates number of specimens with same exposure time.

and less than about 2. Therefore, the preferred system composition was

7V-21CrTi-16Si

with a Cr-Ti: Si ratio of 1.1 to 1.5

6.3 THE Mo-CrTi-Si SYSTEM

The nominal compositions selected for coating investigation were:

Element Weight - mg/cm²		
Mo	Cr,Ti	Si
5	18	12
5	18	18
10	18	12
10	18	18
10	12	12
15	18	12
15	18	18
15	12	12

The molybdenum precoatings were applied in eight chemical vapor depositions runs. The chemical vapor deposition parameters were outlined previously.

The pack coating parameters for the molybdenum coated Cb-752 columbium alloy coupons are summarized in Table XX. The chromium-titanium (Cr,Ti) was applied in Runs 158, 159, and 160. No effect of molybdenum content was discernible on Cr-Ti weight gain, though the premolybdenized coupons picked up less Cr-Ti than did uncoated coupons. The weight gain data for the Cr-Ti coating of the Mo and Mo-V precoated Cb-752 as a function of time are plotted in Figure 45.

The Mo-CrTi precoated samples were siliconized in Runs 162 and 164. Again no effect of molybdenum or Cr-Ti content was observed on silicon transfer, as shown in Figure 46 where the weight gain data are plotted for various diffusion times.

Microstructures after each coating sequence are presented in Figures 47 and 48. A hardness survey of the completed coatings is presented in Figure 48. The molybdenum coatings applied by chemical vapor deposition (CVD) contained either porosity or inclusions, possibly subchlorides, Figure 47. In some cases the interface between the molybdenum and columbium alloy Cb-752 substrate also showed line defects in the form of a second phase or porosity.

Cyclic oxidation data, Table XXI, suggest that coating life increased with increased Mo and Cr-Ti contents, and with decreased Si content within

TABLE XX

COATING DATA FOR THE Mo-CrTi-Si and Mo-V-CrTi-Si SYSTEMS FORMED ON COLUMBIUM ALLOY Cb-752

	Pack Composition		Pack Conditions			Precoating		Average	
Run No.	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run No.	Weight Gain mg/cm^2	Remarks
138	60Cr-40Ti	1KF	2300	8	10^{-2}	1.3Mo	CVD 122, 123	29	CVD & slurry applied Mo-(5TiH$_2$) Blanked-off first 30 min.
						14Mo	CVD 117	27	
						15Mo	135,136, 137	29	
145	Si	1/2KF	2050	5	10^{-2}	Same as 138		9.6	Large Pack;Activator in bottom
								8.3	
								11.9	
146	60Cr-40Ti	1KF	2300	8	10^{-2}	-	-	17.4	
147	Si	1/2KF	2100	6	10^{-2}	17Cr,Ti	146	8.3	
148	Si	1/2KF	2100	6	10^{-2}	17Cr,Ti, 8Si	146,147	8.6	
149	60Cr-40Ti	1KF	2300	4	10^{-2}	1.3-13.7Mo	CVD 117-134	10.4	
						2.4V	103	16.1	
						6.7V	105	21.3	
						2.4V, 7Al	103,106	11.9	
						6V, 7.8Al	104,107	17.1	
						-	-	12.5	
150	V	2NaCl+ .2VCl$_4$	2200	2	150Ar	1-2Mo		3.6	
						8.5-10Mo		5.6	
151	V	2NaCl+ .2VCl$_4$	2200	1	150Ar	3-13Mo		3.7	
152	V	2NaCl+ .2VCl$_4$	2200	12	150Ar	4-6Mo		7.5	
						9-10Mo		8.6	
						11.5-13Mo		9.2	

TABLE XX
(Continued)

	Pack Composition		Pack Conditions			Precoating			
Run No.	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements Mg/cm^2	Run Nos.	Average Weight Gain mg/cm^2	Remarks
153	V	2NaCl+ $.2VCl_4$	2200	10	150Ar	4-12Mo,8-9V	152	2.5	
157	60Cr-40Ti	1KF	2300	6-1/2	10^{-2}	5-15Mo,3-12V	151-153	26.7	
158	60Cr-40Ti	1KF	2300	3	10^{-2}	5-15Mo,3-12V	151-153	12.3	
159	60Cr-Ti	1KF	2300	10	10^{-2}	5-15Mo		18	
160	60Cr-40Ti	1KF	2300	3	10^{-2}	3-13Mo, 4-12V,Si	158	8.3	
						10-13Mo,Si	158	6.2	
162	Si	1/2KF	2100	8	10^{-2}	Mo-V-Cr,Ti Mo-Cr,Ti	159,160	12	Rough spalling coating on some Mo-V-Cr,Ti coupons.
164	Si	1/2KF	2100	18	10^{-2}	Mo-Cr,Ti	159	18.8	
165	Si	1/2KF	2100	4	10^{-2}	Mo-V-CrTi	160	9.7	Spalling coatings on some specimens.

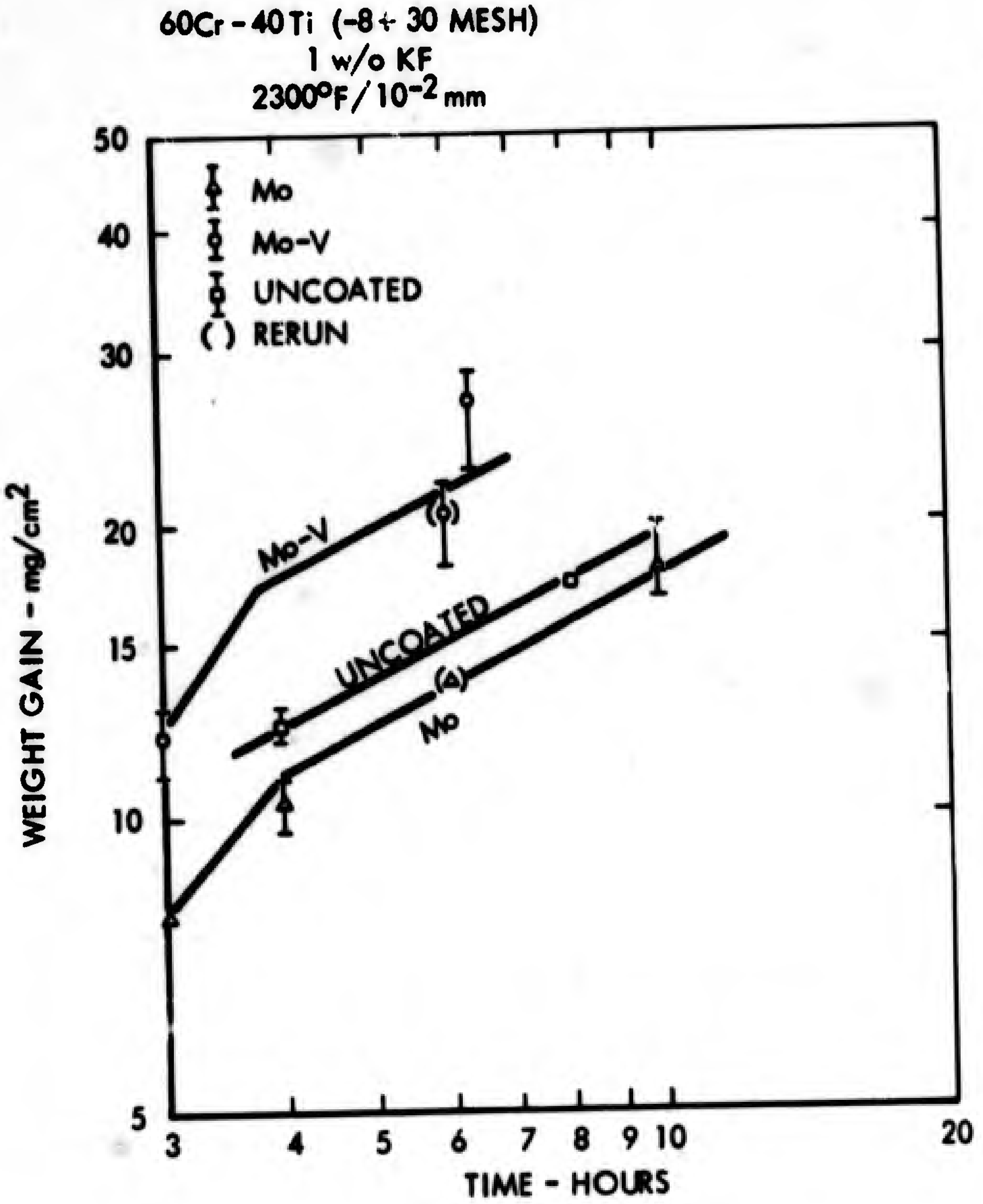


Figure 45 Weight Gain Data for Cr-Ti Coating of Mo and Mo-V Precoated Columbium Alloy Cb-752.

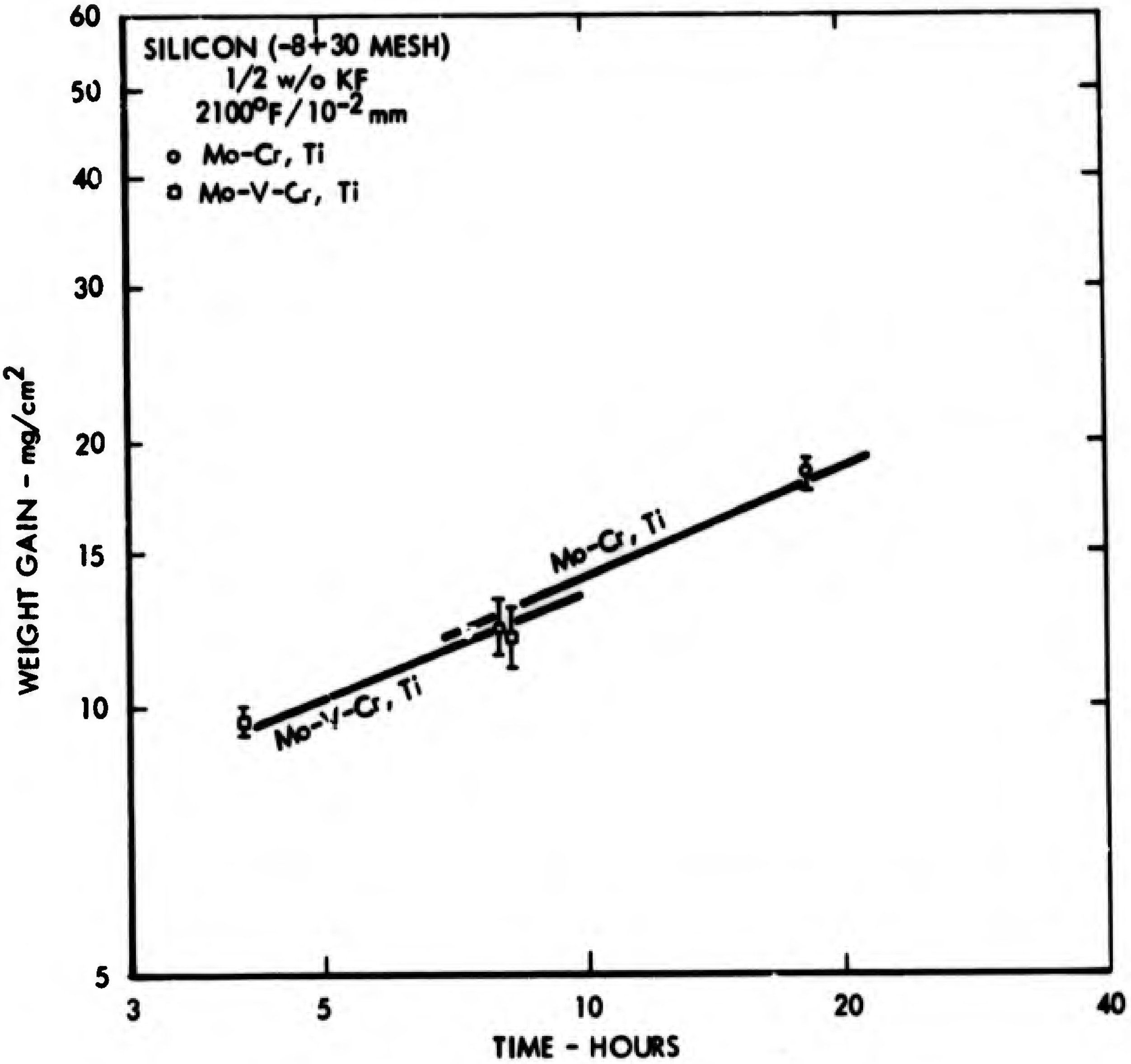
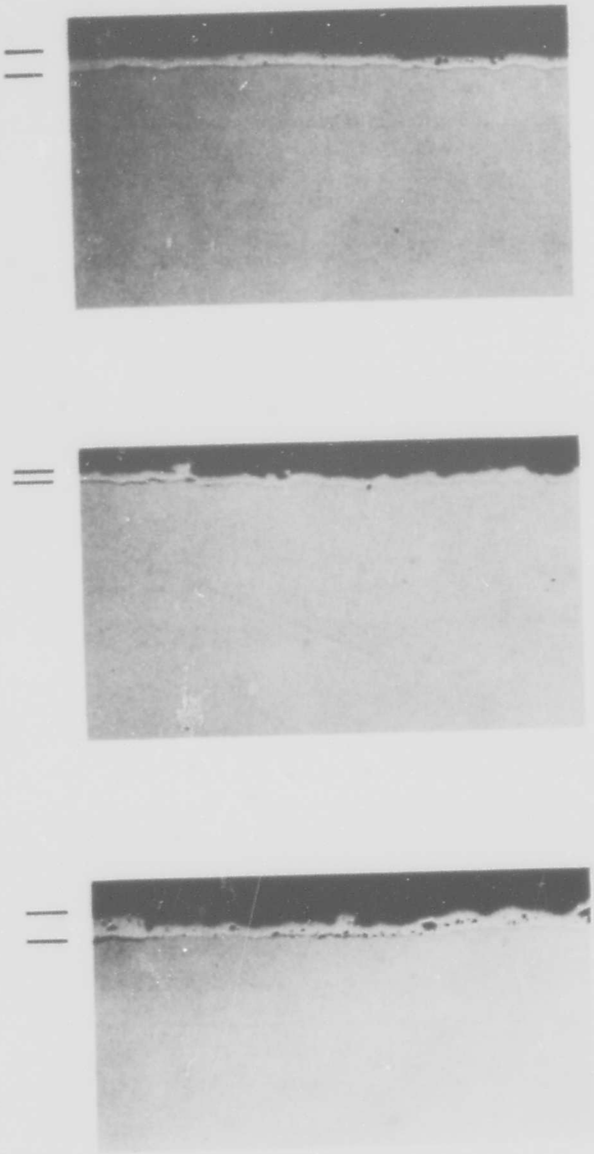


Figure 46 Weight Gain Data for Siliciding of Mo-CrTi and Mo-V-CrTi Precoated Columbium Alloy Cb-752.

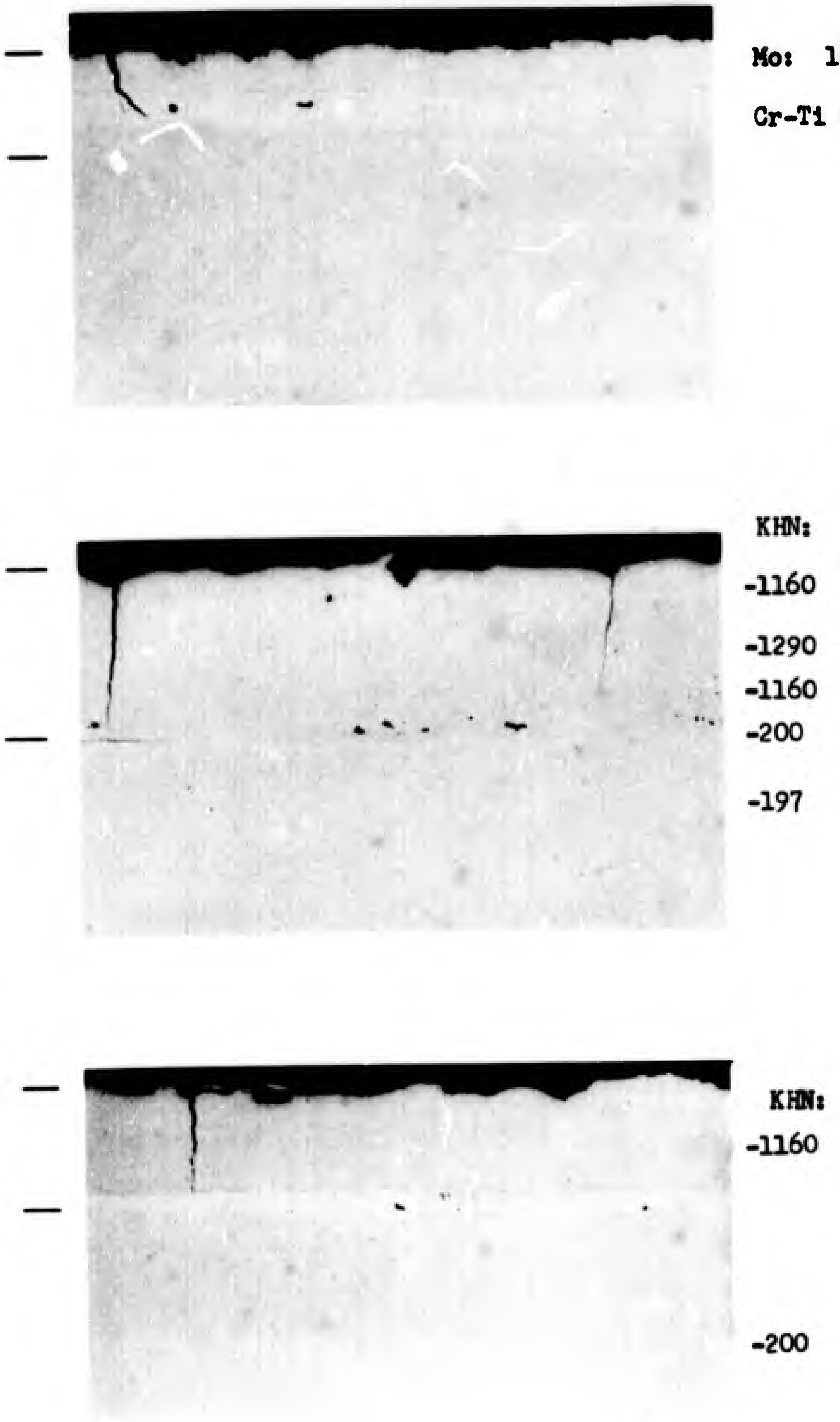


C5

A3, D3

B3, C3

Figure 47 CVD Deposited Molybdenum on Cb-752. 250X



Mo: 10.5 mg/cm^2
Cr-Ti Run 159

Mo: 14.3 mg/cm^2
Cr-Ti Run 159
Si Run 164

Mo: 9.3 mg/cm^2
Cr-Ti Run 159
Si Run 162

Figure 48 Microstructures of Mo-CrTi and Mo-CrTi-Si Coated Cb-752. 250 X

TABLE XXI

PHASE II OXIDATION RESULTS FOR THE Mo-CrTi-Si SYSTEM ON Cb-752

	mg/cm^2			Oxidation Life,[a] Hr.			
Code	Mo	CrTi	Si	1600°F	2000°F	2200°F	2400°F
A2	6.7	18.1	12	183,>575	>283	-	152,246
B2	3.1	18.1	18.8	127,471	-	145,145	139,160^{s}
A1	9.9	14.4	12	79,103	99,251	-	>312,>305
B1	9.3	18.1	18.8	46, 575	-	329,>329	177,>312
B3	10.5	18.1	12	47,49	171,171	-	139^{s},139^{s}
C1	13.4	14.4	12	183,255 [b]	-	>329	>312,>312
D1	13.7	18.1	12	391,>575	-	77^{s}	>305,>305
A3	14.3	18.1	18.8	23,23	19,43	-	77,48,77

---

a. Failures: s-surface; b-surface and edge; unmarked - edge.
b. Failed in stamp mark.

the limits investigated. An oxidation life in excess of 300 hours was obtained at 1600° - 2400°F. Photomicrographs of the exposed coatings, and substrate hardness data, are presented in Figure 49. The preferred composition appeared to be

15Mo-18CrTi-12Si

with a Cr-Ti: Si ratio of 1.3 - 1.5. Electron probe analyses of untested and oxidized coupons are presented in Section 6.8.

6.4 THE Mo-V-CrTi-Si SYSTEM

The nominal compositions selected for coating composition investigation were:

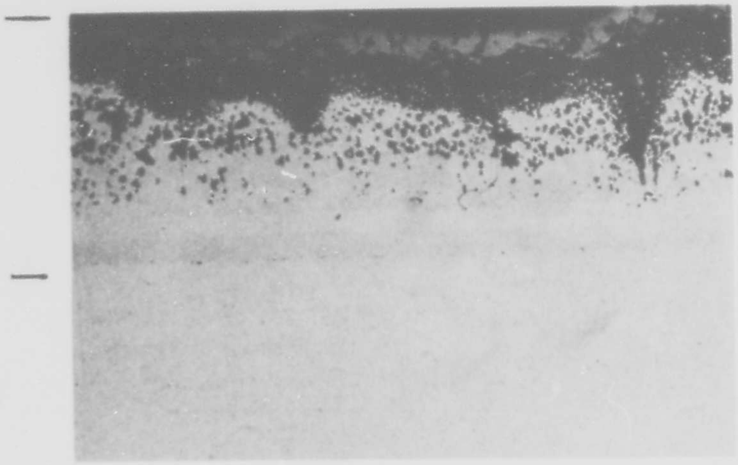
mg/cm^2			
Mo	V	Cr,Ti	Si
5	3	18	15
15	3	18	15
5	7	18	15
10	7	18	12
10	7	18	12
15	7	18	15
5	12	18	15
15	12	18	15

Pack coating parameters are summarized in Table XX, and the molybdenum precoating runs were discussed in the previous section.

The vanadium was applied in three runs (Nos. 151, 152, and 153). One sample run (No. 150) was made prior to the coating runs to determine the effect of molybdenum precoating on vanadium weight gain. This run (2200°F for 2 hours) showed that the amount of molybdenum in the precoating had a slight effect on vanadium transfer. The larger the molybdenum content, generally the larger was the vanadium weight gain, Figure 50.

A Cr-Ti sample run (No.152) was made on the Mo-V precoated coupons to determine the effect of precoating on Cr-Ti weight gain. No effect of Mo or V content on Cr,Ti weight pick-up was discernible. The Mo-V precoated coupons were Cr-Ti coated in Run 158. Weight gain data for the Cr-Ti coating of the Mo-V precoated coupons was shown previously in Figure 45 as a function of time. The Mo-V precoated coupons gained more weight (Cr-Ti) than either the molybdenum precoated or uncoated specimens.

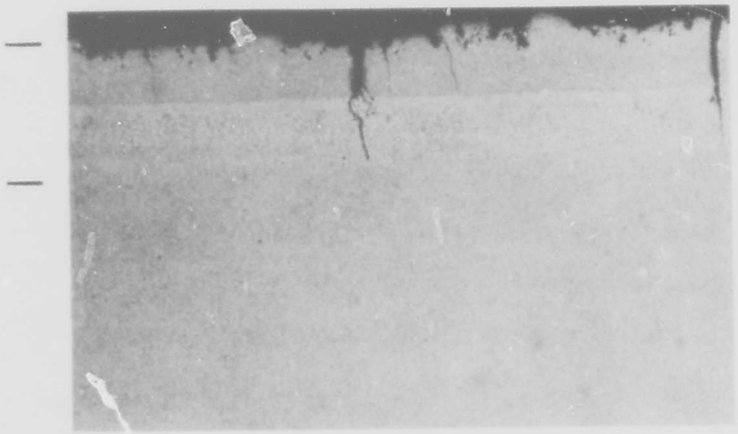
The Mo-V-CrTi precoated coupons were siliconized in Runs 162 and 165. No effect of molybdenum or vanadium content was evident,as shown previously in the weight gain vs diffusion time plot in Figure 46. Some coupons of each composition showed rough and spalling coatings after siliconizing, thus limiting



14Mo-18CrTi-12Si

-193 KHN

> 305 Hr at 2400°F



14Mo-18CrTi-12Si

-194 KHN

> 574 Hr at 1600°F

Figure 49 Photomicrographs of Exposed Phase II Mo-CrTi-Si Coatings on Cb-752. 100 X

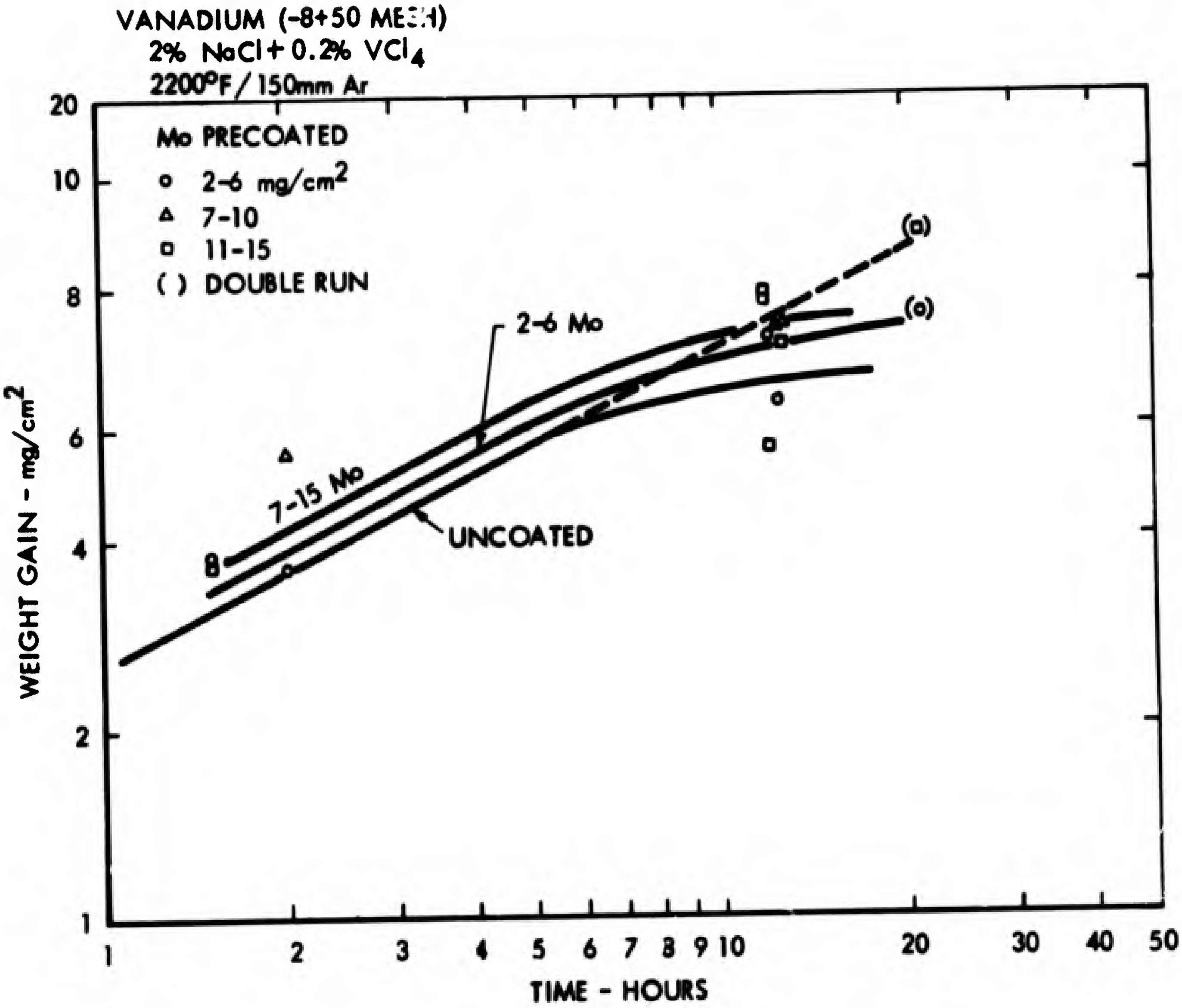


Figure 50 Weight Gain Data for Vacuum Pack Vanadizing of Molybdenum Precoated Columbium Alloy Cb-752 at 2200°F.

the number of available coupons with adherent coatings for testing. The spalling of the silicide layer was associated with the presence of vanadium, since no spalling was noted for the Mo-CrTi precoated coupons silicided in the same pack run (No. 160). The spalling was probably the result of the line defects noted in Figure 52.

Microstructures after each coating sequence are shown in Figures 47, 51 and 52. A hardness survey of the completed coating is presented in Figure 52. Porosity was noted after application of the Cr-Ti coating, Figure 52. In addition, the Mo-V-CrTi diffusion layer contained cracks. The silicide layer also contained cracks, and line porosity was noted at the Mo-V interface as mentioned earlier, Figure52.

Cyclic oxidation data are presented in Table XXII. An oxidation life in excess of 500 hours at 1600°F and 300 hours at temperatures over 2000°F was obtained. A photomicrograph of an exposed coating along with substrate hardness is presented in Figure 53. These data suggested that a medium vanadium content, medium to high molybdenum, and high silicon were conducive to promoting long coating life.The preferred coating composition was

10-14Mo-8V-20CrTi-12Si

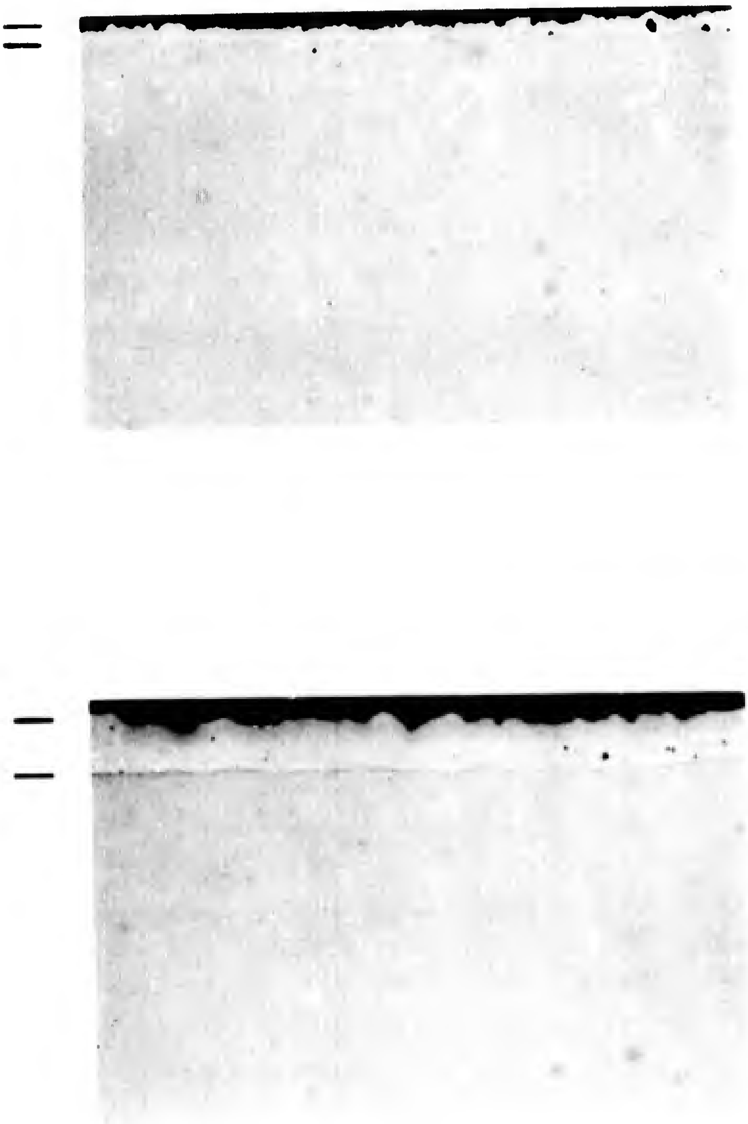
with a CrTi: Si ratio of 1.6 to 1.7 Electron probe analyses of both as coated and oxidized samples are presented in Section 6.8. Since this system offered no apparent advantage over the Mo-CrTi-Si system,involved an additional coating step and presented spalling problems during siliconizing, no further evaluation was conducted.

6.5 THE Ti-Al SYSTEM

The nominal compositions selected for coating investigation were:

mg/cm^2 Ti	mg/cm^2 Al
20	4
20	8
30	4
30	8

The titanizing was performed in runs 120 and 122 and the aluminizing in Runs 127 and 128, Table XXIII. Representative microstructures after each coating step are shown in Figures 54 and 55. The specimens were rough (particle sinter points) after titanizing as mentioned in previous sections. Aluminizing, performed in a 56 w/o Cr-44 w/o Al powder pack, was insensitive to prior titanium content, Figure 56. In fact, uncoated Cb-752 showed weight gains similar to titanized material. The slope for the weight gain data as a function of time was less than predicted by a diffusion controlled process, which may reflect some loss of



Mo: 2.7 mg/cm^2

V Run 151

Mo: 11.7 mg/cm^2

V Run 152

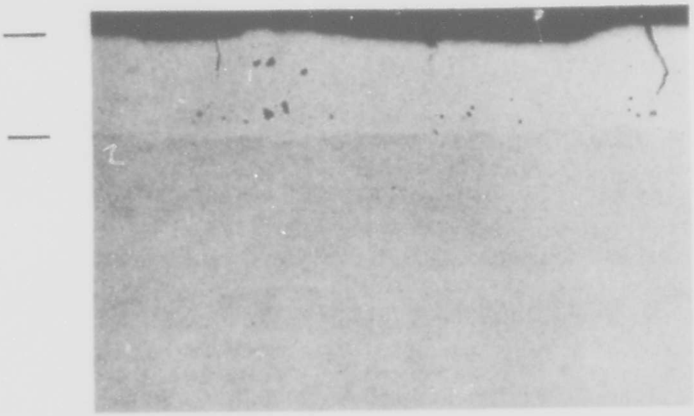
— KHN: 168

Figure 51 Microstructure of Mo-V Coated Cb-752. 250 X

Mo: 11.6 mg/cm^2

V Run 152, 153

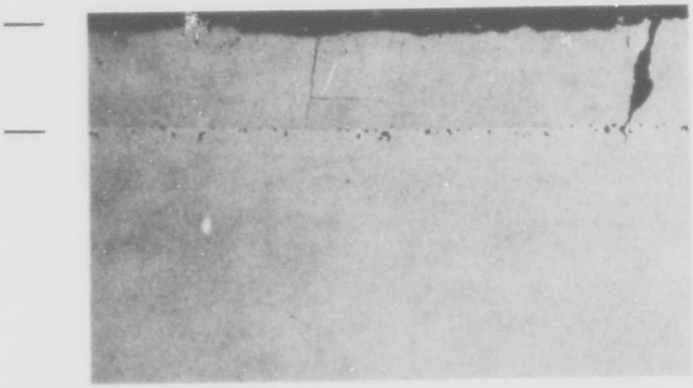
Cr-Ti Run 158, 160



Mo: 4.2 mg/cm^2

V Run 152, 153

Cr-Ti Run 158, 160



KHN:

-1160
-1220
-500
-415
-220
-210

-200

Mo: 11.7 mg/cm^2

V Run 152

CrTi Run 158, 160

Si Run 162

Figure 52 Microstructures of Mo-V-CrTi and Mo-V-CrTi-Si Coated Cb-752. 250 X

TABLE XXII

PHASE II OXIDATION RESULTS FOR THE Mo-V-CrTi-Si SYSTEM ON Cb-752

	mg/cm^2				Oxidation Life^a, Hr.			
Code	Mo	V	CrTi	Si	1600°F	2000°F	2200°F	2400°F
C2	2.7	3.8	20.5	12	>575(2)	19	-	260,216
D2	5.5	8.3	20.5	12	335,>575	-	77^s	>305,>305
C7	4.2	9.1	20.5	12	>575(2)	-	> 329	>305,>305
D3	10.4	8.6	20.5	9.7	>575(2)	> 283	-	78, 98
B5	9.1	8.7	20.5	12	>575(2)	>283	-	>305,>305
C3	13.2	3.6	20.5	12	103,495	-	> 329	>305,>312
A5	12.7	8.0	20.5	9.7	391,>575	171	-	50,75,32
C5	11.7	9.5	20.5	12	>575(2)	-	>329	>305,296
D5	11.6	12.3	20.5	12	>575(2)	>283	-	75,85,>312

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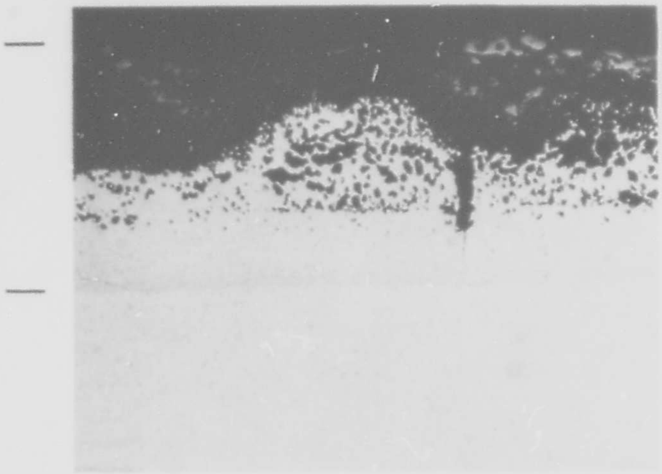
a. Failures: s-surface; b-surface and edge; unmarked-edge.

b. ( ) Indicates number of specimens with same exposure time.



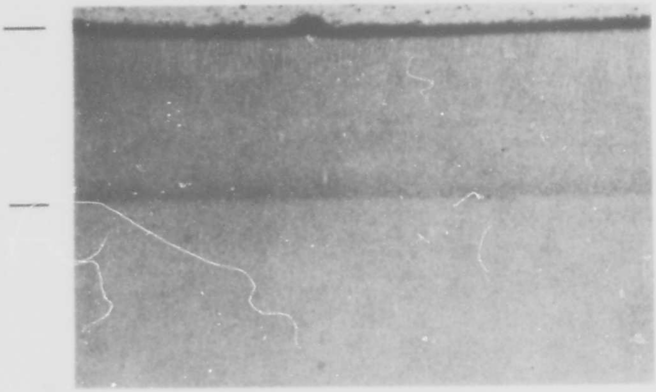
>305 Hr at 2400°F

Figure 53 Photomicrograph of Exposed Phase II Mo-V-CrTi-Si Coating on Cb-752.

TABLE XXIII

COATING DATA FOR Ti-Al, Ti-Al-Si and Ti-Si SYSTEMS FORMED ON COLUMBIUM ALLOY Cb-752

Run No.	Pack Composition		Pack Conditions			Precoating		Average Weight Gain mg/cm^2	Remarks
	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.		
116	Ti	1KF	2000	13	150Ar	-	-	30.1	
120	Ti	1KF	2000	13	150Ar	-	-	30.3	
122	Ti	1KF	2000	7-1/2	150Ar	-	-	22.3	
125	56Cr-44Al	1KF	1900	4	150Ar	22Ti 30Ti	122 120	4.4	
127	56Cr-44Al	1KF	1900	4	150Ar	22,30Ti	122,120	4.1	
128	56Cr-44Al	1KF	2100	10	150Ar	22Ti 30Ti	122 120	10.7 11.8	
133	Ti	1KF	2000	7	150Ar	-	-	24.9	
134	56Cr-44Al	1KF	1900	1-1/2	150Ar	24.9Ti	133	3.3	

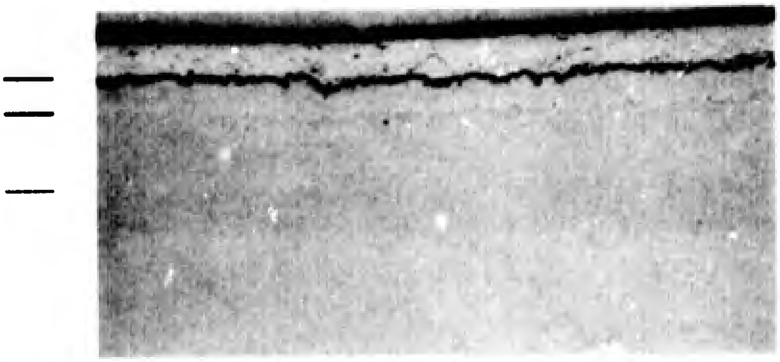


Ti Run 120

Ti Run 122

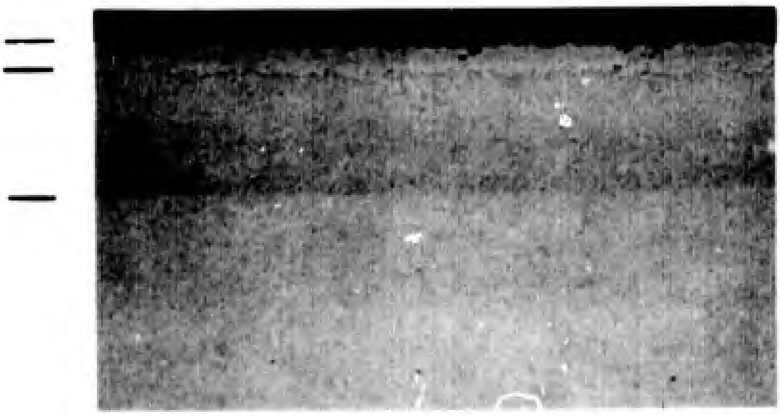
Al Run 128

Figure 54 Microstructures of Ti and Ti-Al Coated Cb-752. 250 X



Ti Run 122

Al Run 127



Ti Run 142

Al Run 183

Figure 55 Microstructure of Ti-Al Coating on Cb-752. 250 X

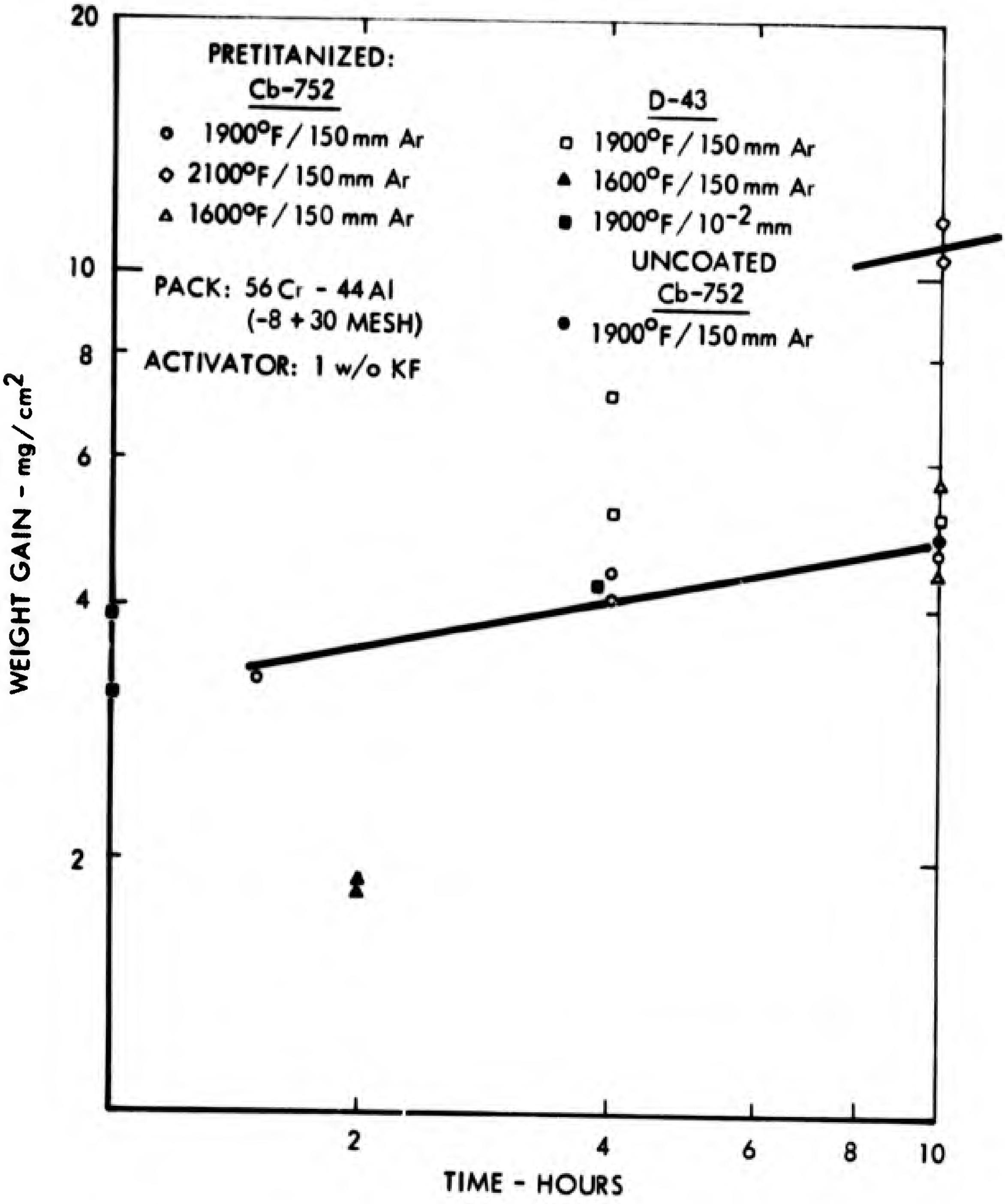


Figure 56 WEIGHT GAIN DATA FOR ALUMINIZING OF PRETITANIZED CB-752 AND D-43.

titanium by reaction with the activator.

Cyclic oxidation test results at 1600°F are presented in Table XXIV.

TABLE XXIV

CYCLIC OXIDATION DATA FOR THE Ti-Al COATING SYSTEM ON CB-752

Code	mg/cm² Ti	mg/cm² Al	Oxidation Life - hrs. 1600°F
E3	22.3	4.1	40, 64, 64, 64, 64, 64
F3	22.3	10.7	96, 96, 120, 144, 200, 200
G3	30.1	4.1	64, 64, 64, 96, 96, 96
H3	30.1	11.8	96, 96, 96, 120, 120, 200

The specimens generally failed at titanium sinter points where the aluminide layer was thin and irregular. Contrary to previous results on columbium alloy D-43, the titanium content had little effect on specimen life for the Phase II coating on columbium alloy Cb-752. On the other hand, the greater aluminum contents yielded longer oxidation protection at 1600°F. Results indicated that the Ti:Al ratio could vary between 2.6 to 5.4 and still yield oxidation life times from about 100 to 500 or more hours for Cb-752. Lifetimes for the Ti-Al system on D-43 were generally longer and ranged between 300 to 900 hours. The longer lifetimes were probably attributable to a more uniform aluminide layer (smaller influence of titanium sintering). Further improvement in the oxidation resistance of this system could be obtained by elimination of the titanium sinter points.

The TiAl system (25Ti-5Al) formed by these vacuum pack techniques was evaluated as a potential blade root coating on columbium alloy Cb 132M by Pratt and Whitney Aircraft (14). Static oxidation tests were performed at 1300 and 1600°F. The performance was good, with no failures observed in 400 hours of exposure at both temperatures.

6.6 THE Ti-Al-Si System

The nominal compositions selected for coating investigation were:

mg/cm² Ti	mg/cm² Al	mg/cm² Si
20	2	2
20	2	4

The titanizing was performed in Runs 122 and 133, and the aluminizing in Runs 127 and 134, Table XXIII. First attempts to siliconize this group of specimens in a pure silicon pack were unsuccessful owing to spalling of the coating. However, siliciding (Run 144) of the Ti-Al precoated coupons in a sample run consisting of a 90 w/o Al_2O_3-Si mixture at 2250°F for 1-1/2 hours (1.5 mm pressure) produced adherent coatings, Table XXV. The Ti-Al precoated coupons were therefore siliconized in a 90 w/o Al_2O_3-Si pack in Runs 161 and 163 Table XXV. The coatings were adherent, and a representative microstructure is shown in Figure 57 along with a hardness traverse through the coating.

Cyclic oxidation tests are summarized in Table XXVI. These coupons generally failed at titanium sinter points similar to the Ti-Al coated specimens. Although the results were inconsistent, the oxidation life appeared to depend more upon the quality of adherence of the silicide layer than the amount of silicon. Previously for the D-43 substrate, introduction of Si into the Ti-Al system shortened oxidation life at 1600°F. However, for the Cb-752 substrate, introduction of Si increased oxidation life over the straight Ti-Al system. A larger aluminum content again produced a longer oxidation life similar to the behavior observed for the Ti-Al system. The preferred composition was close to 22Ti-4Al-1Si since no failures were observed in over 500 hours at 1600°F for the five specimens tested. A photomicrograph of this system after exposure is presented in Figure 58, along with substrate hardness values.

6.7 THE Ti-Si SYSTEM

The nominal compositions selected for coating optimization were:

mg/cm^2	
Ti	Si
20	3
20	6
30	3
30	6

The titanizing was performed in Runs 120, 122 and 133, Table XXIII. Considerable difficulty was experienced in siliconizing the pretitanized Cb-752 coupons even in a large pack. Siliconizing resulted usually, though not always, in flaky and spalled coatings as discussed previously. Siliconizing parameters are summarized in Table XXV.

The Ti-Si microstructure is presented in Figure 57 along with a hardness traverse through the coating. Line porosity evident at the silicide interface.

TABLE XXV

COATING DATA FOR THE TiSi, and Ti-Al-Si SYSTEMS FORMED ON COLUMBIUM ALLOY Cb-752

	Pack Composition		Pack Conditions			Precoating			
Run No.	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.	Average Weight Gain mg/cm^2	Remarks
130	Si	1/2KF	2000	1	10^{-2}	22,30Ti 22 Ti,4Al	120,122 122,127	4.7	Large pack; adherent coatings.
139	Si	1/2KF	2000	1/4	10^{-2}	25,i	133	-	Large pack; rough and flaking coating.
140	Si^a	1/2KF	2000	38 min	10^{-2}	22Ti,4Al	122,127	5.8	Large pack: coating looks O.K.
						25Ti	133	7.5	Flaking coatings.
						30Ti	120	5.8	Flaking coatings.
141	Si^a	1/2KF	2000	1-1/2	10^{-2}	22Ti	122	5.8	Same as 139.
						30Ti	120	10.0	
142	Ti	1KF	2000	6	150Ar	-	-	20	Replace 1-3 specimens.
143	56Cr-44Al	1KF	1900	1	150Ar	20Ti	142	2.1	
144	10Si+90 Al$_2$0	1KF	2250	1-1/2	1.5	22Ti,40Al	122,127	3.3	Coating O.K.
						22Ti	133	5.0	Coating rough and flaking
						30Ti	120	5.0	"
145	Si^a	1/2KF	2050	5	10^{-2}	20Ti,2Al	142,143	6.9	Same as 140.
						22Ti,4Al	122,127	7.2	(O.K.)
						25Ti	133	8.0	
						22Ti	122	8.0	
						30Ti	120	8.3	

TABLE XXV
(Continued)

Run No.	Pack Composition		Pack Conditions			Precoating		Average Weight Gain mg/cm^2	Remarks
	Pack	Activator w/o	Temp. °F	Time Hrs.	Pressure mm	Elements mg/cm^2	Run Nos.		
155	Si[a]	1/2KF	2050	3	10^{-2}	22Ti	122	6.8	Large pack
						30Ti	120	7.3	
161	10Si+90 Al_2O_3	1KF	2250	3/4	1.5	20Ti,2Al	142,143	3.0	
163	10Si+90 Al_2O_3	1KF	2250	1-1/4	1.5	20Ti,4Al	122,127	1.1	
						25Ti	133	2.5	Rough flaky coatings.
						30Ti	120	3.4	Rough flaky coatings.

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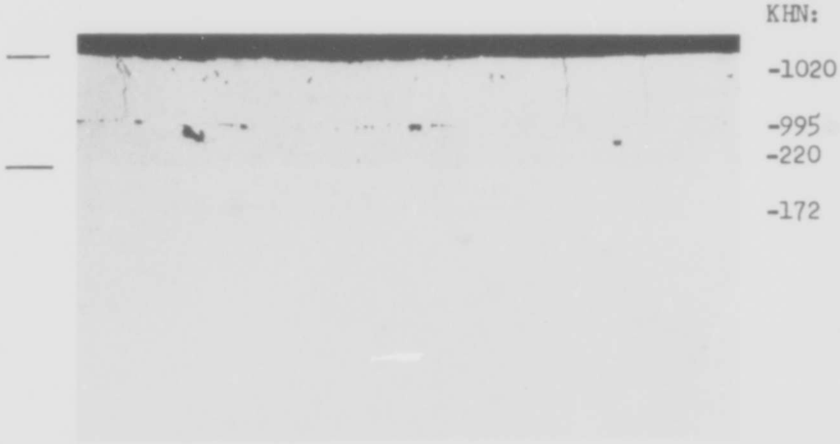
a. Activator mixed in bottom of pack.



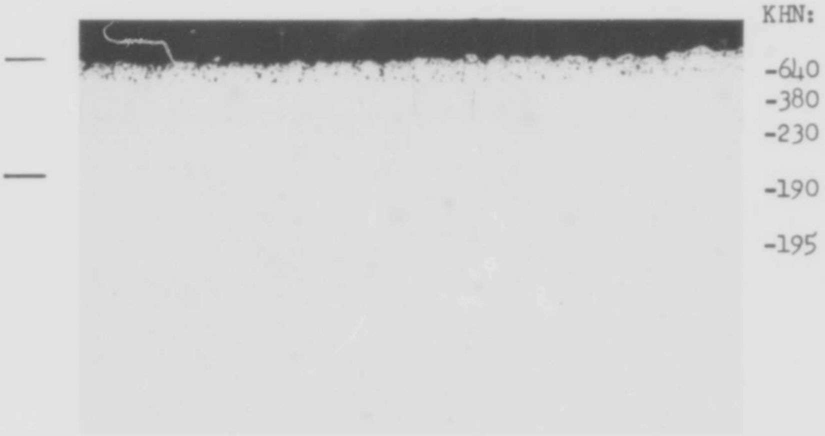


Figure 57 Microstructures of Ti-Si and Ti-Al-Si Coatings on Cb-752. 250 X

TABLE XXVI

PHASE II OXIDATION RESULTS OF THE Ti-Al-Si SYSTEM ON Cb-752

mg/cm^2			Oxidation Life[a], Hrs.	
Ti	Al	Si	1600°F	Coating Run Nos.
22	4	4.7	56	122,127,130
22	4.1	5.8	232	122,127,140
22	4.1	3.3	> 693	122,127,144
22	4.1	7.2	>866	122,127,145
20	2.1	3.0	79,207,335 >575(3)	142,143,161
22	4.1	1.1	>575(5)	122,127,163

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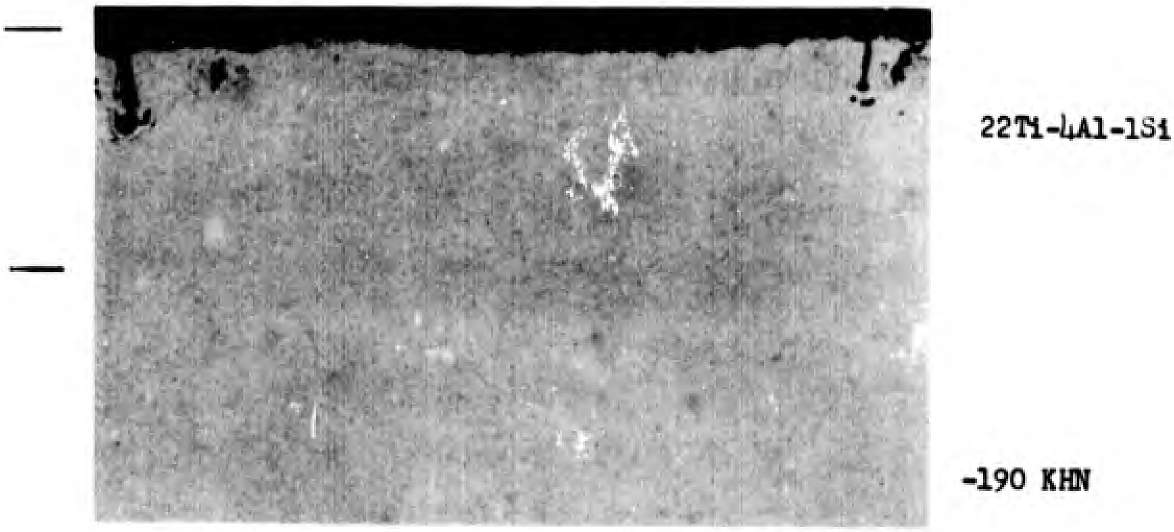
a. Failures: s-surface; b-surface and edge; unmarked-edge.
b. ( ) Indicates number of specimens with the same exposure time.



> 866 Hr at 1600°F

Figure 58 Photomicrograph of Exposed Phase II Ti-Al-Si System on Cb-752.

TABLE XXVII

PHASE II OXIDATION RESULTS OF THE Ti-Si SYSTEM ON Cb-752

mg/cm^2		Oxidation Life, Hr.	
Ti	Si	1600°F	Coating Run Nos.
22	5	56	122,130
22	5	412	122,130
30	5	412	120,130
30	4	412	120,130
22	8.0	264	122,145
30	8.3	240	120,145
22	7.3	8,8,8,16,16,16	122,155
30	6.8	32,32,32,32,32,32	120,155
24.9	2.5	24,24,24,24,24,24	133,163
30	3.4	24,24,24,24,24,24	120,163

Cyclic oxidation data are presented in Table XXVII. These, in general, showed poor oxidation life for the Ti-Si coated Cb-752 samples, primarily because the silicide layer was not adherent. Based on the difficulties associated with siliconizing the pretitanized substrate, this system was not pursued in subsequent experimentation.

6.8 MICROPROBE ANALYSES OF PHASE II COATINGS

Microprobe analyses were conducted on as-applied coatings and on coatings which were exposed in cyclic oxidation tests at 2400°F. The analyses were performed on a Norelco-Phillips electron microprobe analyzer, Model AMR/3, capable of simultaneously scanning two elements over a given traverse. The coupons subjected to analysis were selected on the basis of oxidation performance from each group (V-Al-CrTi-Si, V-CrTi-Si, Mo-CrTi-Si and Mo-V-VrTi-Si) formed within a range of coating compositions. Scans for seven elements, Cb, Si, Ti, Cr, Al, Mo and V, were made. Appropriate pure element standards were included in each mount to permit semi-quantitative values to be calculated for each element. The measured relative intensities as a function of distance from the coating surface are presented in Figures 59 through 62 for the as-applied coatings, and in Figures 63 through 66 for the coatings after 2400°F exposure. These traces provide a semi-quantitative picture of the distribution of the elements in the coatings. They are not suitable, however, for accurate quantitative interpretation. The electron bean scanning images as a rule were not recorded on the identical areas shown in the photomicrographs.

Corrections for matrix absorption, fluorescence and atomic number were calculated only for the V-CrTi-Si system. For the as-applied coating at 1.5 mils from the coating surface the corrected composition based on weight was: 53% Si; 30.3% Cr, 3.0% Ti, 8.4% V and 4.9% Cb. This corresponded to the phase $MeSi_2$. At 2.5 mils from the surface the corrected composition was: 38% Si, 19% Cr, 1.7% Ti, 7% V and 32% Cb(bal). The phase based on composition was Me_2Si_3. This phase is not reported in the literature for V-Cr-Ti modified silicides, however, many compounds are possible in a complex system such as this. At 3 mils from the surface the composition was: 36.8%Si, 22.5% Cr, 2.7% Ti, 20.4% V and 17.6% Cb (bal). The probable phase present was again Me_2Si_3. At 3.4 mils the composition was: 3.5% Cr, 4.9% Ti, 12.6% V and 78.9% Cb (bal).

Comparison of the coatings prior to and after exposure at 2400°F showed that coating element loss occurred by both element diffusion into the matrix and by conversion to oxide. Thus, of the three layers visible in the etched photomicrograph of the V-CrTi-Si coating shown in Figure 59, the first two layers were silicides and the third light layer at the substrate coating interface was a columbium rich phase containing Cr, Ti and V. Silicon was the element which showed the greatest penetration of the columbium alloy matrix during exposure of each coating system, Figures 63 through 66. For the V-CrTi-Si system, after a 294 hour exposure at 2400°F at 5 mils from the surface corrected silicide composition corresponded to 14.6% Si and 80.4% Cb.

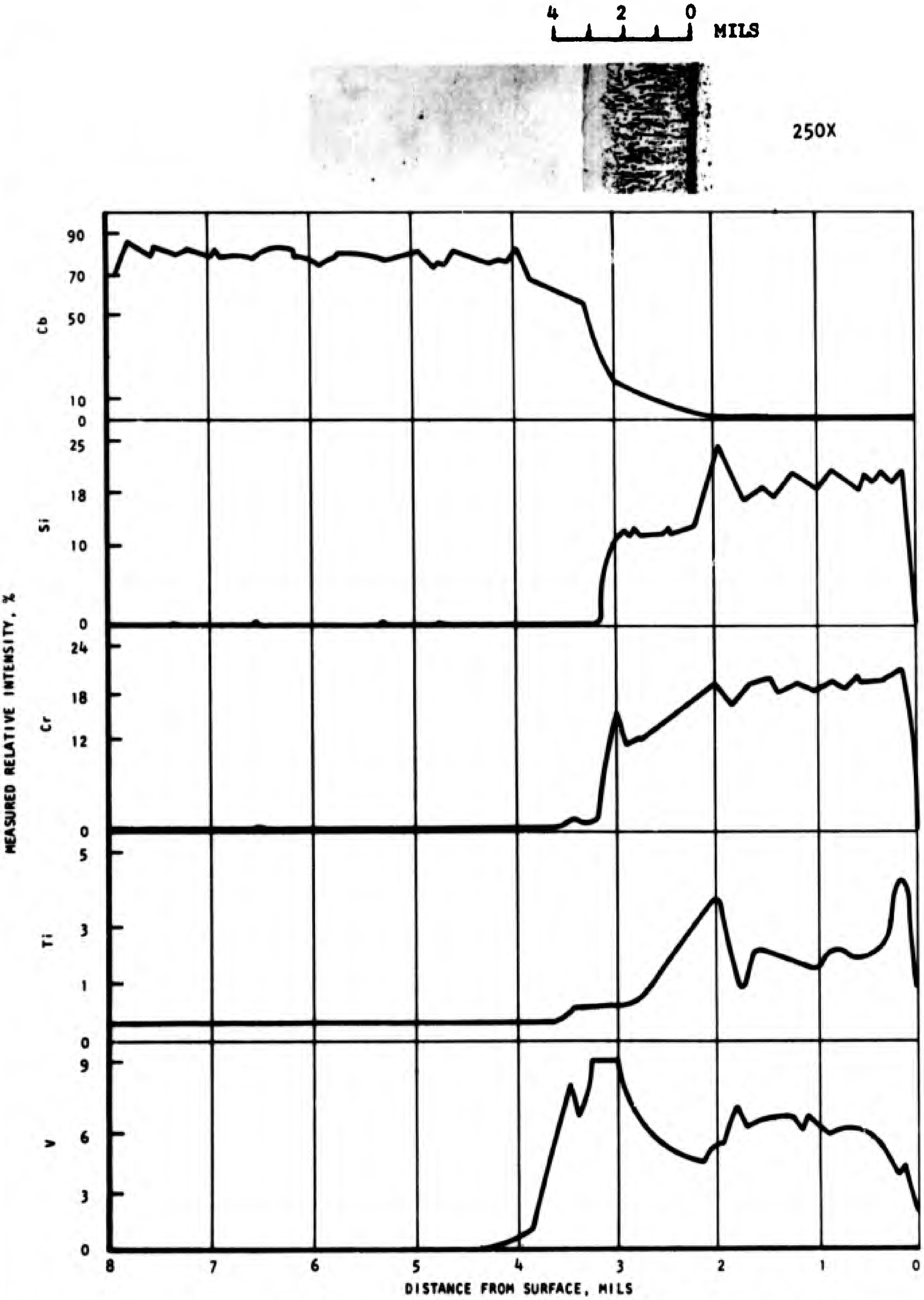


FIGURE 59. ELECTRON MICROPROBE ANALYSIS OF 7V-21CrTi-14Si COATING SYSTEM ON Cb752.

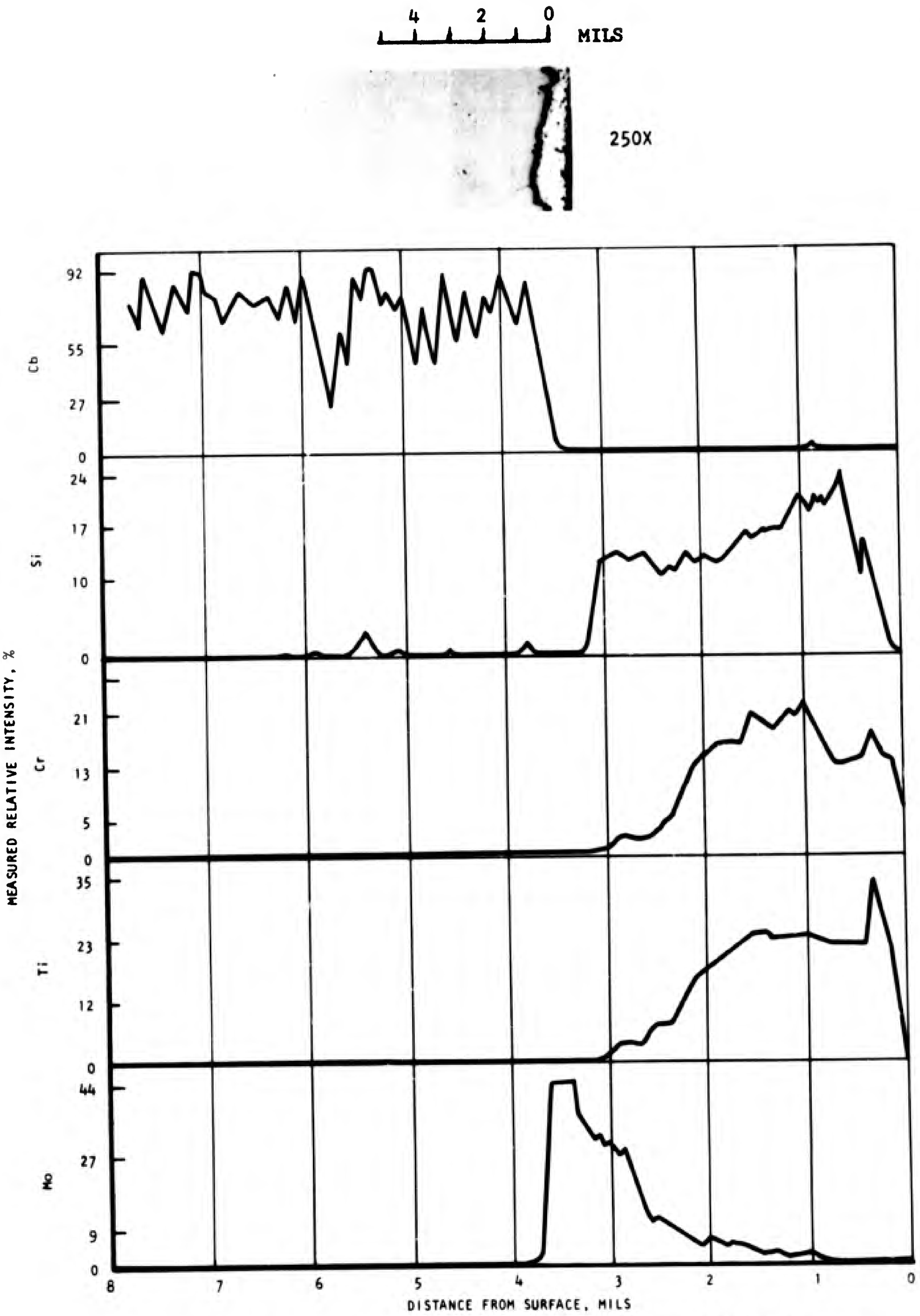


FIGURE 60. ELECTRON MICROPROBE ANALYSIS OF 10Mo-14CrTi-12Si COATING SYSTEM ON Cb752.

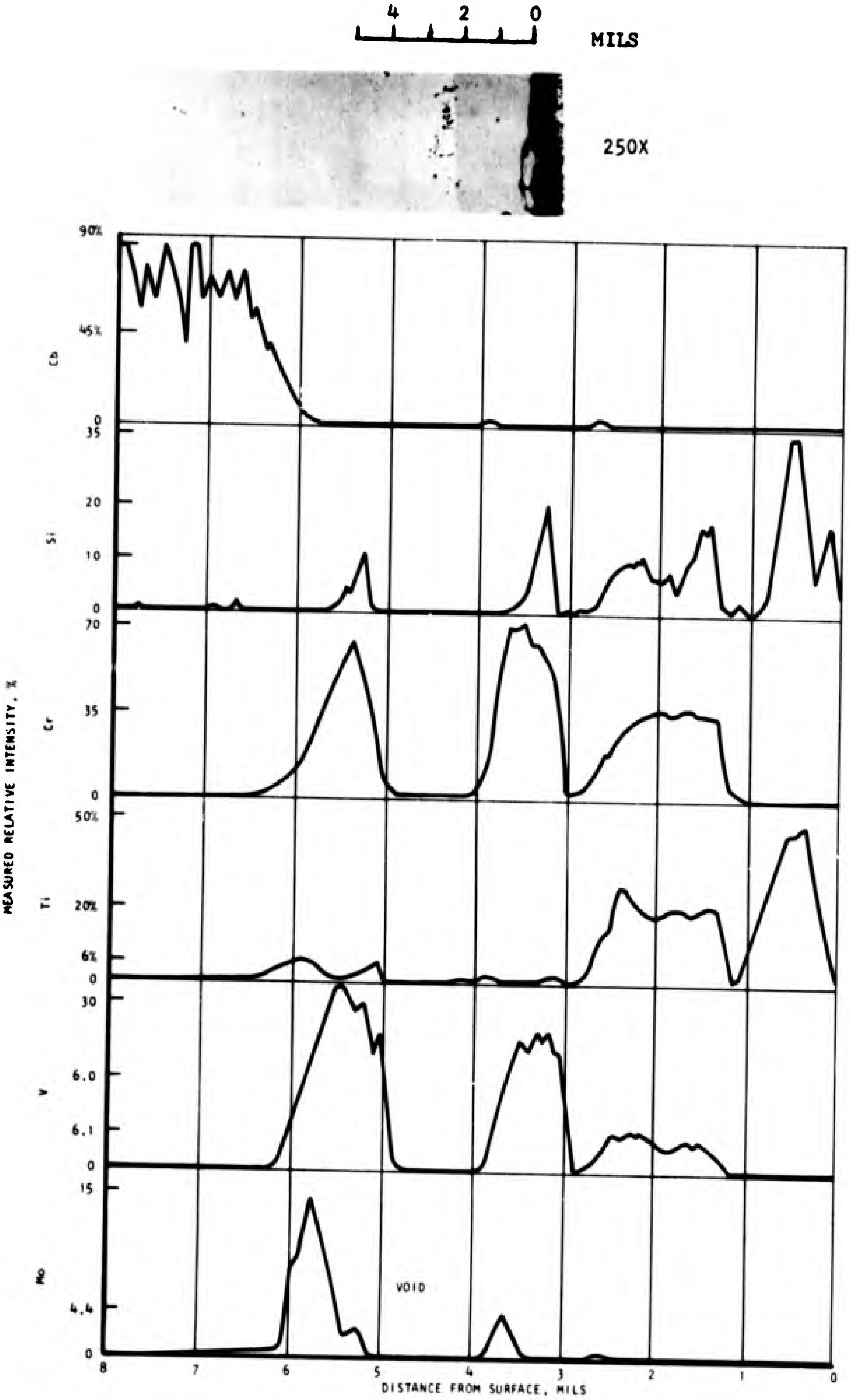


FIGURE 61. ELECTRON MICROPROBE ANALYSIS OF 4Mo-9V-18CrTi-12Si COATING SYSTEM ON Cb752.

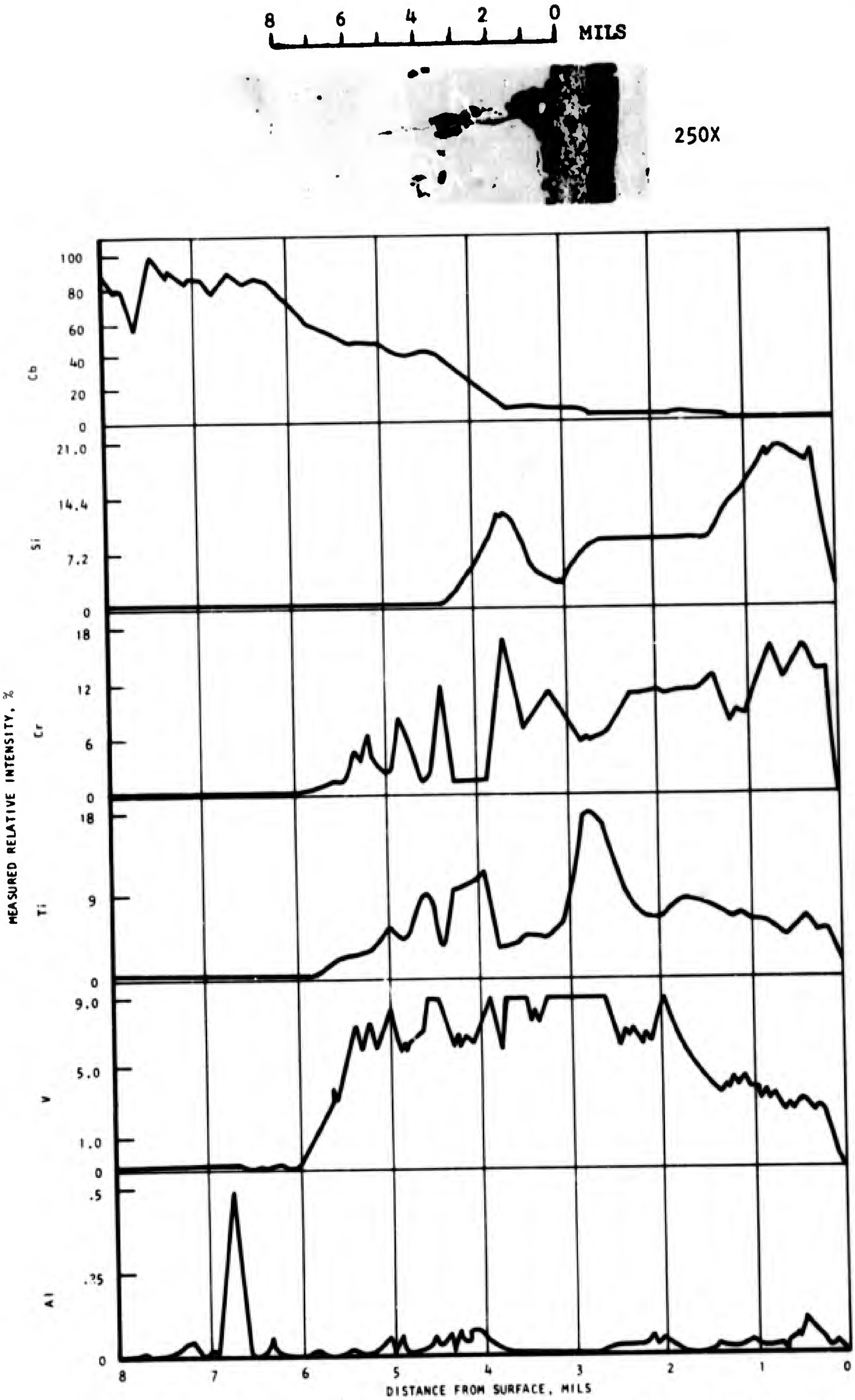


FIGURE 62. ELECTRON MICROPROBE ANALYSIS OF 9.5V-6Al-15CrTi-16Si COATING SYSTEM ON Cb752.

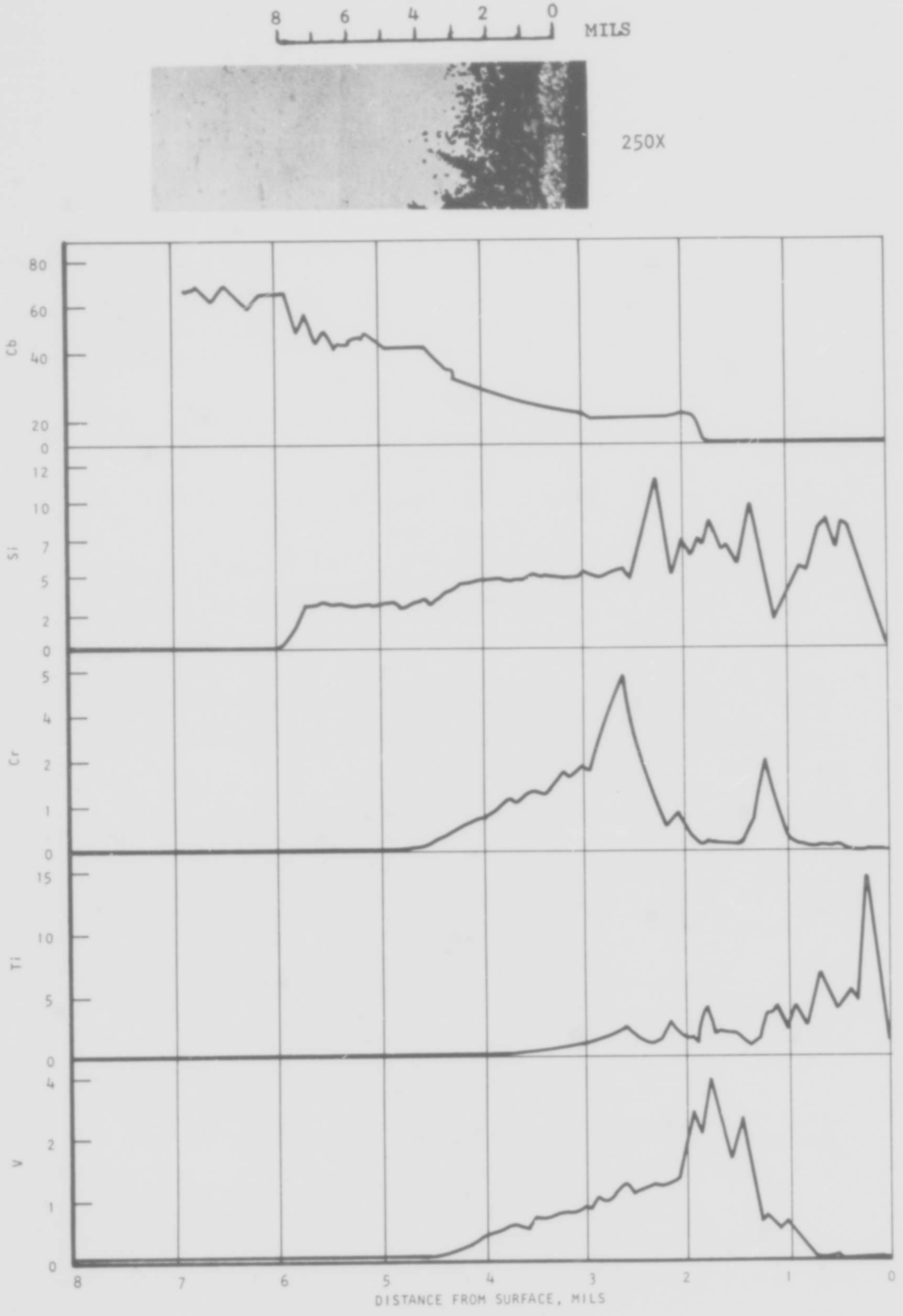


FIGURE 63. ELECTRON MICROPROBE ANALYSIS OF 7V-21CrTi-14Si COATING SYSTEM ON Cb752 AFTER A 294 HOUR CYCLIC EXPOSURE AT 2400°F.

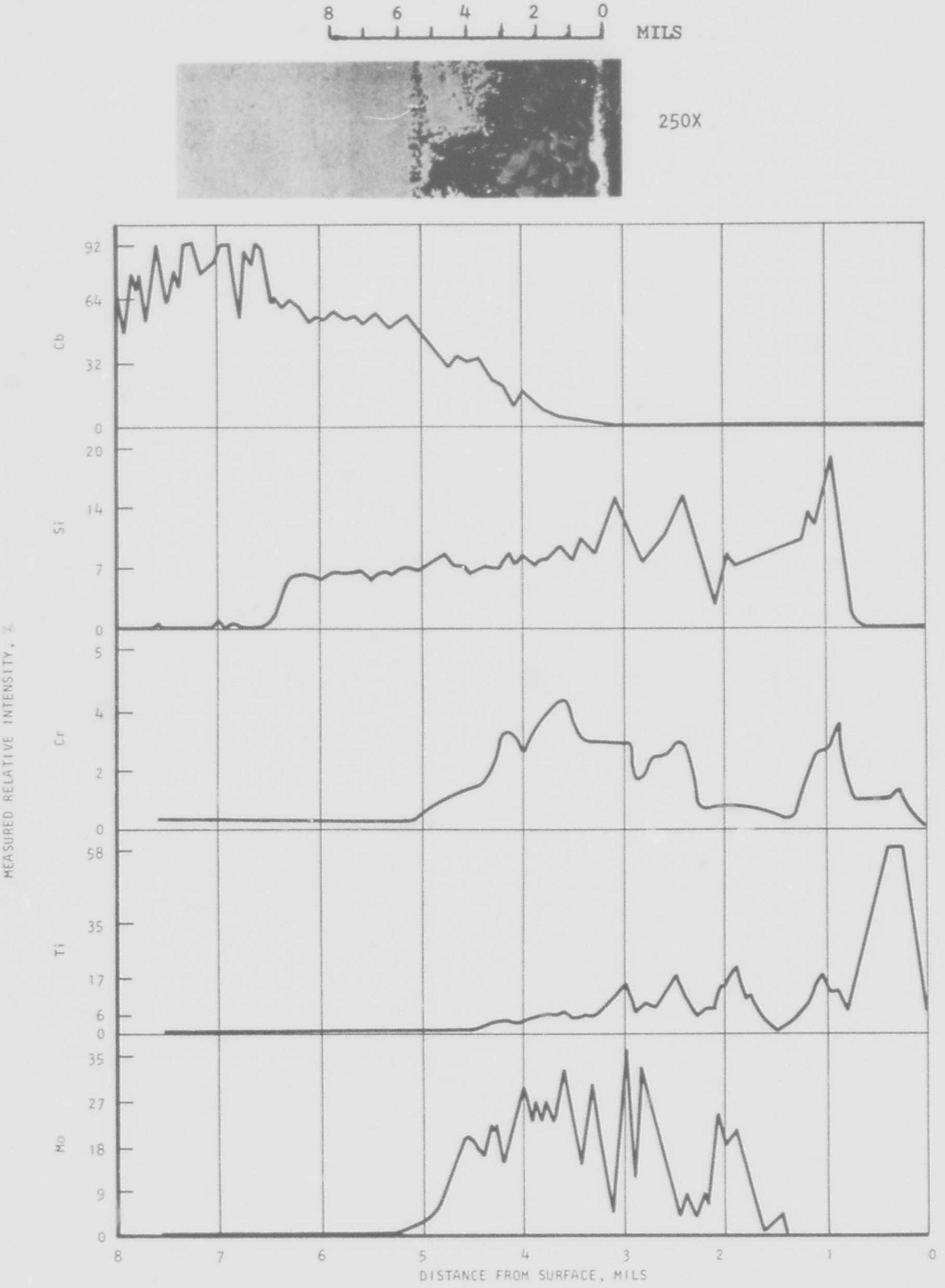


FIGURE 64. ELECTRON MICROPROBE ANALYSIS OF 10Mo-14CrTi-12Si COATING SYSTEM ON Cb752 AFTER A 300 HOUR CYCLIC EXPOSURE AT 2400°F.

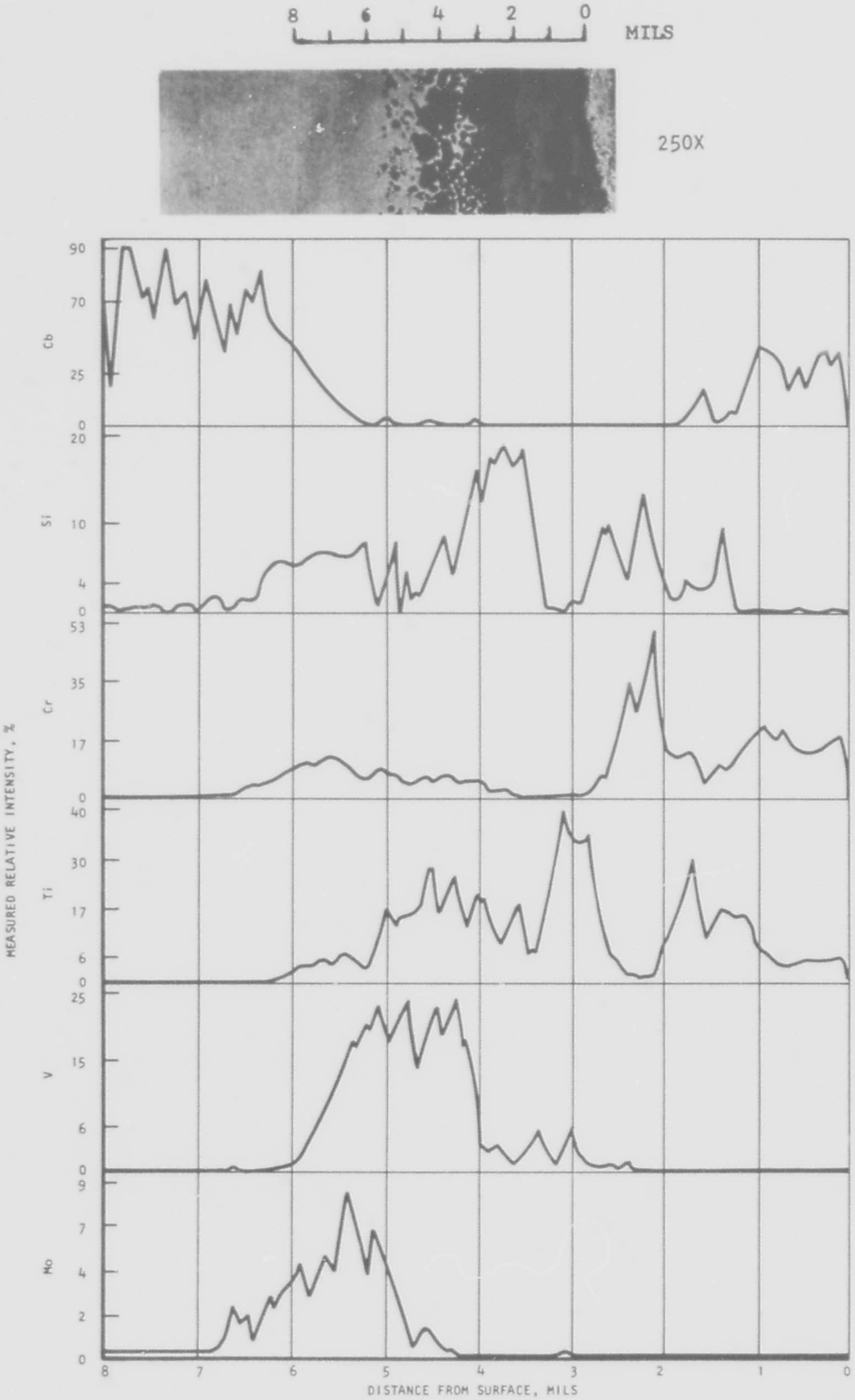


FIGURE 65. ELECTRON MICROPROBE ANALYSIS OF 4Mo-9V-18CrTi-12Si COATING SYSTEM ON Cb752 AFTER A 300 HOUR CYCLIC EXPOSURE AT 2400°F.

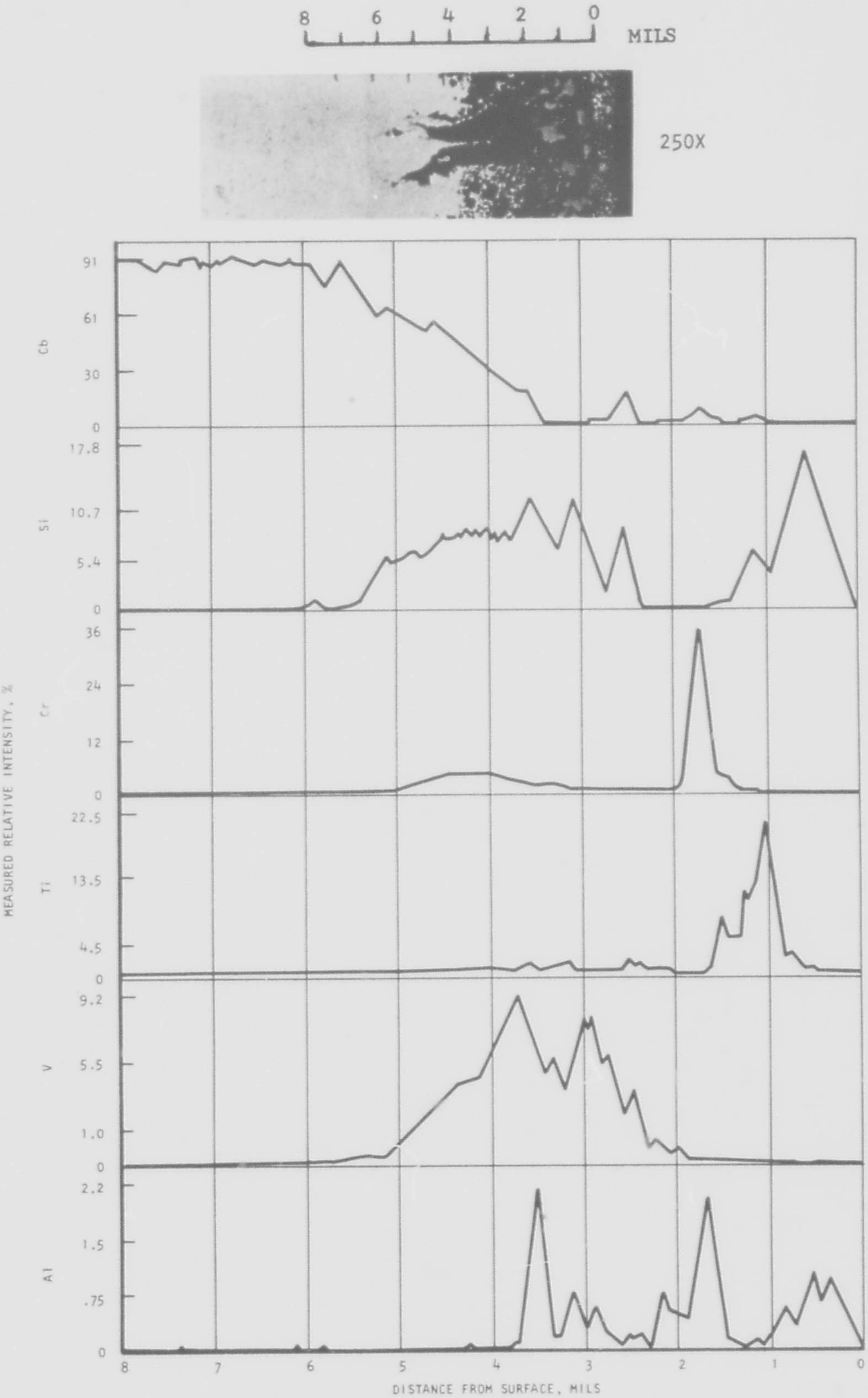


FIGURE 66. ELECTRON MICROPROBE ANALYSIS OF 9.5V-6Al-15CrTi-16Si COATING SYSTEM ON Cb752 AFTER A 280 HOUR CYCLIC EXPOSURE AT 2400°F.

The trace for the V-CrTi-Si coating system after exposure at 2400°F, Figure 63, showed the vaporization loss of chromium and vanadium from the coating surface. Both elements undoubtedly vaporized as oxides. The trace for the Mo-CrTi-Si system, Figure 64, showed that protection was offered at 2400°F by titanium and chromium oxides at the surface. No molybdenum was present in the surface oxide, which suggests this element was lost by vaporization as a volatile oxide. Silicon oxide was located below the surface oxides.

The trace for the Mo-V-Cr,Ti-Si coating after the 2400°F exposure, Figure 65, showed columbium, chromium.titanium and silicon oxides.Presence of columbium oxide indicates failure or imminent failure of the system. Molybdenum and vanadium were absent from the oxidized layers, due to vaporization.

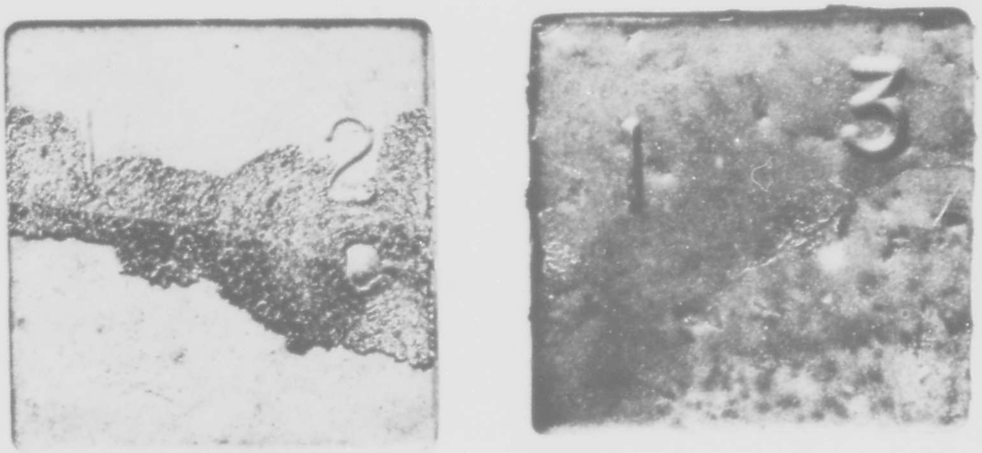
The trace for the V-Al-Cr,Ti-Si coating, Figure 66, showed that the surface oxide consisted of silicon and aluminum, probably a silicate. Below this surface oxide layer, the oxides of titanium, chromium and aluminum were formed. No vanadium or chromium were noted in the oxide layers, indicating loss of these elements by vaporization as oxides.

6.9 BALLISTIC IMPACT TESTING OF PHASE II COATINGS

Ballistic impact tests were conducted at room temperature and at 2000°F on some of the available systems. Impacting with a o.156 inch diameter steel pellet (total weight of pellet and pell ranged between 1.17 to 1.19 grams) was performed at a velocity of 340 ft/sec. This was the minimum velocity with which sufficient accuracy could be maintained to hit the test coupons. The energy of impact was 4.6-4.7 ft-lb.

Typical surface appearances after impact at room temperature are shown in Figures 67 and 68 and after impact at 2000°F in Figures 69 and 70. Specimens were of insufficient thickness (0.030 in) to prevent deformation effects on the reverse sides.As the photographs show, ballistic impact at the elevated temperature caused much less damage to the coating and substrate than impact at room temperature. Some coating spalling was notedin the areas impacted at 2000°F. However, impact at room temperature resulted in specimen cracking, particularly for the V-CrTi-Si, V-Al-CrTi-Si, CrTi-Si and Ti-Al-Si coating systems. In addition, coating flaking was evident on both the front and back sides of the specimens in the impact area. Substrate cracking was not evident for any of the systems containing a molybdenum precoating (i.e., Mo-CrTi-Si and Mo-V-CrTi-Si).

Cyclic oxidation life at 2400°F of the ballistic impact tested coupons is summarized in Table XXVIII. Cracked specimens were not tested. Examination of the data shows that 2000°F is well above the impact transition temperature of the coating-base metal systems. The tests show that the cotings and substrate can absorb impact energy by local deformation without a catastrophic destruction of the protective characteristics of the coatings.

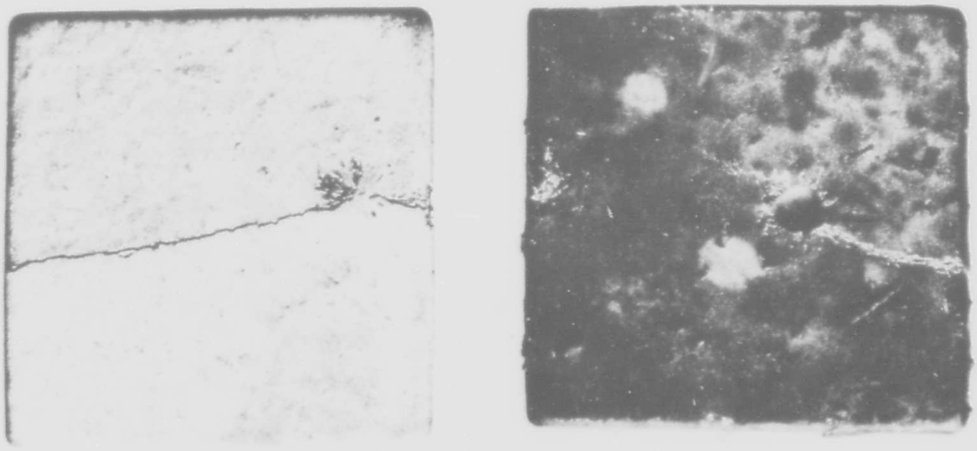


Rear

Front

7V-21CrTi-14Si

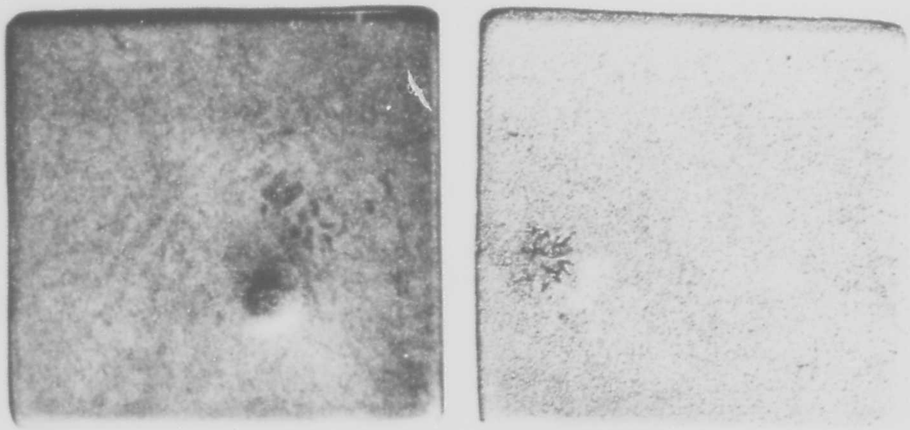
20Ti-2Al-3Si



Front

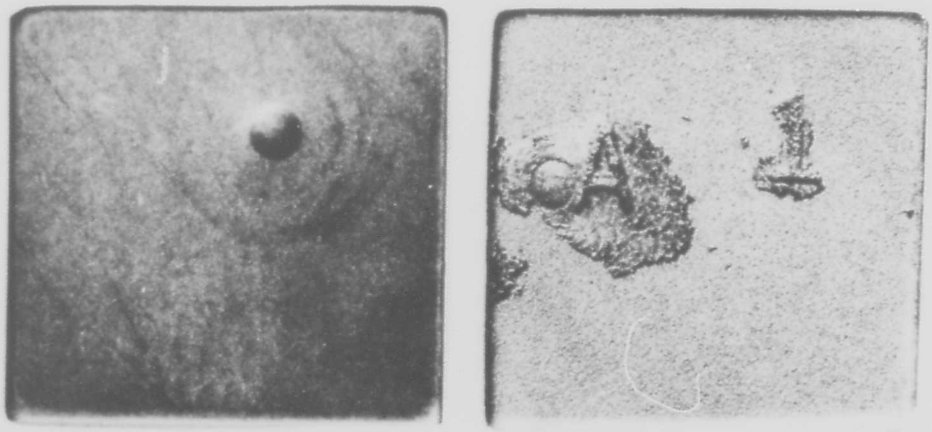
Rear

Figure 67 Surfaces of Coated Cb-752 after Ballistic Impact at Room Temperature. 5X



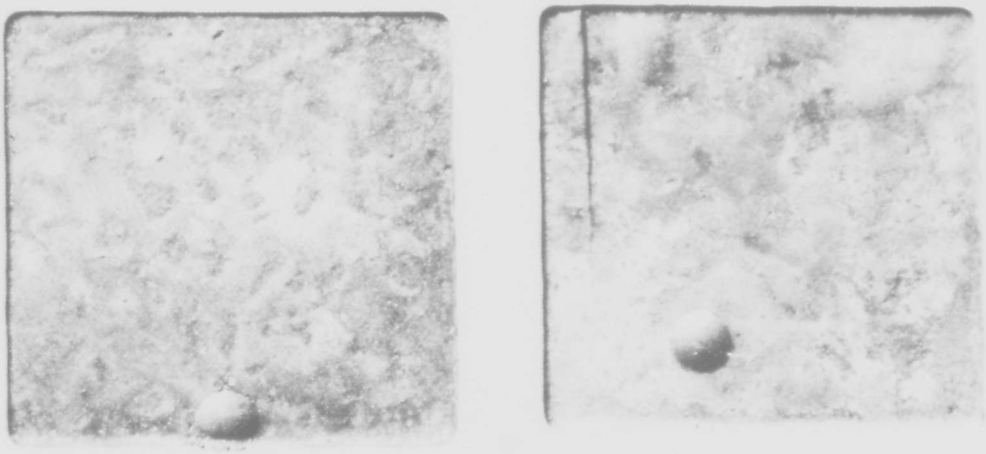
Front Front

Uncoated 10Mo-14CrTi-12Si



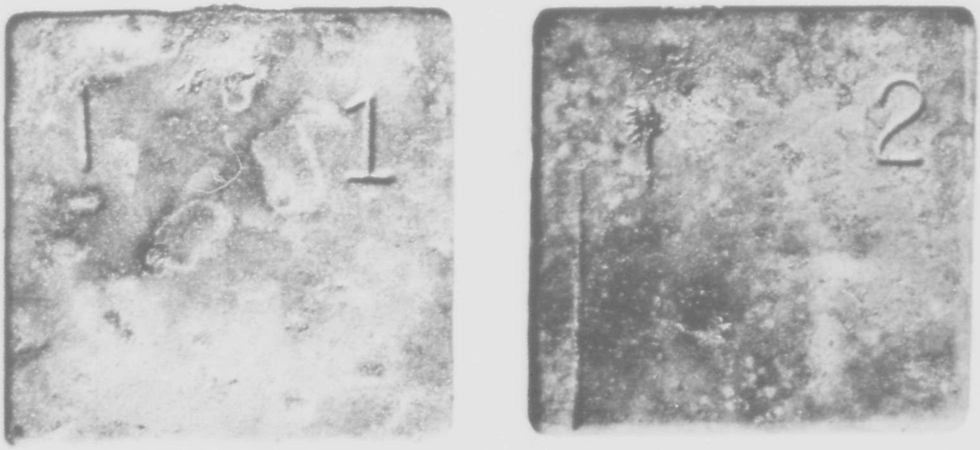
Rear Rear

Figure 68 Surfaces of Coated Cb-752 after Ballistic Impact at Room Temperature. 5X



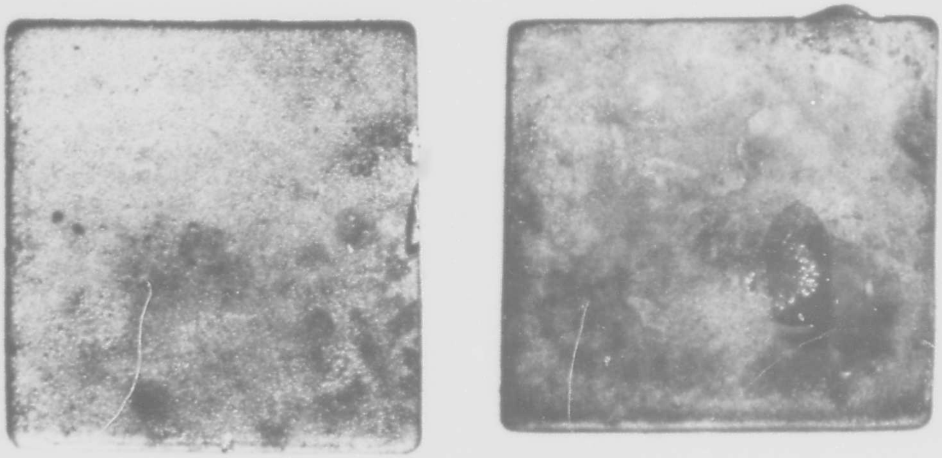
Rear Rear

6V-8Al-12CrTi-16Si 7V-21CrTi-14Si



Front Front

Figure 69 Surfaces of Coated Cb-752 after Ballistic Impact at 2000°F. 5X

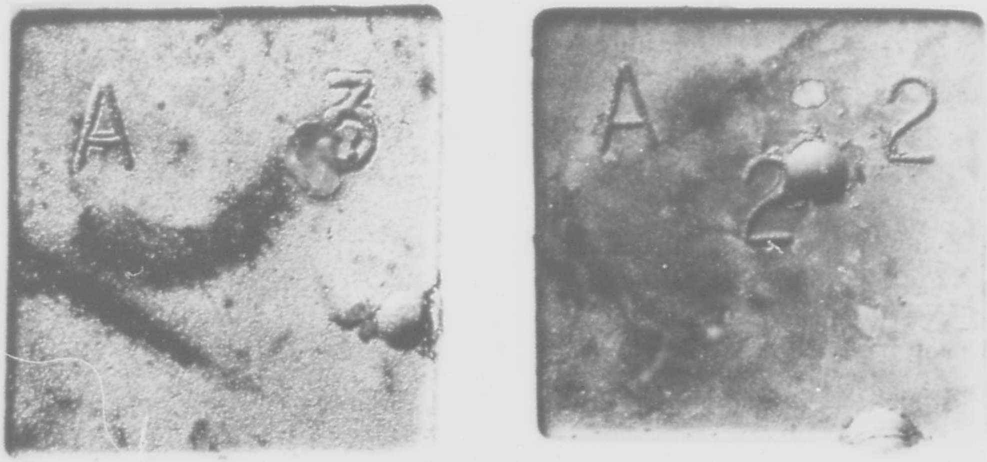


Front

14Mo-18CrTi-18.8Si

Front

7Mo-18CrTi-12Si



Rear

Rear

Figure 70 Surfaces of Coated Cb-752 after Ballistic Impact at 2000°F. 5X

TABLE XXVIII

RESULTS OF PHASE II BALLISTIC IMPACT TESTING OF VARIOUS COATING SYSTEMS ON COLUMBIUM ALLOY Cb-752

Code	Coating	Specimen Temp. at Impact, °F	Oxidation Life after Impact at 2400°F, Hr.	Observed Condition after Oxidation Exposure	
				Surface at Impact Point	Surface Behind Impact Point
A2	7Mo-18CrTi-12Si	RT	4	Oxide surrounding impact depression.	No oxide noted.
C2	3Mo-4V-21CrTi-12Si	RT	2	Oxide surrounding impact depression.	No oxide noted.
A3	14Mo-18CrTi-19Si	RT	2	Oxide in impact depression	Oxide.
C1	13Mo-14CrTi-12Si	RT	2	Oxide impact depression	Oxide.
C5	12Mo-10V-21CrTi-12Si	RT	2	Oxide in impact depression.	Oxide.
K1	6V-10Al-14CrTi-16Si	RT	2	Oxide surrounding depression.	No oxide noted.
K2	10V-21CrTi-15Si	RT	2	Oxide in depression.	Oxide.
D5	12Mo-12V-18CrTi-12Si	RT	2	Oxide in depression.	Oxide.
A1	10Mo-14CrTi-12Si	RT	2	Oxide in depression.	Oxide.
D3	10Mo-9V-21CrTi-10Si	RT	2	Oxide in depression.	Oxide.
A2	7Mo-18CrTi-12Si	2000	$>3^a$	No oxide noted.	No oxide noted.
D3	10Mo-9V-21CrTi-10Si	2000	$>1^a$	No oxide noted.	No oxide noted.
D5	12MO-12V-18CrTi-12Si	2000	1	Oxide in depression.	Oxide.
C5	12Mo-10V-21CrTi-12Si	2000	1^a	Oxide in depression.	No oxide noted.
A3	14Mo-18CrTi-19Si	2000	1^a	Oxide in depression.	Oxide.
A1	10Mo-14CrTi-12Si	2000	1^a	Oxide in depression	Oxide

TABLE XXVIII

(Continued)

Code	Coating	Specimen Temp. at Impact, °F	Oxidation Life after Impact at 2400°F, Hr.	Observed Condition after Oxidation Exposure: Surface at Impact Point	Observed Condition after Oxidation Exposure: Surface Behind Impact Point
C1	13Mo-14CrTi-12Si	2000	6	Oxide adjacent to depression.	Oxide adjacent to depression.
I1	6V-8Al-12CrTi-16Si	2000	6^a	Oxide adjacent to depression.	Oxide adjacent to depression.
A4	17CrTi-17Si	2000	13	Oxide surrounding depression.	Oxide.
I2	7V-21CrTi-14Si	2000	13	No oxide noted.	Oxide adjacent to depression.
K1	6V-10Al-14CrTi-16Si	2000	13	No oxide noted	Oxide.
K2	10V-21CrTi-15Si	2000	13^a	No oxide noted	Oxide adjacent to depression.

---

a. Edge hit
Weight of Steel projectile: 1.17 - 1.19 grams (weight of pell included)

Thickness of substrate: 0.030 in.
Velocity: 340 ft/sec.
Impact energy: 4.6 - 4.7 ft-lb.

6.10 DEMONSTRATION OF IMPROVED COATINGS

The V-CrTi-Si, V-Al-CrTi-Si and Mo-CrTi-Si coating systems along with the standard CrTi-Si system were selected for assessing the influence of substrate material on coating behavior. The columbium alloys included in the evaluation were Cb 752, D43, Cb132M and C129Y. The coating compositions selected for further evaluation were:

1) 7V-10Al-18CrTi-17Si
2) 7V-21CrTi-16Si
3) 18CrTi-16Si

The evaluation tests were:

a) furnace cyclic oxidation,
b) erosion-oxidation, and
c) ballistic impact.

6.10.1 Specimen Preparation

The coating runs are summarized in Table XXIX and representative microstructures after each coating step are presented in Figures 71 through 81.

The V-Al-CrTi-Si system specimens were vanadized in Runs 179 and 180, and aluminized in Run 181. The coupons and erosion bars were chromium-titanium coated in Runs 184 and 185 and siliconized in Run 187, Table XXIX. Microstructures are presented in Figures 63, 64 and 66. After Cr-Ti coating, the V-Al precoated specimen surfaces displayed craze cracks. This condition was not in evidence for the sample Run (No. 183) nor on vanadized specimens. Microscopic examination of the coupons showed porosity and crevice formation as a result of aluminum loss, Figure 72. The crevice generation was more pronounced when the V-Al precoated coupons were CrTi coated in a large pack versus a small pack, c.f. Figures 41 and 72. More activator, and a longer residence time of the activator is experienced with the larger pack. These are factors which may have influenced the loss of aluminum from the precoat. Thus, this system was not directly amenable to process scale-up, because of the aluminum loss incurred during the Cr-Ti coating step.

The V-CrTi-Si system coupons and erosion bars were vanadized in Run 179, chromium-titanized in Run 182 and siliconized in Run 187, Table XXIX. Representative microstructures are presented in Figures 71, 73 and 75. No problems were encountered in forming this system.

TABLE XXIX

Coating Data for Various Columbium Alloy Substrates

	Pack Composition		Pack Conditions			Precoating		
Run No.	Pack	Activator w/o	Temperature °F	Time Hr.	Pressure mm	Elements mg/cm^2	Run Nos.	Average Weight Gain mg/cm^2
170	60Cr-40Ti	1 KF	2300	8	10^{-2}	-	-	19.0
171	Si	1/2 KF	2100	8	10^{-2}	19 Cr Ti	170	9.4
179	V	1NaCl+. 2VCl$_4$	2200	12	150 Ar	-	-	8.2-9.4
180	V	"	"	"	"	-	-	6.4
181	56Cr-44Al	1 KF	2100	7	150 Ar	6V	179, 180	13.7-15.6
182	60Cr-40Ti	1/2 KF	2300	6	10^{-2}	6V	179, 180	28
183	"	"	2300	4½	10^{-2}	6V-14Al	179, 181	25.4
184[a]	60Cr-40Ti	1/2 KF	2300	3	10^{-2}	6V-14Al	179, 180, 181	3.4-5.8
185	"	"	2300	4	"	V-Al-CrTi	184	19.5
186	"	"	2340	7	"	-	-	17.0
187	Si	"	2100	15	"	V-Al-CrTi V-CrTi	185 182	17.0 16.0
188	Si	"	2100	4½	"	CrTi	186	12.0
189	60Cr-40Ti	1/2 KF	2300	12	"	12-17 Mo	CVD 135-141	21.5
190[b]	Si	"	2100	8	"	Mo-CrTi	189	13
433	60Cr-40Ti	"	2340	7	"	-	-	19
434	Si	"	2150	4	"	CrTi	433	10

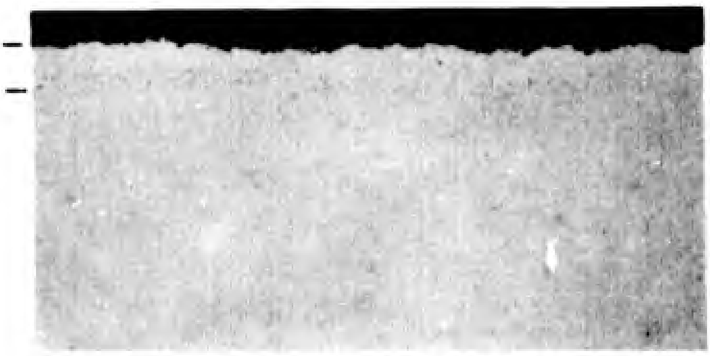
---

a. Activator in bottom 1/2. Coating craze cracked.

b. Three specimens blistered.

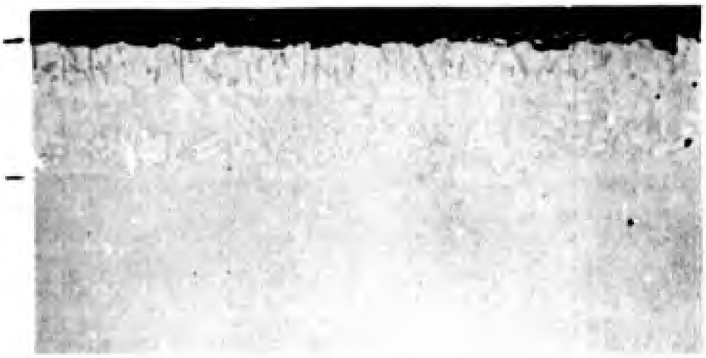
V Run 179

D-43



V Run 179

Cb 132M

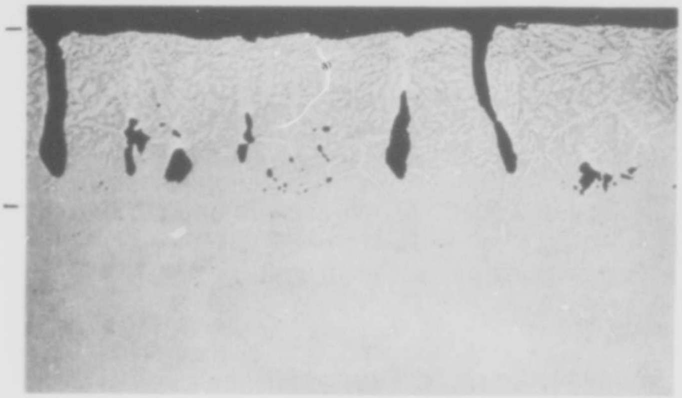


V Run 179

CrTi Run 182

Cb 132M

Figure 71 Microstructures after V and V-CrTi Coating.
250X

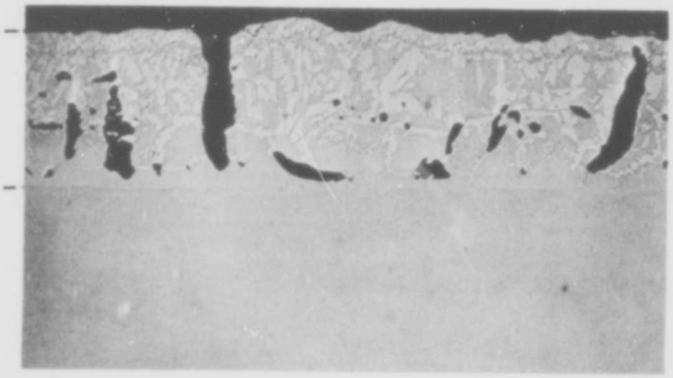


V Run 179

Al Run 181

Cr-Ti Runs 184, 185

Cb 132M



V Run 179

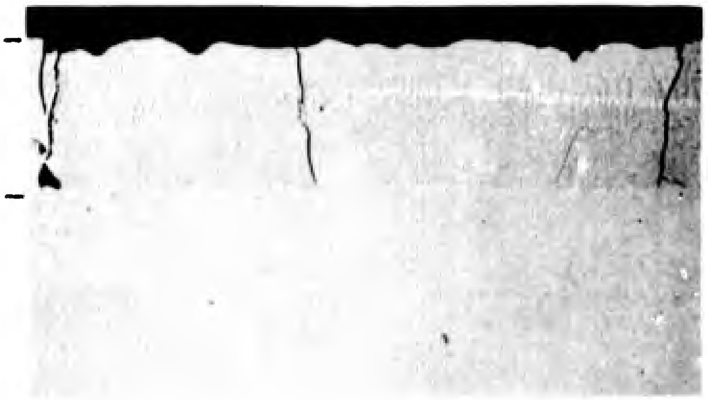
Al Run 181

Cr-Ti Run 184,185

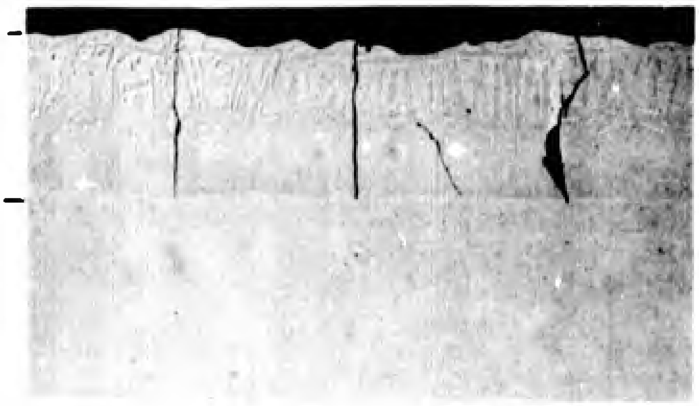
D43

Figure 72 Microstructures after V-Al-CrTi Coating. 250X

D 43



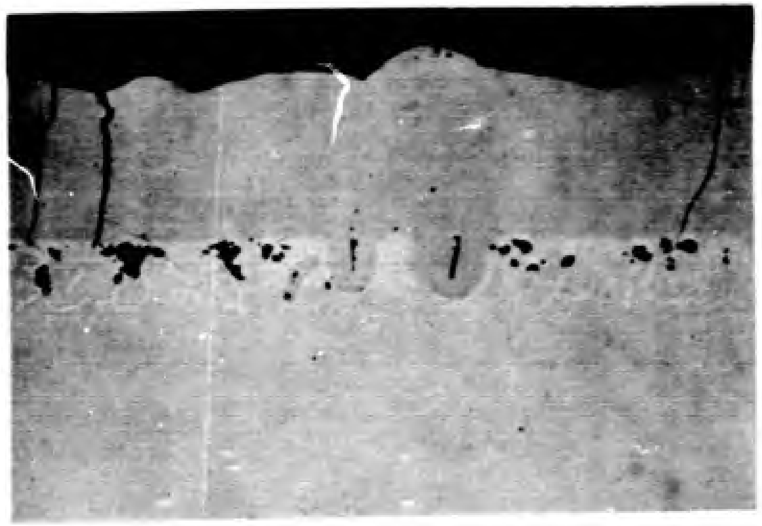
Cb 132M



D 43

Figure 73 Microstructures after V-CrTi, and V-Al Coating
250X

Cb 752

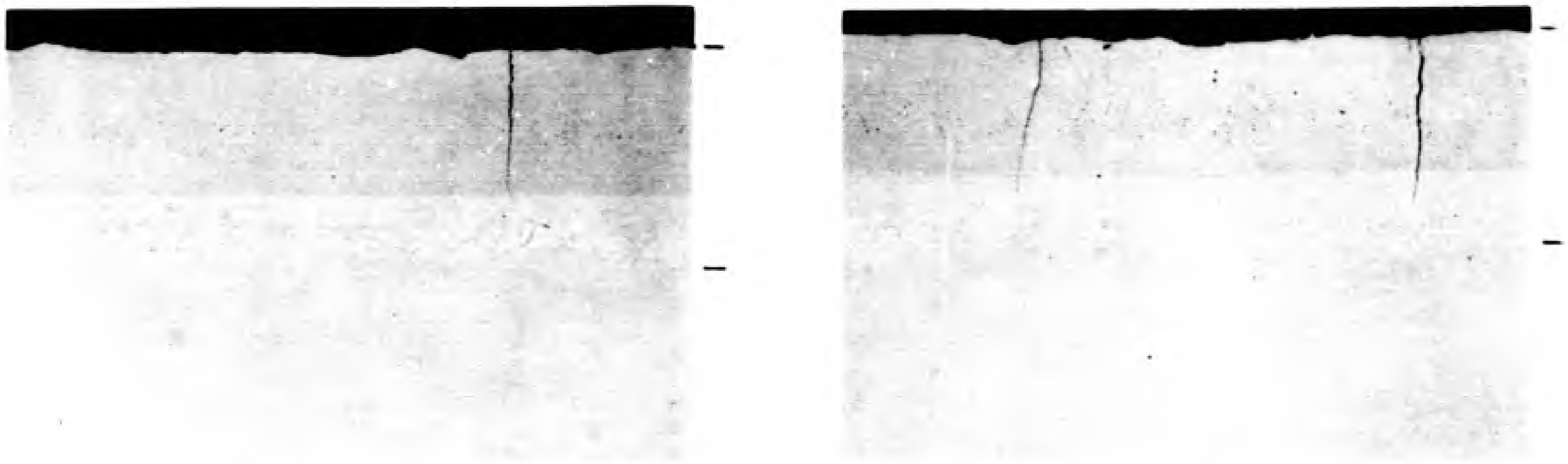


Cb 132M

D 43

C129Y

Figure 74 The 8.7V - 14.8Al - 19.5 CrTi - 17Si Coating System on Various Columbium Alloy Substrates. 250X



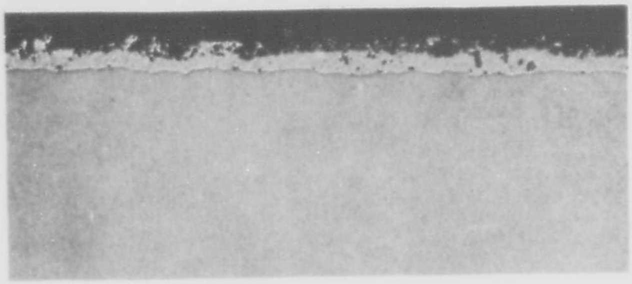
CB 752

Cb 132M

D 43

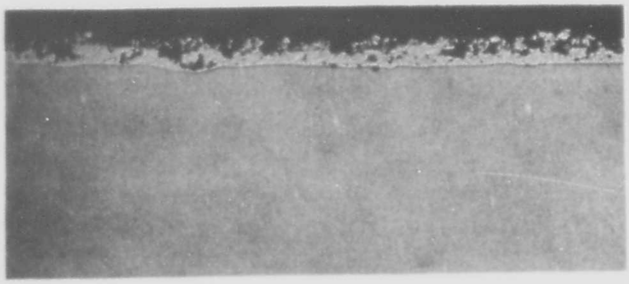
C129Y

Figure 75 The 8.8V-28.3CrTi-16Si Coating System on Various Columbium Alloy Substrates. 250X



Mo
CVD Run 136, 139

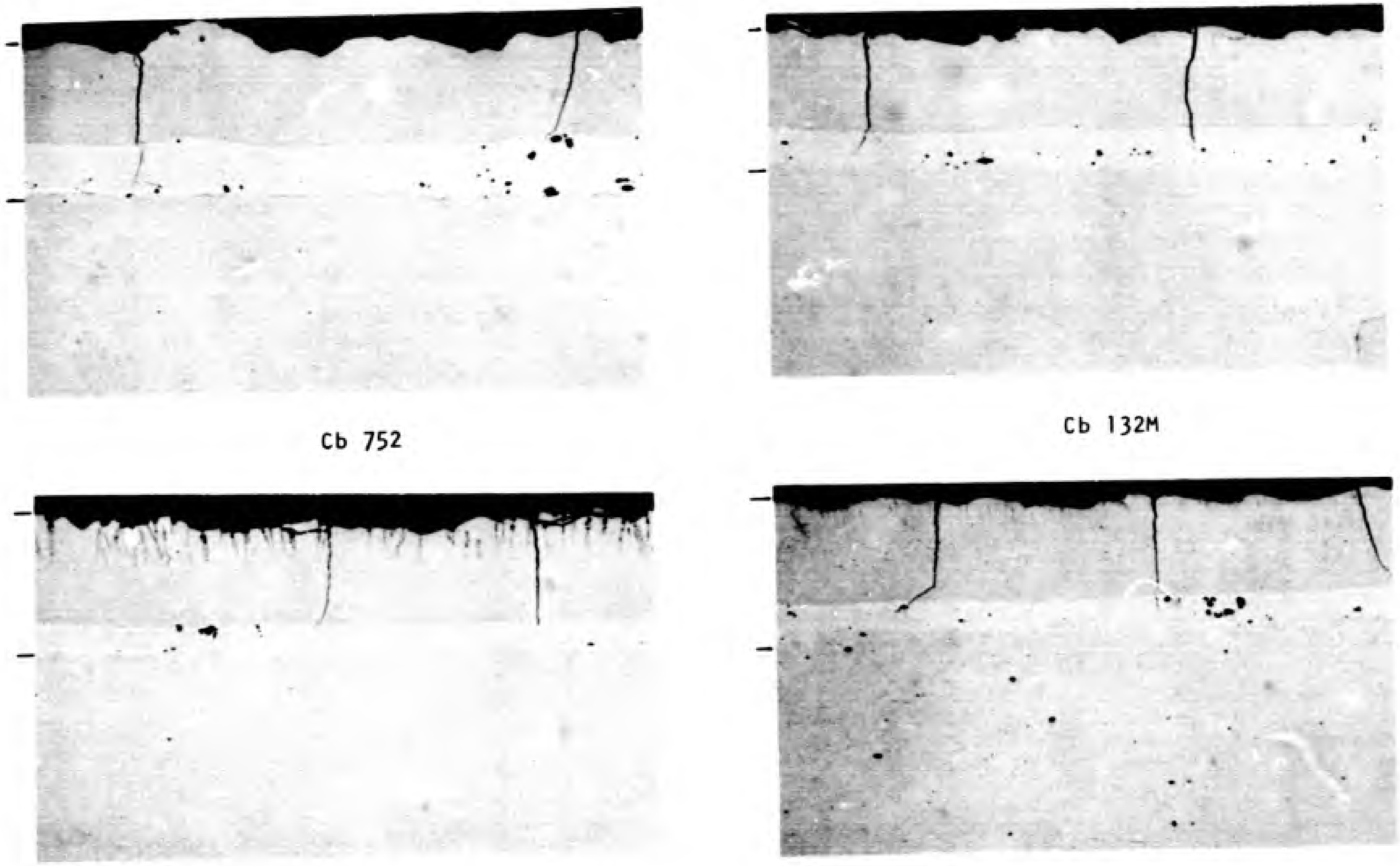
Cb 132M



Mo
CVD Run 136, 139

D-43

Figure 76 Microstructures after Molybdenizing. 250X



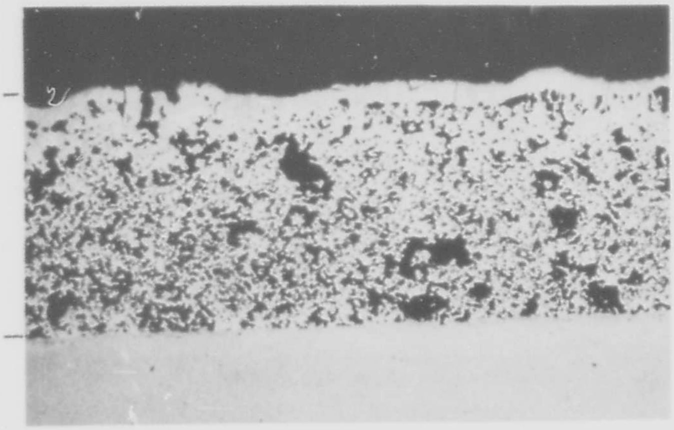
Cb 752

Cb 132M

D 43

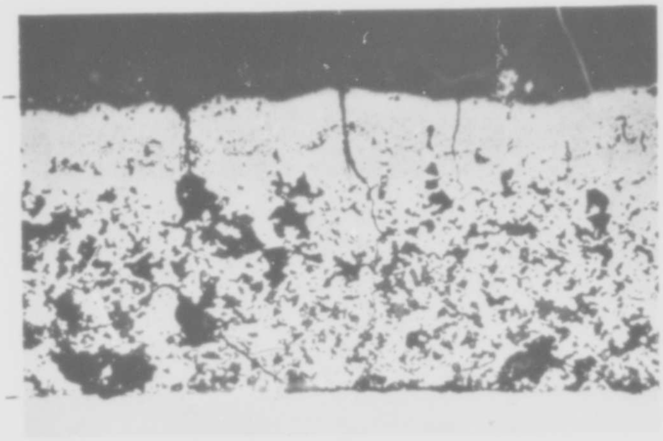
C 129Y

Figure 77 The 15 Mo - 21.5 CrTi-13Si Coating System on Various Columbium Alloy Substrates. Molybdenum Applied by CVD. 250X

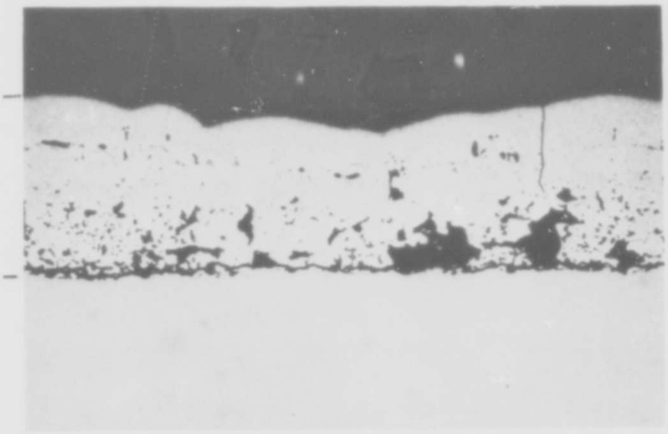


Mo-CrTi: Run Nos. 197 and 198

Figure 78 Microstructure Mo-CrTi Coated Columbium Alloy C129Y. Molybdenum applied as Mo-10 w/oAg Slurry. 250X

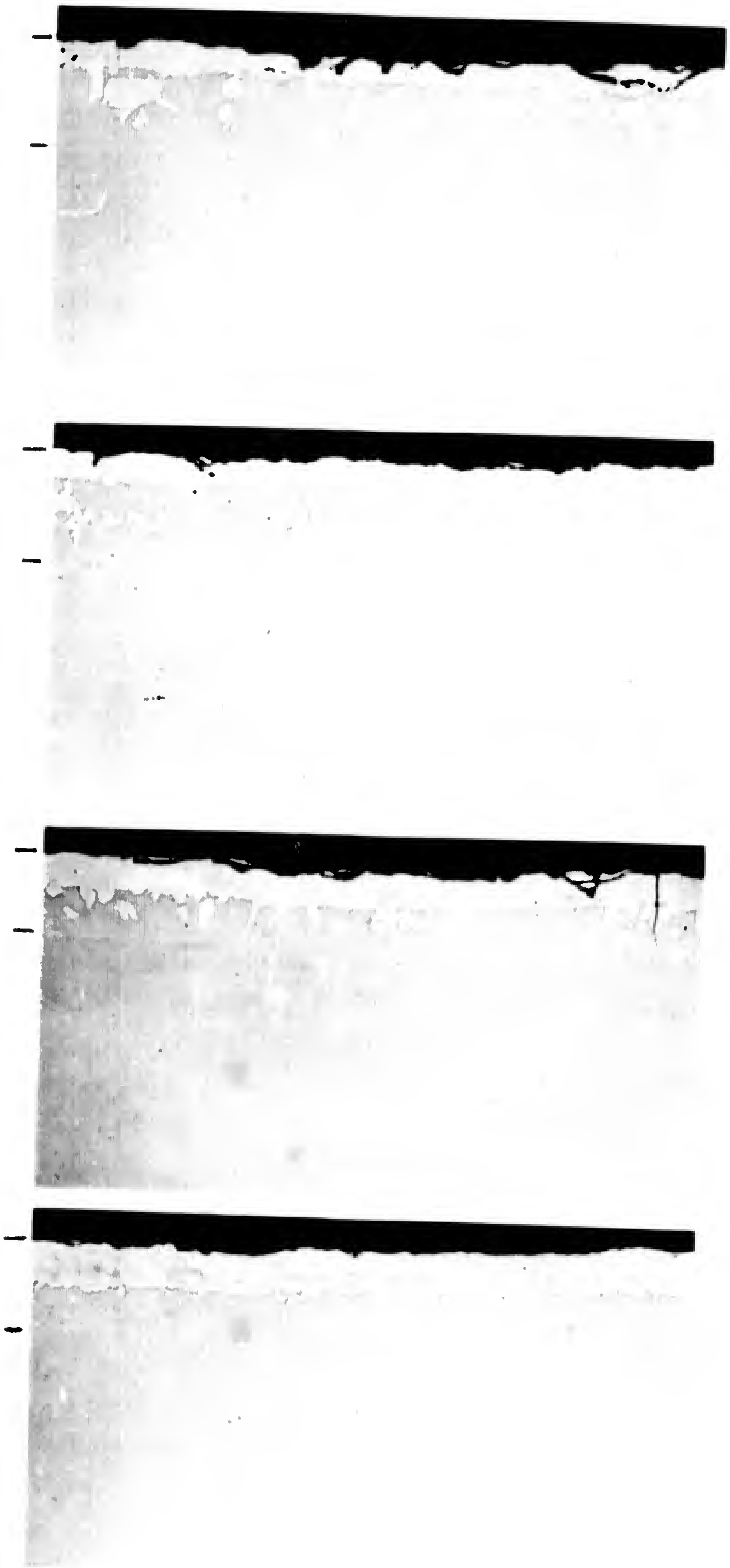


C129Y



CB 752

Figure 79 Microstructures of Mo-CrTi-Si Coatings on Columbium Alloys C129Y and Cb 752. Molybdenum Applied as Mo-10 w/o Ag Slurry. Run Nos. 197, 198 and 199. 250X



Cr-Ti Run 186:

Cb752

C129Y

Cb132M

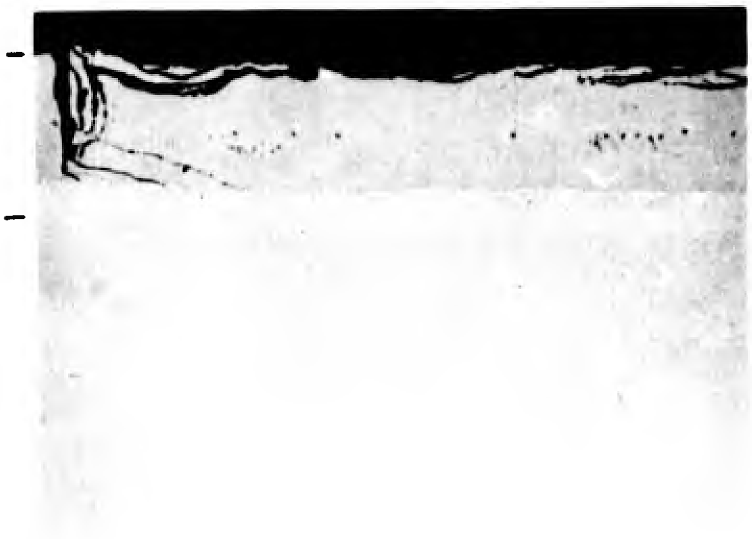
D43

Figure 80 Microstructures after CrTi Coating. 250X

Cr-Ti Run 186

Si Run 188

D43



Cb132M

Figure 81 Microstructures after CrTi-Si Coating. 250X

The Mo-CrTi-Si system coupons were molybdenum precoated by the CVD technique in Runs CVD 135 - 141, chromium-titanized in Run 189 and siliconized in Run 190. Representative microstructures are presented in Figures 76 and 77. The erosion bars could not be uniformily precoated with molybdenum by the CVD technique. due to equipment limitations. The bars were therefore molybdenized by the slurry method using fine molybdenum powder (particle size less than one micron). The amount of slurry applied was 15 mg/cm^2. Representative microstructures are presented in Figures 12, 78 and 79. Coating spalling was observed after CrTi and Si coating on some of the specimens,although after the initial molybdenum application the coating was adherent.

The CrTi-Si system specimens (standards) were coated in Runs 186 and 188, Table XXIX. Microstructures after Cr-Ti and Si coating are presented in Figures 80 and 81, respectively.

6.10.2 Furnace Cyclic Oxidation Results

Cyclic oxidation data obtained for the optimum coatings applied to the various columbium-alloy substrates are summarized in Table XXX.

The V-CrTi-Si system displayed a fairly consistent protective capability of over 350 hours at 1600° to 2400°F for all coated substrates. The standard CrTi-Si system also showed a reasonably consistent protective trend; however, the oxidation life at 2400°F was shorter than the V-CrTi-Si coating life, probably due to the lower Cr-Ti content. The V-Al-CrTi-Si and Mo-CrTi-Si systems showed erratic behavior during oxidation testing because of the crevice formation during the Cr-Ti coating cycle for the former, and possible lack of molybdenum adhesion during the CVD coating cycle for the latter.

To determine the effects of transient temperature overshoots such as may occur in a gas turbine environment, several of the V-CrTi-Si coated Cb752 specimens were cyclic oxidation tested at 2600 and 2800°F. No failures were observed on two specimens at 2600°F in 171 hours of testing. At 2800°F both specimens failed in 9 and 10 hours.

6.10.3 Erosion-Oxidation Rig Test Results

Erosion-oxidation rig data are presented in Table XXXI, and surface appearances after testing are shown in Figures 83 through 87.Bars were rotated at 1750 rpm in a burner rig shown in Figure 82 utilizing a mixture of jet type A (ASTM-1655) fuel containing o.4 w/o sulfur and air. Failure was defined as the first appearance of substrate oxide on the specimen airfoil surface. Specimens were inspected after each 10 hours of testing.

The V-CrTi-Si and CrTi-Si systems(Figures 83, 86 and 87) showed good performance at the 2200°F test temperature with life times in excess of 200 hours,whereas the V-Al-CrTi-Si and Mo-CrTi-Si systems displayed relatively short lives (less than 10 hours) similar to the reduced lives noted in the furnace cyclic oxidation test results. The molybdenized coatings spalled

TABLE XXX

CYCLIC OXIDATION DATA FOR VARIOUS COLUMBIUM ALLOY SUBSTRATES

Code	Coating System	Alloys	Cyclic Oxidation Life, Hours 1600°F	2000°F	2200°F	2400°F
3A	8.7V-14.8Al-19.5CrTi-17Si	Cb-752	5,12	345,>378	7,>413	12,>265
3B		Cb-132M	29,157	282,>378	7,>413	289,>393
3C		C129Y	5,5	23,28[1]	7,>413	5,109
3D		D-43	5,29	4,>378	157[1],413	29,29
4A	8.8V-28.3CrTi-16.1Si	Cb-752[2]	>421,>421	>378,>378	>413,>413	>393,>393
		Cb-132M	>421,>421	>378,>378	>413,>413	>393,>393
		C129Y	>421,>421	>378,>378	>413,>413	165[1],>393
		D-43	>421,>421	>378,>378	>413,>413	>393,>393
5A	15Mo-21CrTi-13Si	Cb-752	328,>362	20,51	6,48	24, 332
5B		Cb-132M	24,96	51,51	6,>352	24,72[1]
5C		C129Y	>362,>362	68,>378	>352,>352	276,324
5D		D-43	>362,>362	68,240	>352,>352	27,>332
6A	18CrTi-15Si	Cb-752	>421,>421	>378,>378	381,504	185,217
6B		Cb-132M	213,>421	>378,>378	333,285	165,165
6C		C129Y	>421,>421	>378,>378	285,285	233[1],233
6D		D-43	>421,>421	>378,>378	285,357	185,185

---

1. Surface failure, otherwise edge.
2. Cyclic oxidation life at 2600°F > 171 hr (2 spec) and at 2800°F-9,10 hours.

TABLE XXXI

EROSION-OXIDATION RIG TEST RESULTS

Coating System	Alloy	Temperature, °F	Time, Hr.
8.7V-14.8Al-19.5CrTi-17Si	Cb-752	2200	4 (SF)[a]
	"	2200	4 (SF)
	Cb 132 M	2200	6 (SF)
	"	2200	6 (SF)
	D-43	2200	100 (NF)
	"	2200	100 (NF)
8.8V-28.3CrTi-16.1Si	Cb-752	2200	113 (NF)
		+	+
		2400	106 (SF)
	"	2200	123 (NF)
		+	+
		2400	106 (SF)
	Cb 132 M	2200	110 (NF)
	"	"	217 (NF)
	D-43	2200	217 (NF)
		"	255 (NF)
30Mo-17CrTi-10Si	Cb-752	2200	8 (SF)
	"	"	10 (SF)
	Cb 132 M	2200	8 (SF)
	"	"	8 (SF)
18CrTi-15Si	Cb-752	2200	217 (NF)
		+	+
		2400	106 (NF)
	Cb-752	2200	113 (NF)
	Cb 132 M	2200	113 (NF)
		+	+
		2400	106 (NF)
	Cb 132 M	2200	92 (SF)

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a. NF - no failure; SF - spot failure

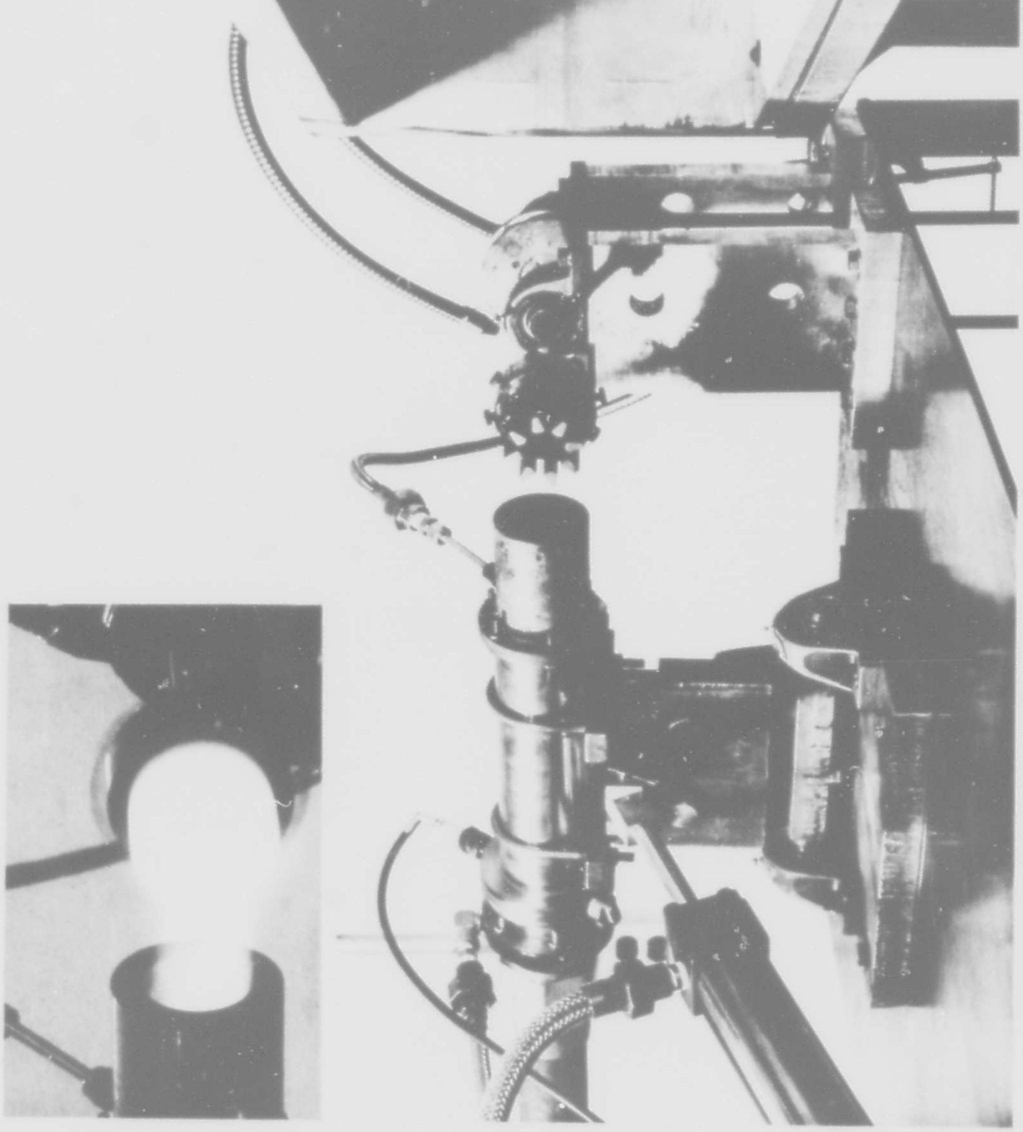
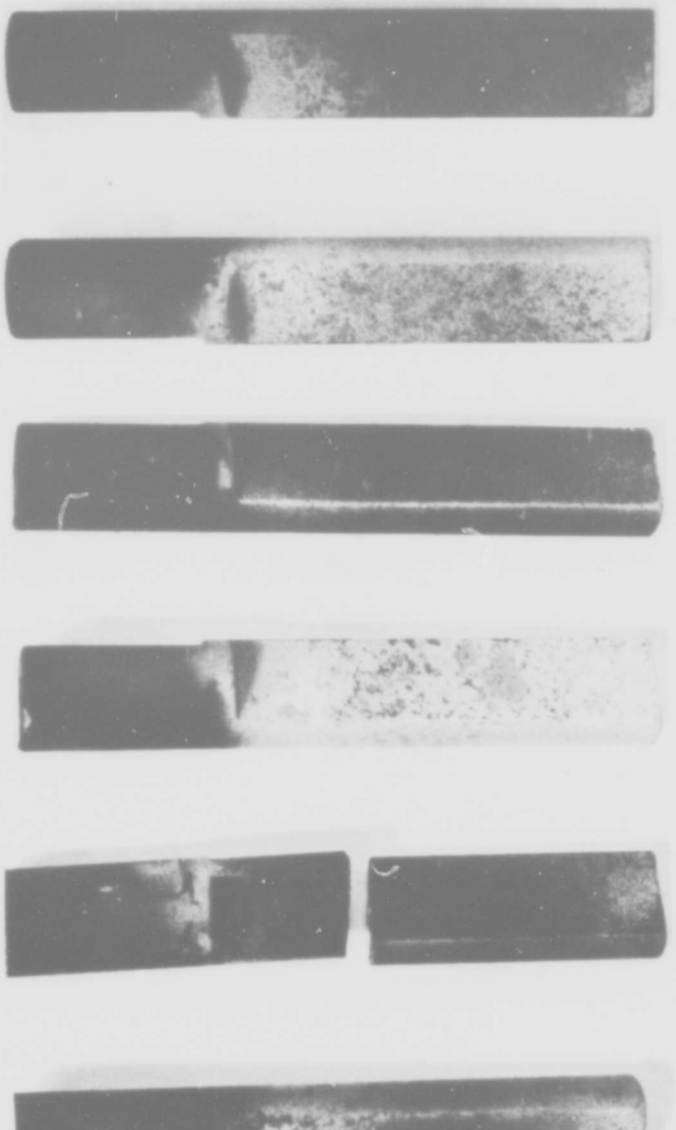


Figure 82 Erosion-Oxidation Burner Test Rig.



V-CrTi-Si

Figure 83 Columbium Alloy Bars Coated with the 8.8V-28.3CrTi-16Si System after Oxidation-Erosion Testing at 2200°F for the Indicated Times. 125X

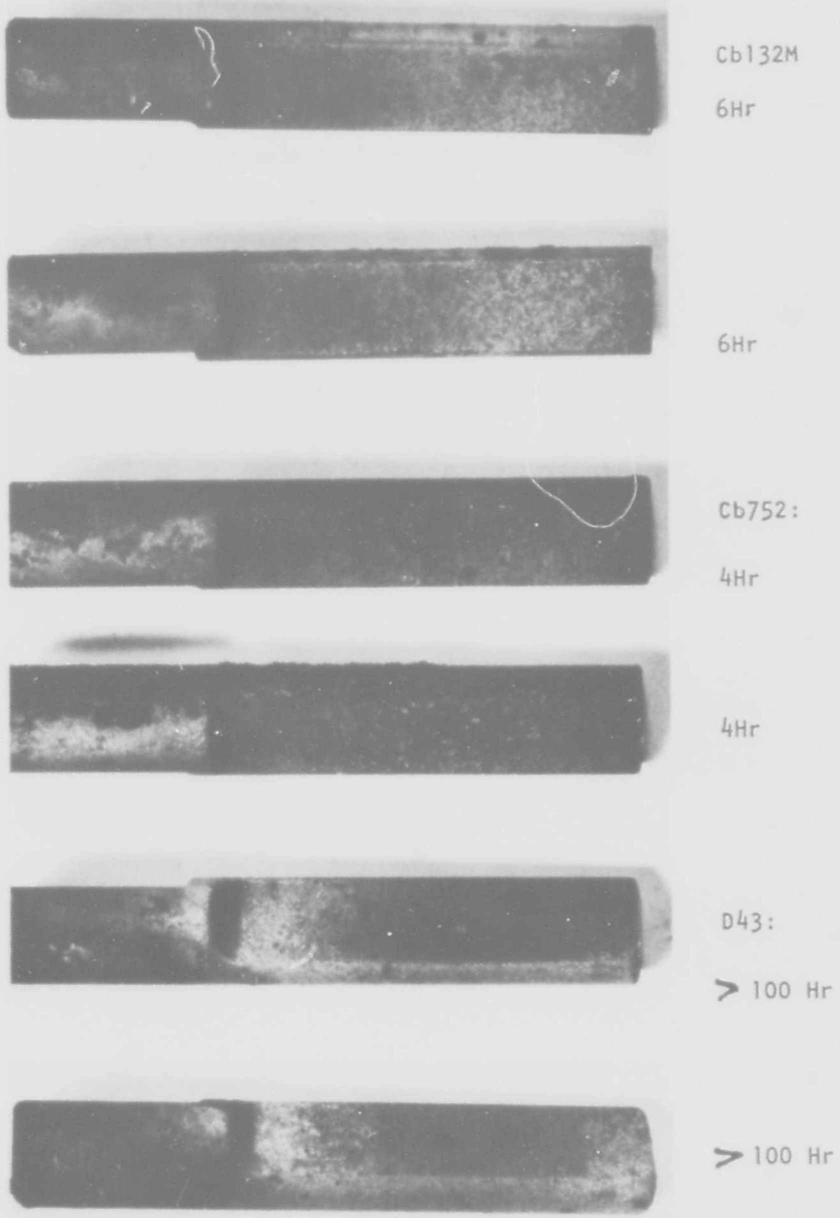


Figure 84 Columbium Alloy Bars Coated with the 8.7V-14.8Al-19.5CrTi-17Si System after Oxidation-Erosion Testing at 2200°F for the Indicated Times. 125X

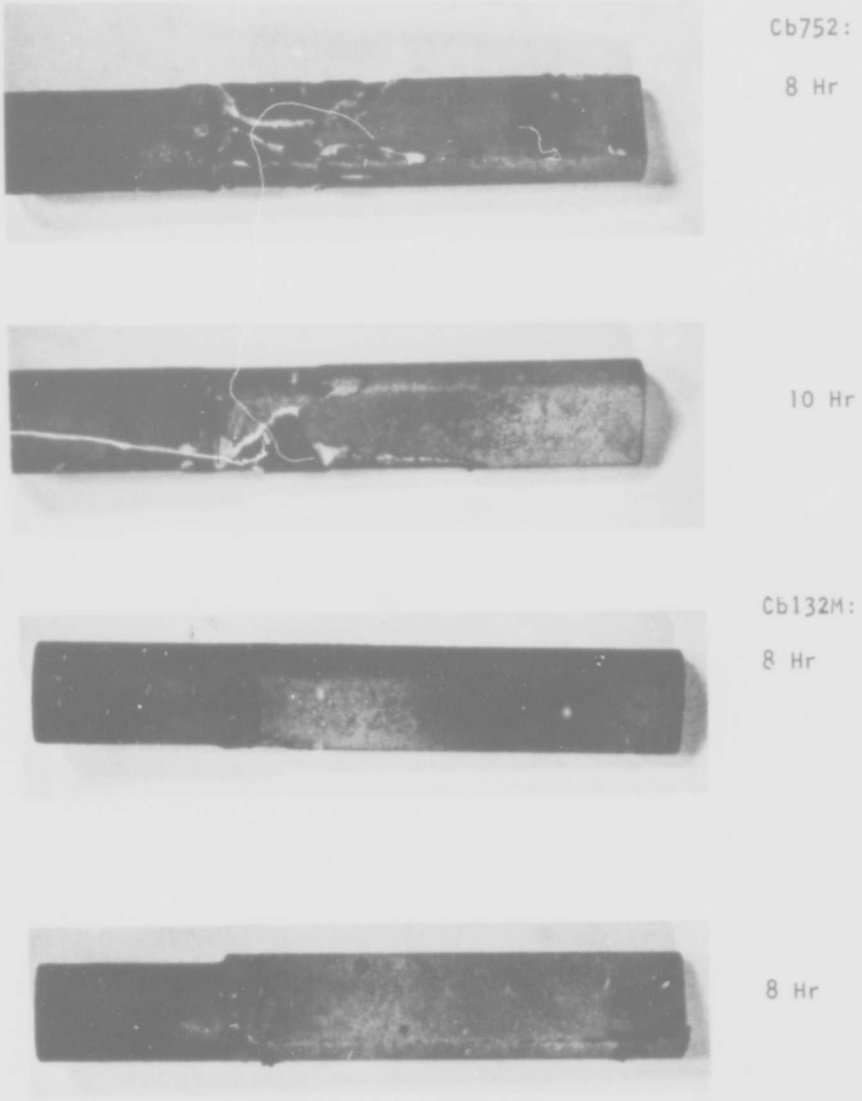


Figure 85 Columbium Alloy Bars Coated with the 30Mo-17CrTi-10Si System after Oxidation-Erosion Testing at 2200°F for the Indicated Times. Molybdenum applied as a Mo-10 w/o Ag Slurry. 1.25X

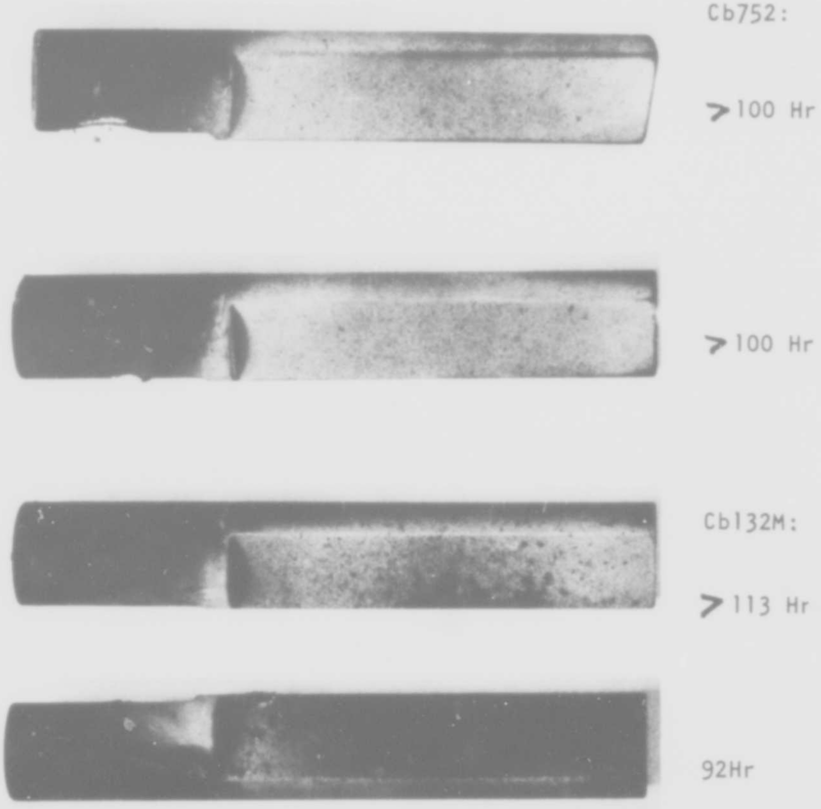


Figure 86 Columbium Alloy Bars Coated with the 18CrTi-15Si System after Oxidation-Erosion Testing at 2200°F for the indicated Tines. 1.25X

whereas the aluminized containing coatings developed large failure areas, Figures 84 and 85.

The V-CrTi-Si and CrTi-Si coated erosion bars were given additional exposures at 2400°F in the erosion rig after the initial exposure at 2200°F. A useful lifetime of 100 hours at 2400°F was indicated for both the V-CrTi-Si and CrTi-Si coated specimens. Photographs of the erosion bars at test termination are presented in Figure 87 and typical cross-sections of the coatings after exposure are presented in Figures 88 and 89. Visually, no coating failures were observed after testing at 2200°F for either the V-CrTi-Si or CrTi-Si coated Cb752, D43 and Cb132M columbium alloys. After 100 hours at 2200°F plus 106 hours at 2400°F, the V-CrTi-Si coated Cb752 samples developed small failure spots or tubercles which grew very slowly. The slow growth of these failure areas indicates a margin of reliability for this coating system

Microscopic examination of cross-sections removed from the exposed erosion bars showed oxidation in cracks or fissures of the silicide coatings which penetrated the rough silicide layer in many instances. In addition, oxygen penetration of the substrate was observed for both the V-CrTi-Si and CrTi-Si coating systems. Thus, it appears that the useful life time of either coating is at least 200 hours at 2200°F or 100 hours at 2200°F plus 100 hours at 2400°F

6.10.4 Ballistic Impact Test Results

Ballistic impact tests were conducted at room temperature and at 2000°F on the various substrates coated with the optimum coating systems. The energy of impact was 4.6 - 4.7 ft.-lb. as in previous impact tests.

Surface appearances after impact at room temperature are shown in Figures 90 and 91, and after impact at 2000°F in Figure 92. With exception of the Cb132M material (0.053in) specimens were of insufficient thickness (.030-.040in) to prevent deformation on the reverse side. Impact at room temperature generally resulted in specimen cracking or total fracture for the Cb132M and Cb752 columbium alloy substrates, regardless of the coating system, whereas the C-129Y and D43 substrates were virtually free of substrate cracking. As previously noted, impact at 2000°F caused less damage than evidenced at room temperature, with no cracking or fracture noted for any of the substrates tested. Coating flaking was generally evidenced on the surfaces opposite the impact side, both in the room temperature and 2200°F impact tests

Cyclic oxidation life at 2200°F of the ballistic impact tested coupons is presented in Table XXXII. Fractured or cracked specimens were not tested. With exception of the V-Al-CrTi-Si system, all of the coating systems demonstrated a capability to protect the impacted substrates at 2200°F for periods ranging from 1 to over 15 hours. The CrTi-Si system showed a longer protective life after damage than the V-CrTi-Si system on the D43 and C129Y substrates. Many of the specimens suffered edge hits during impact testing. This condition materially reduced oxidation life due to the severity of the damage in these areas.

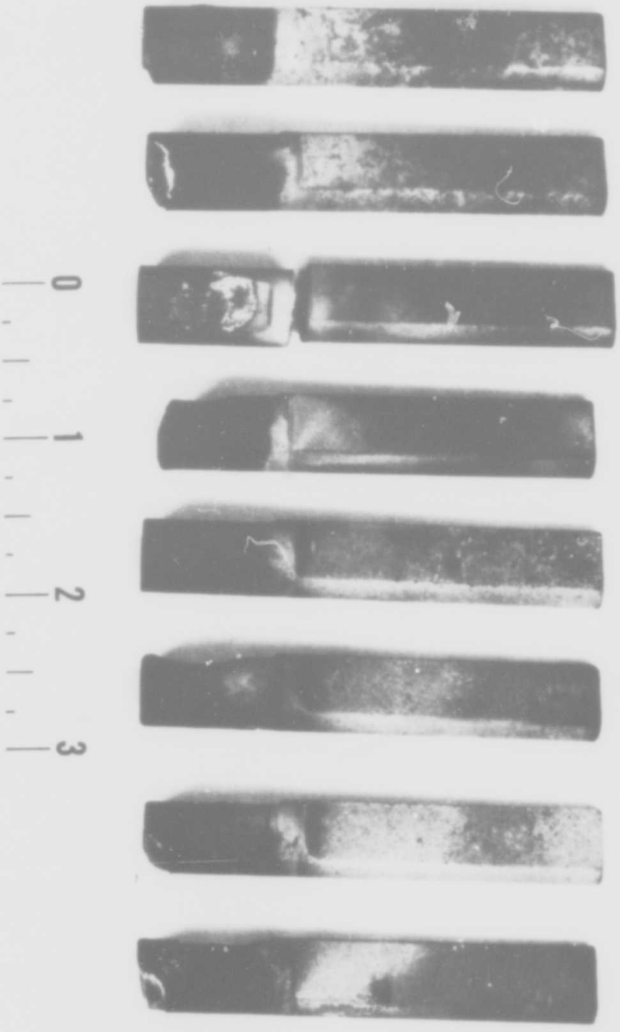
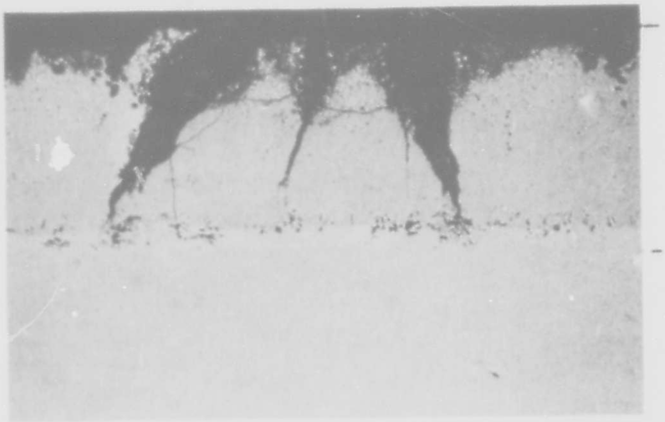
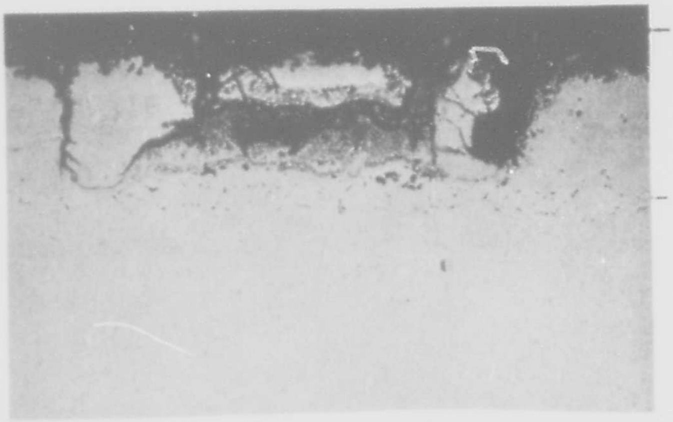


Figure 87 Phase II Erosion-Oxidation Bars after Additional Exposure at 2200 and 2400°F for the Indicated Times. All of these Bars previously tested for at least 100 hours at 2200°F. IX

D-43:
8.8V-28.3CrTi-16Si
>255 Hours



Cb-132M:
8.8V-28.3CrTi-16Si
>217 Hours



Cb-752:
18CrTi-15Si
>217 Hours

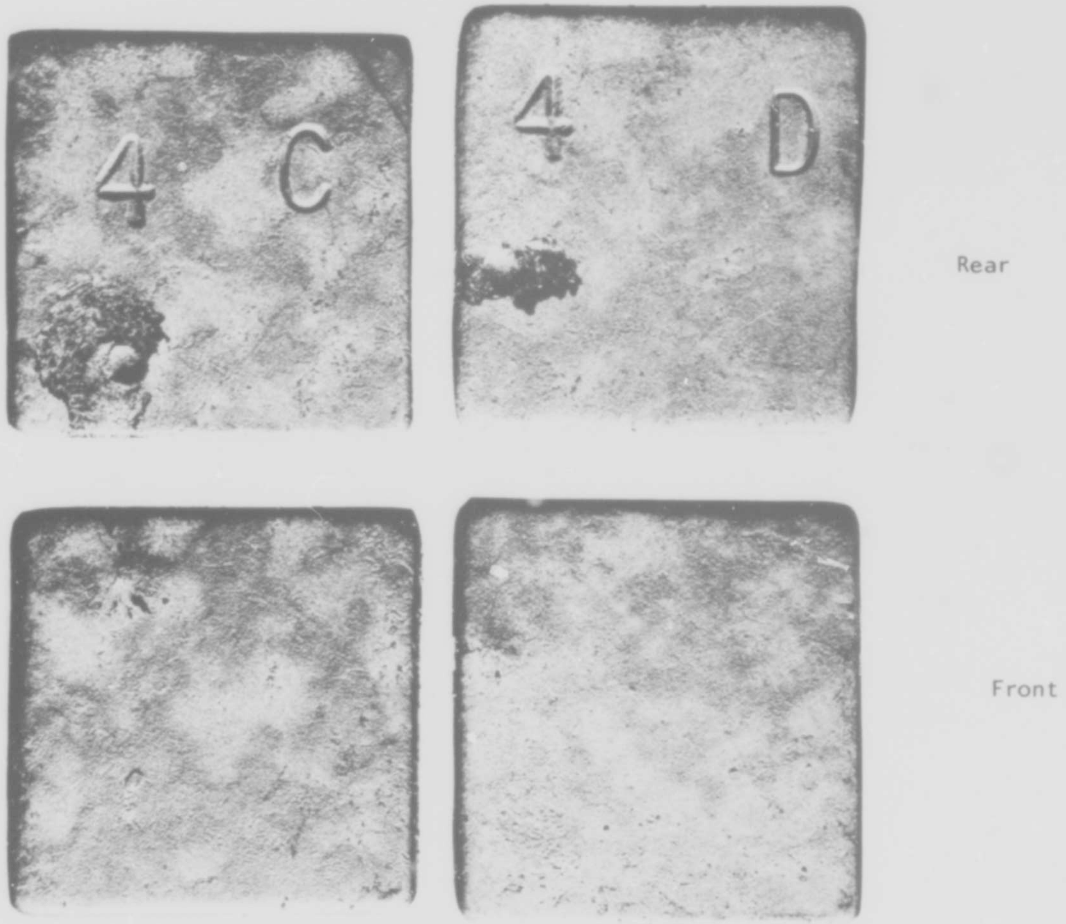
Figure 88 Microstructures of Coated Columbium Alloys Erosion Bars after Exposures for the Indicated Times at 2200°F in the Erosion Rig. 250X

Cb-752:
8.8V-28.3CrTi-16.1Si

Cb-752:
18CrTi-15Si

Cb-132M:
18CrTi-15Si

Figure 89 Microstructures of Coated Columbium Alloy Erosion Bars after 100 Hours at 2200°F plus 106 hours at 2400°F in the Erosion Rig. 250X



C129Y D43

Figure 90 Surfaces after Ballistic Impact at Room Temperature of the 8.8V-28.3CrTi-16.1Si Coating System on Various Substrates. 5X

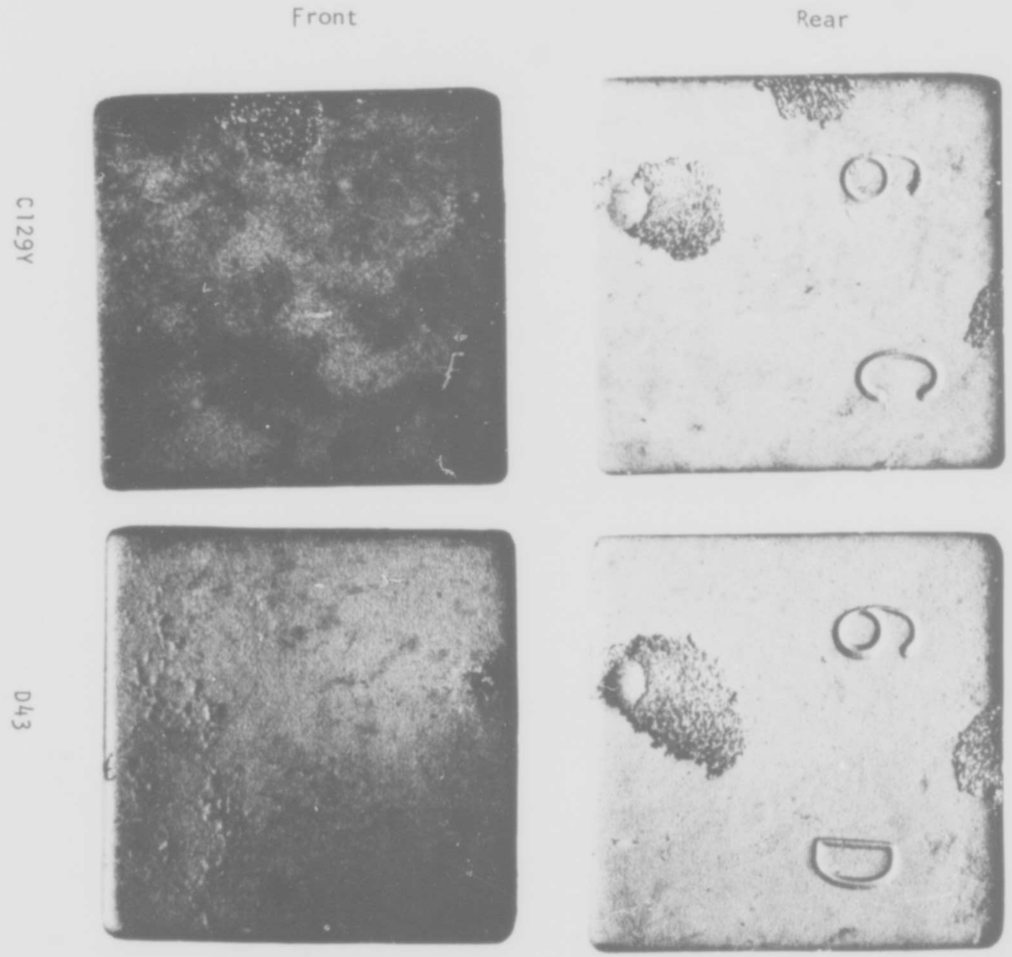
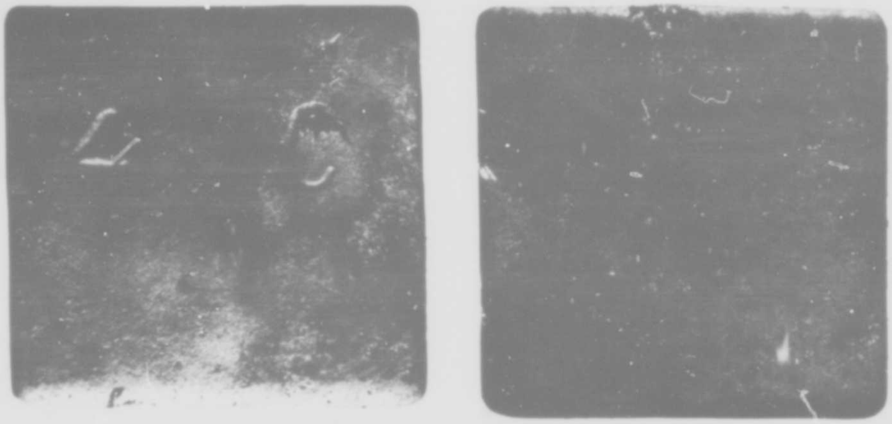
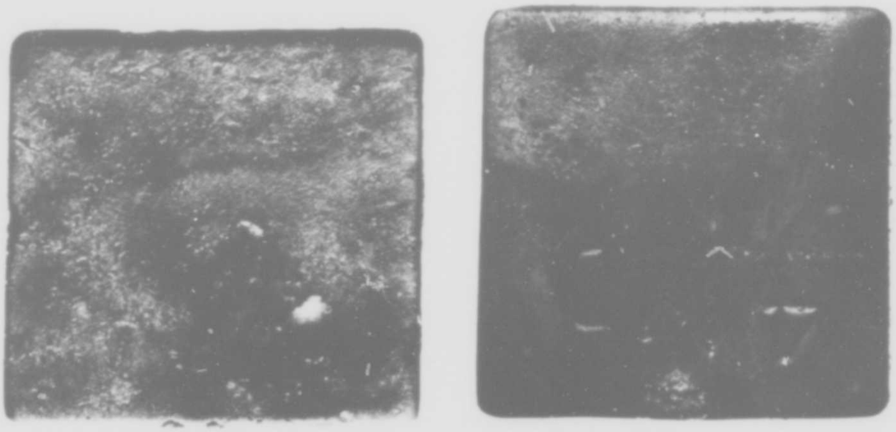


Figure 91 Surfaces after Ballistic Impact at Room Temperature of the 18CrTi-15Si Coating System on Various Substrates. 5X



Front



Rear

C129Y D43

Figure 92 Surfaces after Ballistic Impact at 2000°F of the 8.8V-28.3CrTi-16Si Coating System on Various Substrates. 5X

TABLE XXXII

RESULTS OF BALLISTIC IMPACT TESTING OF OPTIMUM COATINGS ON VARIOUS COLUMBIUM ALLOY SUBSTRATES

Coating	Alloy	Specimen Temp. at Impact, °F	Oxidation Life at 2200°F After Impact, Hr.	Observed Condition After Oxidation Exposure	
				Surface at Impact Point	Surface Behind Impact Point
8.7 V-14.8 Al-19.5 CrTi-17 Si	Cb752	75	[a]		
	Cb132M		[a]		
	C129Y		1[b]	oxide	oxide
	D43		1[b]	oxide	oxide
	Cb752	2000	1	oxide adjacent to depression	oxide
	Cb132M		1[b]	oxide " " "	oxide
	C129Y		1	oxide " " "	oxide
	D43		>1	no oxide	no oxide
8.8 V-28.3 CrTi-16.1 Si	Cb752	75	[a]		
	Cb132M		[a]		
	C129Y		4[b]	oxide adjacent to depression	no oxide
	D43		1[b]	oxide " " "	no oxide
	Cb752	2000	1[b]	oxide adjacent at edge	oxide
	Cb132M		3[b]	no oxide	oxide adjacent on edge
	C129Y		6	oxide adjacent to depression	oxide
	D43		3[b]	oxide " " "	oxide adjacent on edge
15 Mo-21.5 CrTi-13 Si	Cb752	75	1	oxide adjacent to depression	no oxide
	Cb132M		[a]		
	C129Y		11	oxide	oxide
	D43		2	oxide on edge away from depr.	no oxide
	Cb752	2000	2	oxide away from depr. on edge	no oxide
	Cb132M		2[b]	oxide adjacent to depr. on edge	oxide on edge
	Cb129Y		11	oxide adjacent to depression	no oxide
	D43		2	oxide " " "	no oxide
18 CrTi-15 Si	Cb752	75	[a]		
	Cb132M		[a]		
	C129Y		10[b]	oxide adjacent to depression	no oxide
	D43		7	oxide in depression	oxide
	Cb752	2000	>15	no oxide	no oxide
	Cb132M		8[b]	oxide adjacent to depr. on edge	no oxide
	C129Y		8[b]	no oxide	oxide adjacent to depression
	D43		10	oxide adjacent to depression	oxide

---

a. Specimen cracked or broke into pieces.
Thickness of Substrate: Cb752-0.030 in; Cb132M-0.052 in; C129Y-0.037 in; and D43-0.030 in.
Velocity: 340 ft/sec
Impact Energy: 4.6-4.7 ft-lbs.

b. Edge Hit.

6.11 SELECTION OF COATING-BASE METAL SYSTEMS FOR PHASE III COMPREHENSIVE EVALUATION.

The V-CrTi-Si system was selected for a comprehensive evaluation in Phase III. The selection was based on the consistent protective capability displayed by the system in comparison to the others in cyclic oxidation and erosion-oxidation tests. Furthermore, no adverse effect of substrate chemistry upon the protective life was discernible with any of the substrates evaluated In addition, the formation of this system presented no insurmountable processing problems; therefore, it appeared to be well suited to being scaled-up.

SECTION VII

PHASE III: ADVANCED TESTING AND EVALUATION

The primary objective of Phase III was to demonstrate the potential of the V-CrTi-Si coating system for application to advanced jet engine components and re-entry vehicles.

The 7 V-21CrTi-16Si Coating system was selected for Phase III on the basis of its performance, its ease of formation, and its capability of being scaled-up. The columbium alloy substrates selected for evaluation with the coating included the sheet vane materials Cb-752 and D-43, and the blade materials Cb-132 M and XB-88. The blade materials are experimental alloys currently being developed for turbojet engine applications. The test parameters were selected for each metal-coating system on the basis of the environmental conditions that would be experienced by coated components in either re-entry vehicle (2400°F max.) or turbojet engine applications (2200°F max. for the blade materials and 2400°F max. for the vane materials).

The Phase III tests were:

Furnace cyclic oxidation

Low-pressure exposure

Thermal fatigue

Oxidation-erosion rig tests

Ballistic impact

Oxidation after coating damage

Re-entry simulation tests

Two other tests were included to evaluate the effects of the coating and processing conditions on the mechanical properties of the alloys:

Tensile tests

Stress-oxidation tests

7.1 SPECIMEN PREPARATION

The coating parameters and weight gain data are presented in Tables XXXIII and XXXIV and microstructures after each coating cycle are presented in Figures 93 through 96, after chromium-titanium coating of the prevanadized coupons, some of the coupons showed shiny areas similar to those observed occasionally when the Cr-Ti coating is applied directly to columbium base alloys. After siliconizing in the large pack (Table XXXIV) flaky coatings were observed on some specimens. This condition was apparent only on the edges of specimens facing the outside of the pack,

TABLE XXXIII

PACK RUN DATA FOR THE PHASE III V-CrTi-Si COATED COLUMBIUM ALLOY EVALUATION SPECIMENS

Run Nos.	Pack	Activator, w/o	Temperature °F	Time Hr.	Pressure mm.
200,202,204,205, 209,211,213,219	V[a]	2 NaCl+0.2VCl_4	2200	12	150 Ar
203	60Cr-40Ti	1 KF	2300	3 1/2	10^{-2}
206	60Cr-40Ti	1 KF	2200	3	10^{-2}
212	60Cr-40Ti	1 KF	2300	8	10^{-2}
214	60Cr-40Ti[a]	1 KF	2300	7	10^{-2}
220	60Cr-40Ti[a]	1 KF	2300	4	10^{-2}
221	60Cr-40Ti[a]	1 KF	2300	3	10^{-2}
208,215	Si	1 KF	2100	15	10^{-2}
216,217	Si	1 KF	2050	15	10^{-2}
222	Si	1 KF	2100	7	1.5

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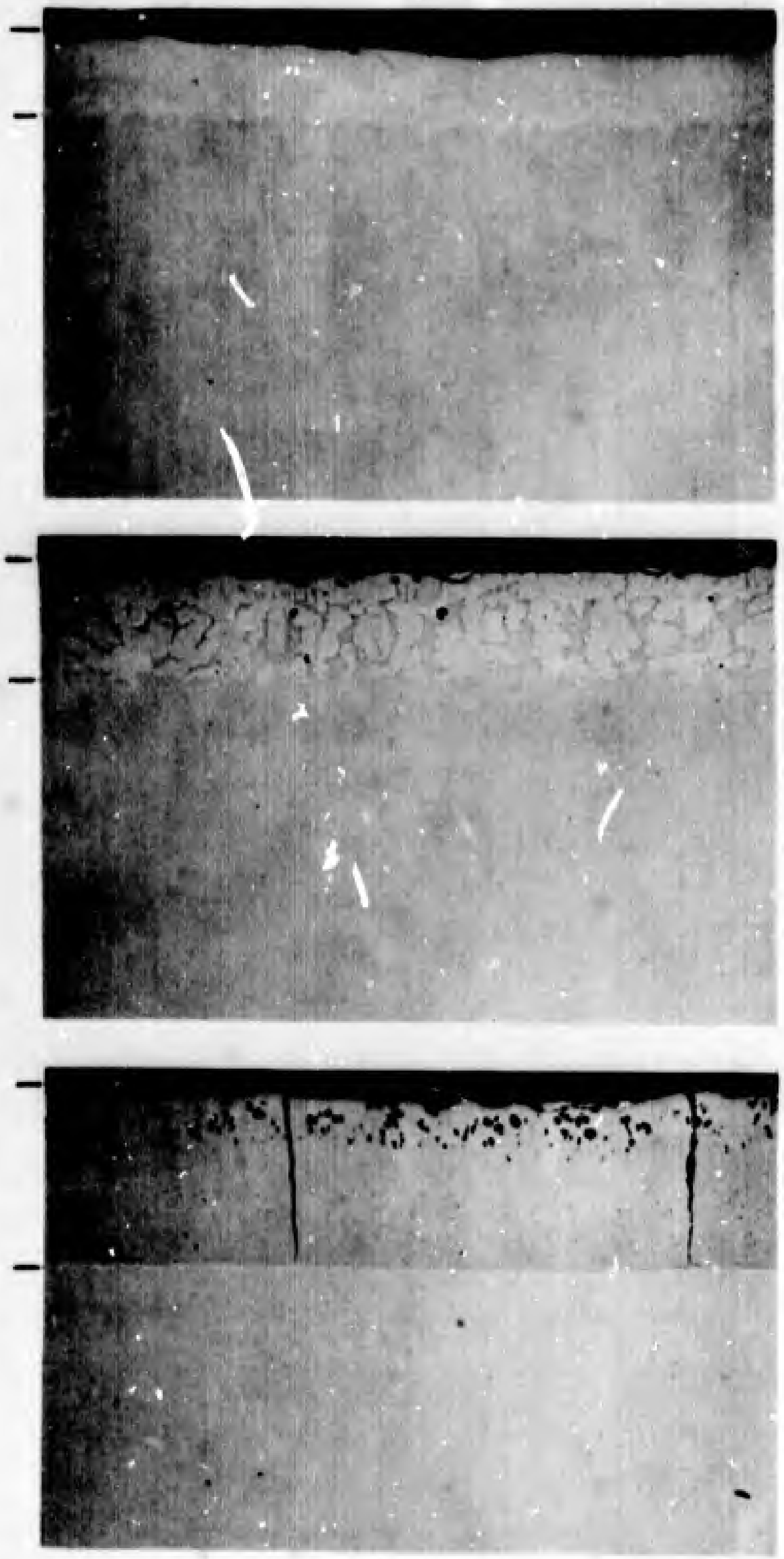
[a] 3.5 in. dia. retort - otherwise 7.25 in. dia. retort.

TABLE XXXIV

WEIGHT GAIN DATA FOR PHASE III
V-Cr Ti-Si COATED COLUMBIUM ALLOY EVALUATION SPECIMENS

Specimen Description	Alloy	V		Cr Ti		Si	
		mg/cm^2	Run No.	mg/cm^2	Run No.	mg/cm^2	Run No.
Oxidation	Cb-752	7.2	209	23.5	212	14.7	217
	XB-88	6.6	209	23.0	212	17.0	216
	Cb 132M	5.8	200	21.8	203,206	15.0	208
	D-43	5.9	200	22.5	203,206	14.8	208
Impact	Cb-752	7.2	209	23.5	212	14.1	216
	XB-88	6.6	209	23.0	212	17.0	216
	Cb 132M	5.8	200	21.8	203,206	15.0	208
	D-43	7.2	209	25.8	212	15.4	216
Erosion Bars	Cb-752	8.0	211	26.7	212	15.4	216
	XB-88	6.8	211	24.8	212	14.4	216
	Cb 132M	6.9	211	26.3	212	14.1	216
	D-43	7.3	211	25.8	212	14.1	216
Thermal Shock	Cb-752	7.6	202	26.7	212	14.1	216
	XB-88	7.6	202	25.0	212	15.4	216
	Cb 132M	7.6	202	24.8	212	14.7	217
	D-43	7.6	202	26.3	212	14.7	217
Tensile	Cb-752	7.7	204	26.7	212	17.8	215
	D-43	6.6	205	25.8	212	17.8	215
(RT)	XB-88	5.7	213	26.	214	16.9	211
	XB-88	5.6	219	21.9	220,221	19.2	222
Stress Oxidation	Cb-752	7.7	204	26.7	212	14.7	217
	D-43	6.6	205	25.8	212	14.7	217
	XB-88	5.6	219	21.9	220,221	19.2	222

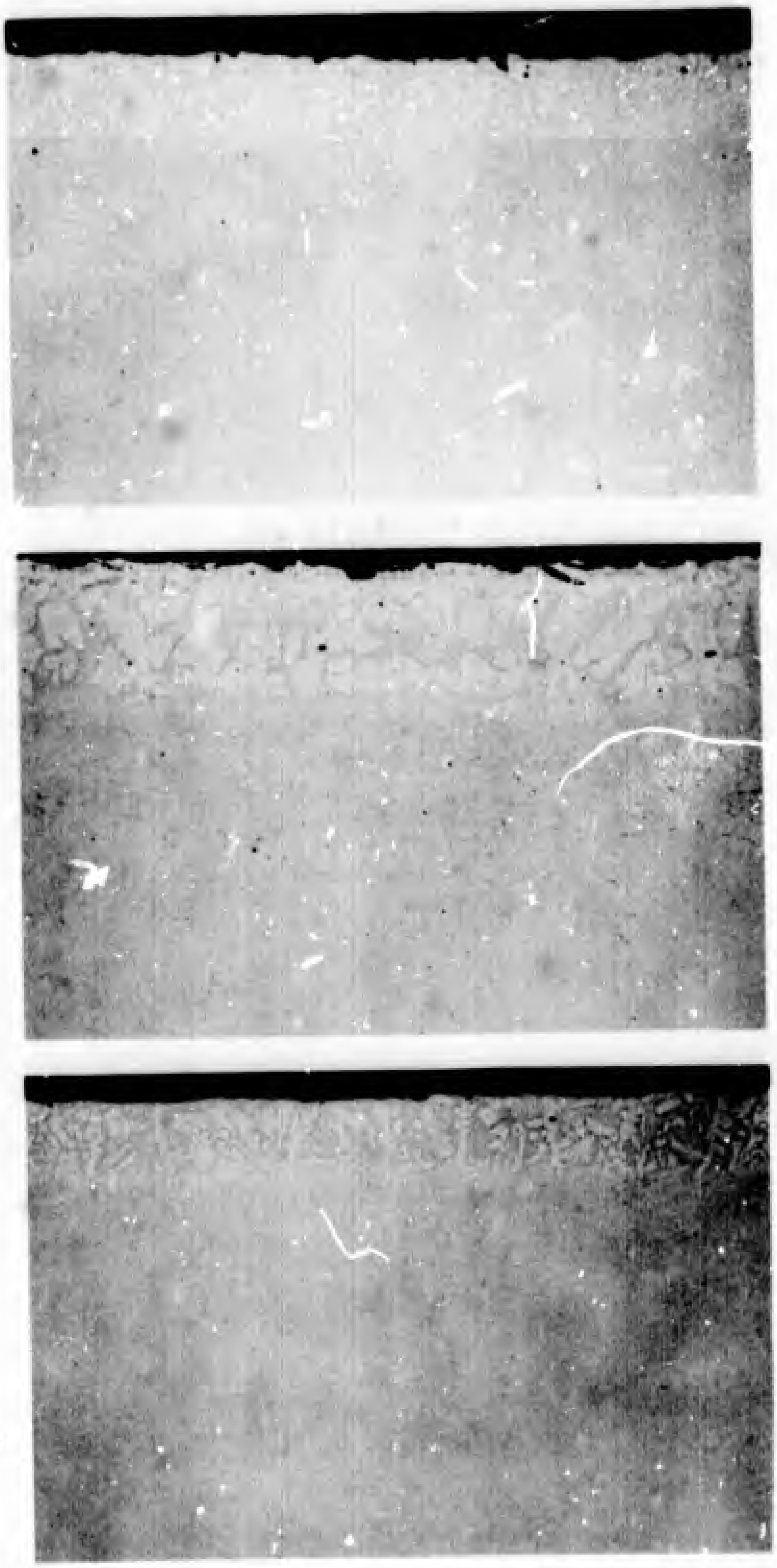


V Run 209

V Run 209
CrTi Run 212

V Run 210
CrTi Run 212
Si Run 215

Figure 93 Microstructures of Columbium Alloy XB-88 after V,CrTi and Si Coating. 250X

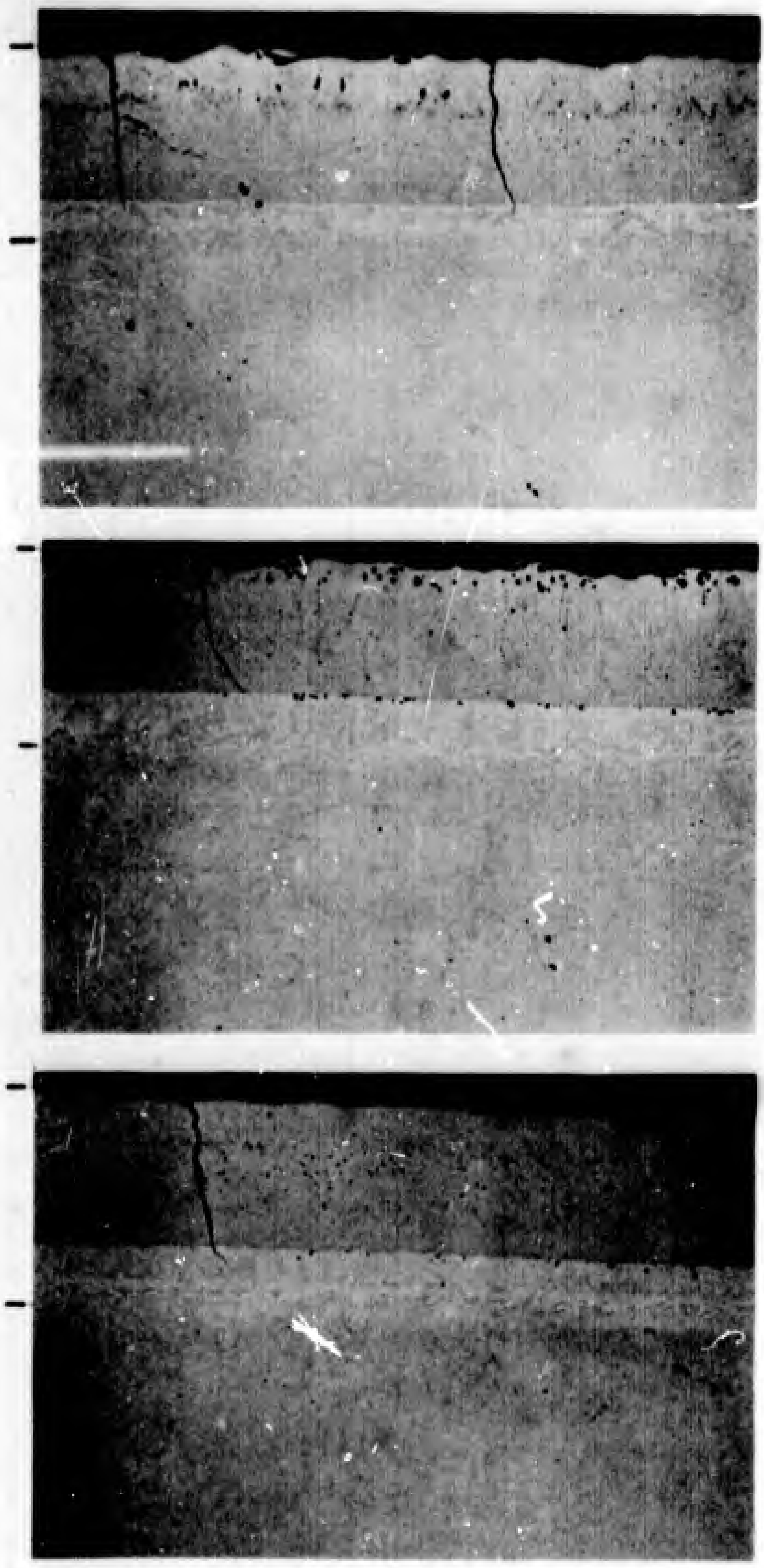


D43:
V Run 200
CrTi Run 203

Cb752
V Run 209
CrTi Run 212

Cb132M:
V Run 200
CrTi Run 203

Figure 94 Microstructures of Columbium Alloys D43, Cb752 and Cb132M after V and CrTi Coating. 250X



D43:

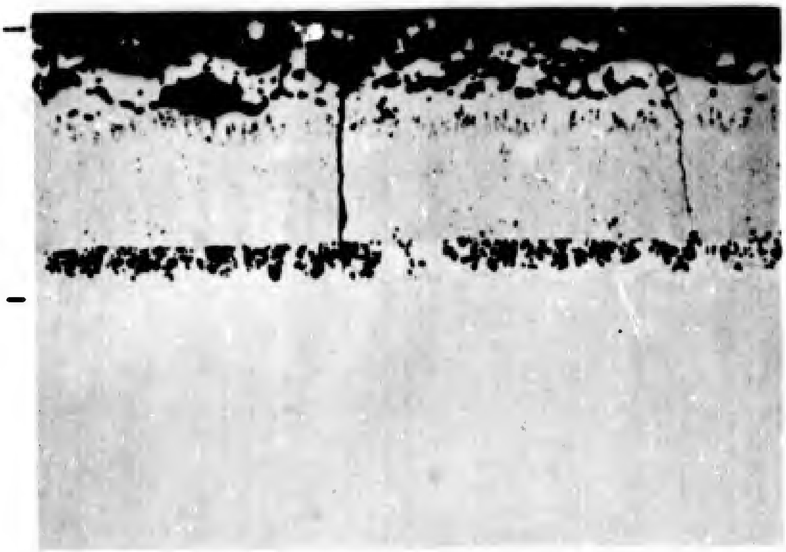
V Run 200
CrTi Run 206
Si Run 208

Cb752:

Cb752
V Run 205
CrTi Run 212
Si Run 215

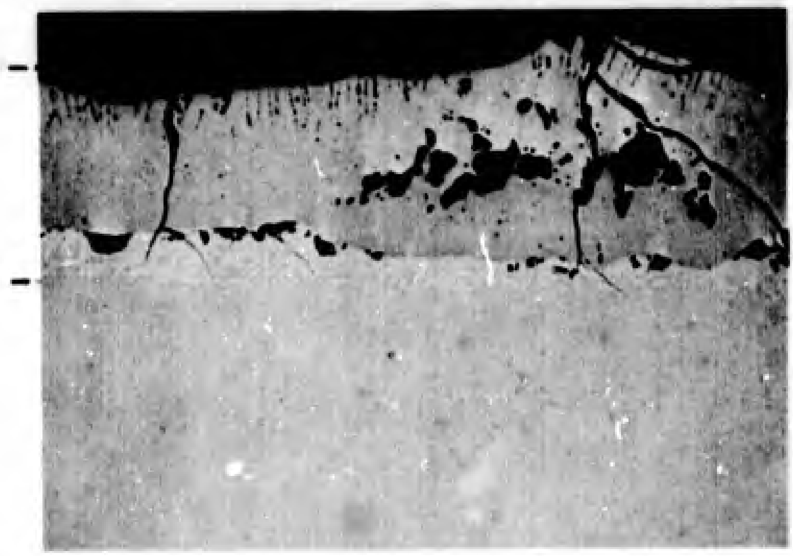
Cb132M:
V Run 200
CrTi Run 206
Si Run 208

Figure 95 Microstructures of Columbium Alloys D-43, Cb752 and Cb132M after V,CrTi and Si Coating. 250X



D-43:

V Run 200
CrTi Run 206
Si Run 208



XB88:

V Run 209
CrTi Run 212
Si Run 215

Figure 96 Photomicrographs Showing Porosity on Specimen Edges. 250X adjacent to the retort surface. This condition was not noted in previous siliconizing runs. The flaking was due to coating porosity predominant in the Laves phase, Figure 96. Solar (1) also reported problems during the silicon deposition cycle when forming the V-CrTi-Si system. The flaking was observed on virtually all substrates, and was probably associated with the growth of a titanium rich silicide which has a relatively large volume change and expansion coefficient in comparison with the chromium rich silicide which normally forms on siliciding the Cr-Ti precoat. The shiny areas generally reflect the absence of the continuous Laves phase, and a titanium rich columbium solid solution region on the precoated surface.

7.2 CYCLIC OXIDATION RESULTS

The high temperature protective capabilities of the V-CrTi-Si coating system on columbium alloys Cb-752, Cb-132M, D-43 and XB-88 were evaluated for up to 1000 hours using the standard MAB cyclic oxidation test at 1600, 2000, 2200 and 2400°F. Test results are summarized in Table XXXV and microstructures after exposure are presented in Figures 97 through 100.

Expected lifetimes at a reliability of 50 and 90% estimated from Weibull plots(at a cumulative failure time of 50 and 10%, respectively) are presented in Table XXXVI. Example of a Weibull plot for the 1600°F cyclic oxidation data is presented in Figure 101. At 1600°F, the failure mechanisms were random type failures for all coated substrates except XB-88 which showed a wearout type failure. At 2000°F, the Cb-752 and Cb-132M coated samples showed infant mortality failures, whereas the others showed wearout failures. At 2200°F, the Cb-752 and D-43 coated materials showed wear-out type failures and the XB-88 and Cb-132M random type failures. Virtually all failures occurred on edges. At 2400°F, no failures were observed in 200 hours of exposure on any of the substrates. This suggests that any defects that are present in the coating are amenable to self-repair at this temperature due to the fluid nature of the oxide, whereas at lower tempratures, this mechanism is not operative.

Microscopic inspection of coated coupons exposed for 1000 hours at 1600°F showed cracks through the coating into the Laves phase. Similar cracks were more heavily oxidized at higher exposure temperatures, and in addition, at 2000° and 2200°F, a thicker oxide surface layer was evident. No oxygen penetration was observed for any of the specimens examined with exception of the 2000°F exposed Cb-132M and XB-88 specimens, Figures 98 and 100. The stability of the intermediate chromide layer can also be observed from these photographs. After 1000 hours at 1600°F, the thickness of the chromide layer is virtually unchanged from the as-coated condition. Dissolutioning of this phase is observed to increase with increasing temperature, and the layer is nearly consumed after 1000 hours at 2200°F.

TABLE XXXV

CYCLIC OXIDATION DATA FOR THE V-CrTi-Si COATING SYSTEM ON VARIOUS COLUMBIUM ALLOY SUBSTRATES

Alloy	Cyclic Oxidation Life, Hours 1600°F	 2000°F	 2200°F	 2400°F[a]
Cb-752	408[b],1008,1008+[c](6)[d]	48,48,72,520,1008+(4)	816,1008+(7)	200+(8)
Cb-132M	312,792,1008+(2)	72,648,864(2)	176[e],464,696,1008+	200+(4)
D-43	96,232,256,648,792, 1008+(3)	384,672,888,1008+(5)	544,1008+(7)	200+(8)
XB88	648,816,960,1008	520,1008+(3)	232,360,984,1008+	200+(4)

---

a. Furnace malfunction at 200 hours.
b. All edge failures unless otherwise indicated.
c. Plus signs indicates no failure - test terminated.
d. Numbers in parentheses refer to number of specimens with identical life.
e. Surface failure.

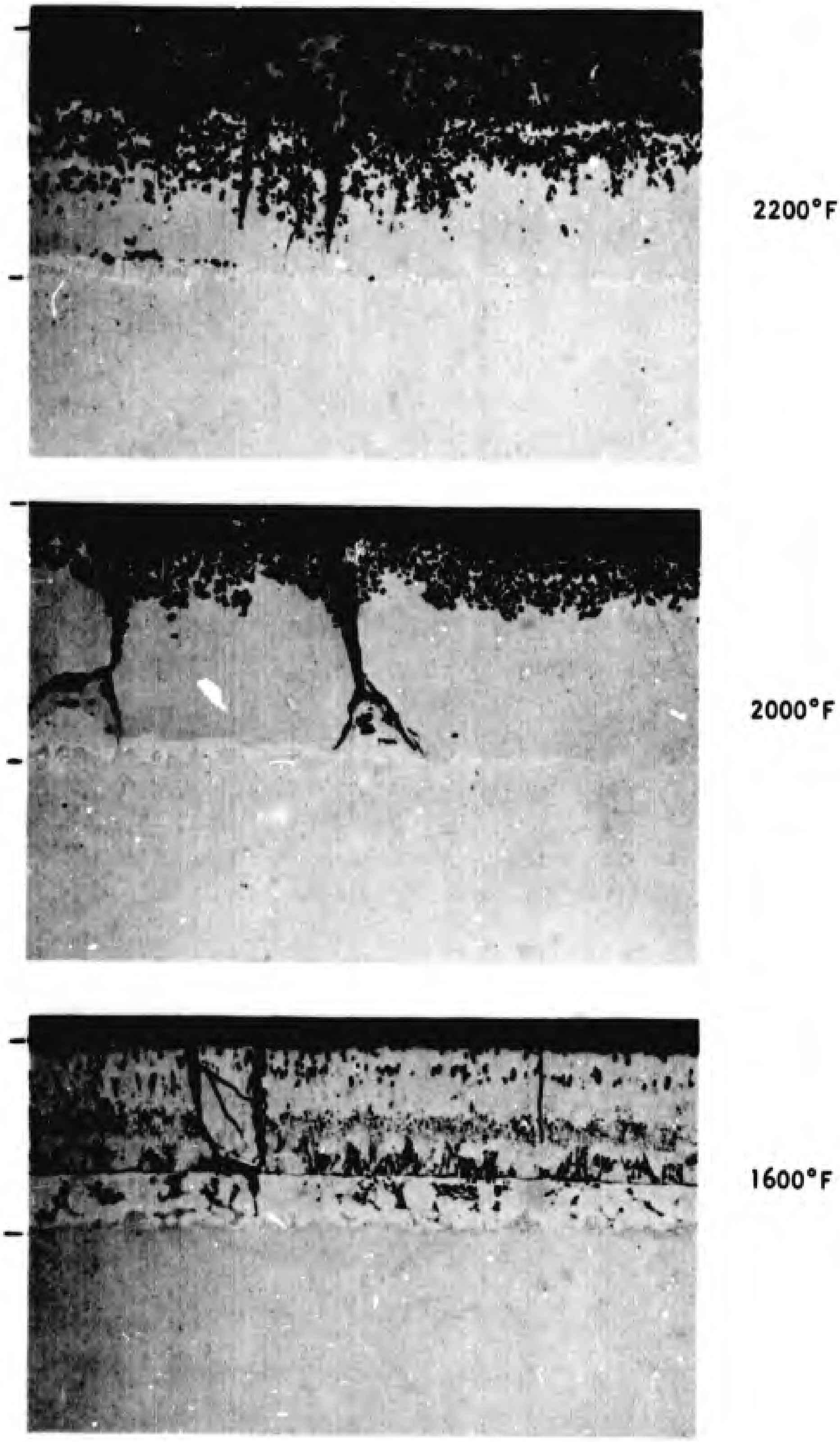


Figure 97 Microstructures of V-CrTi-Si Coated Columbium Alloy Cb752 after 1000 hour Cyclic Exposure at the Indicated Temperatures. 250X

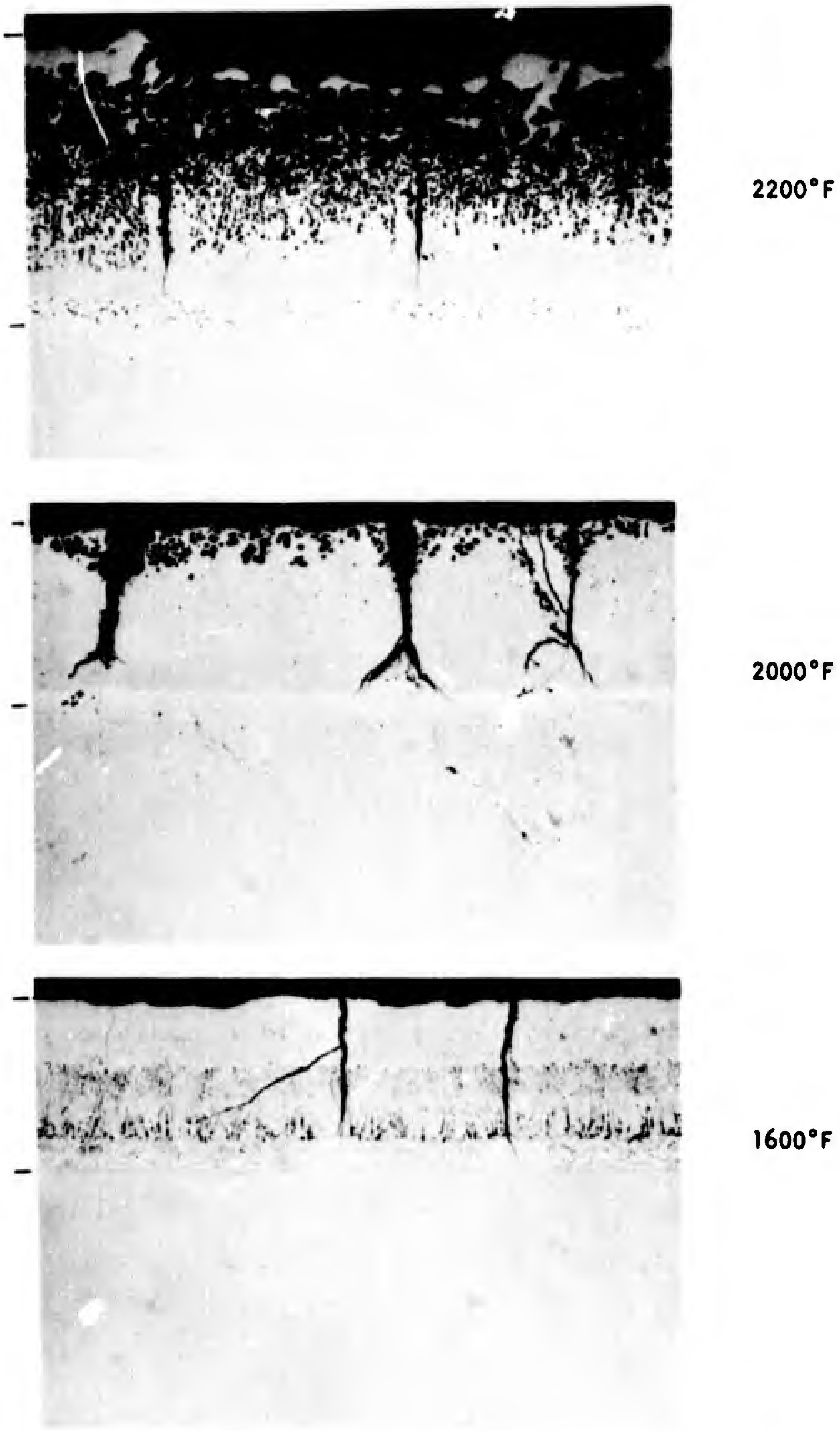
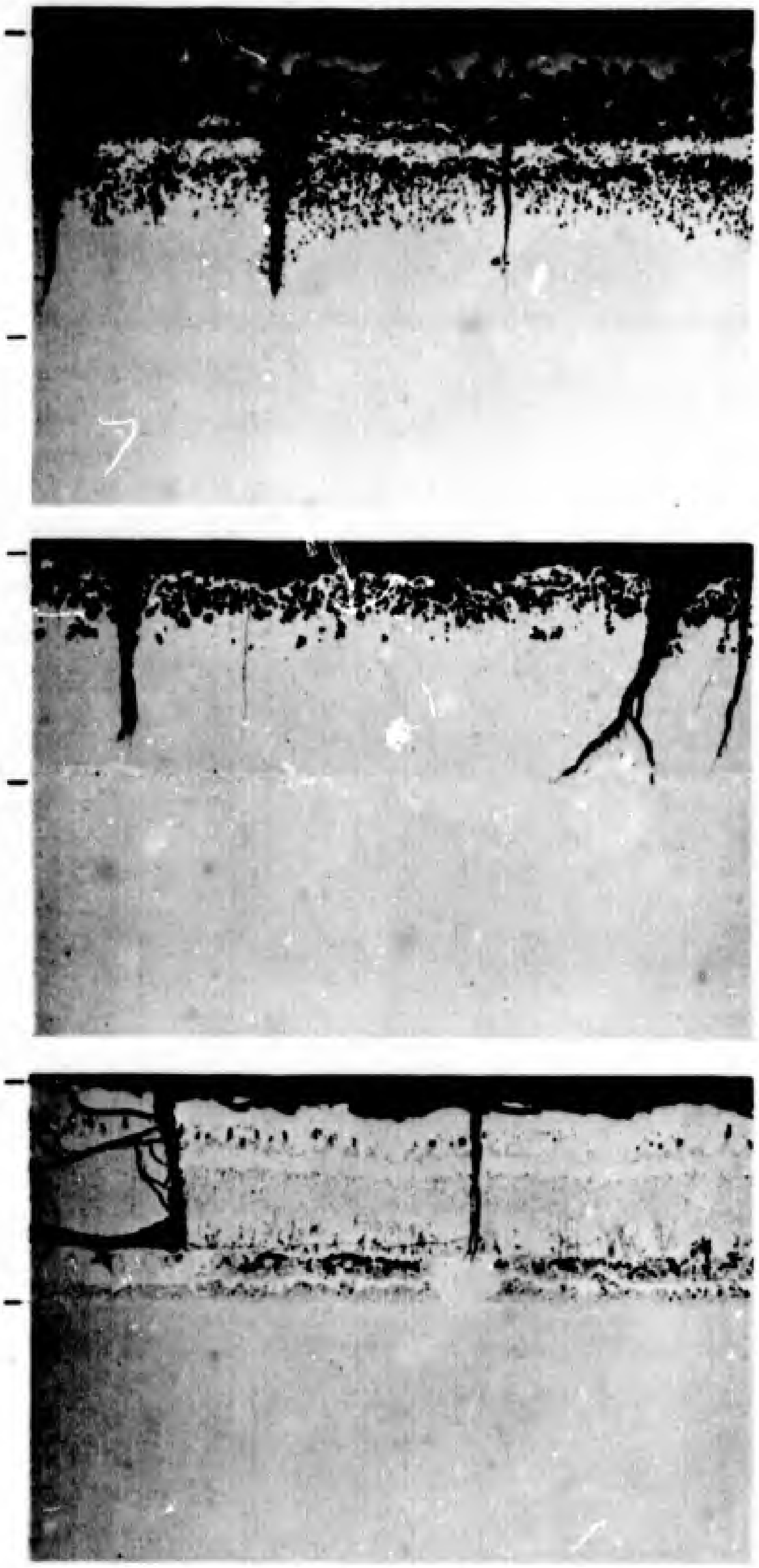


Figure 98 Microstructures of V-CrTi-Si Coated Columbium Alloy Cb-132M after 1000 hour Cyclic Exposure at the Indicated Temperatures. 250X


2200°F

2000°F

1600°F

Figure 99 Microstructures of V-CrTi-Si Coated Columbium Alloy D-43 after 1000 hour Cyclic Exposure at the Indicated Temperatures. 250X

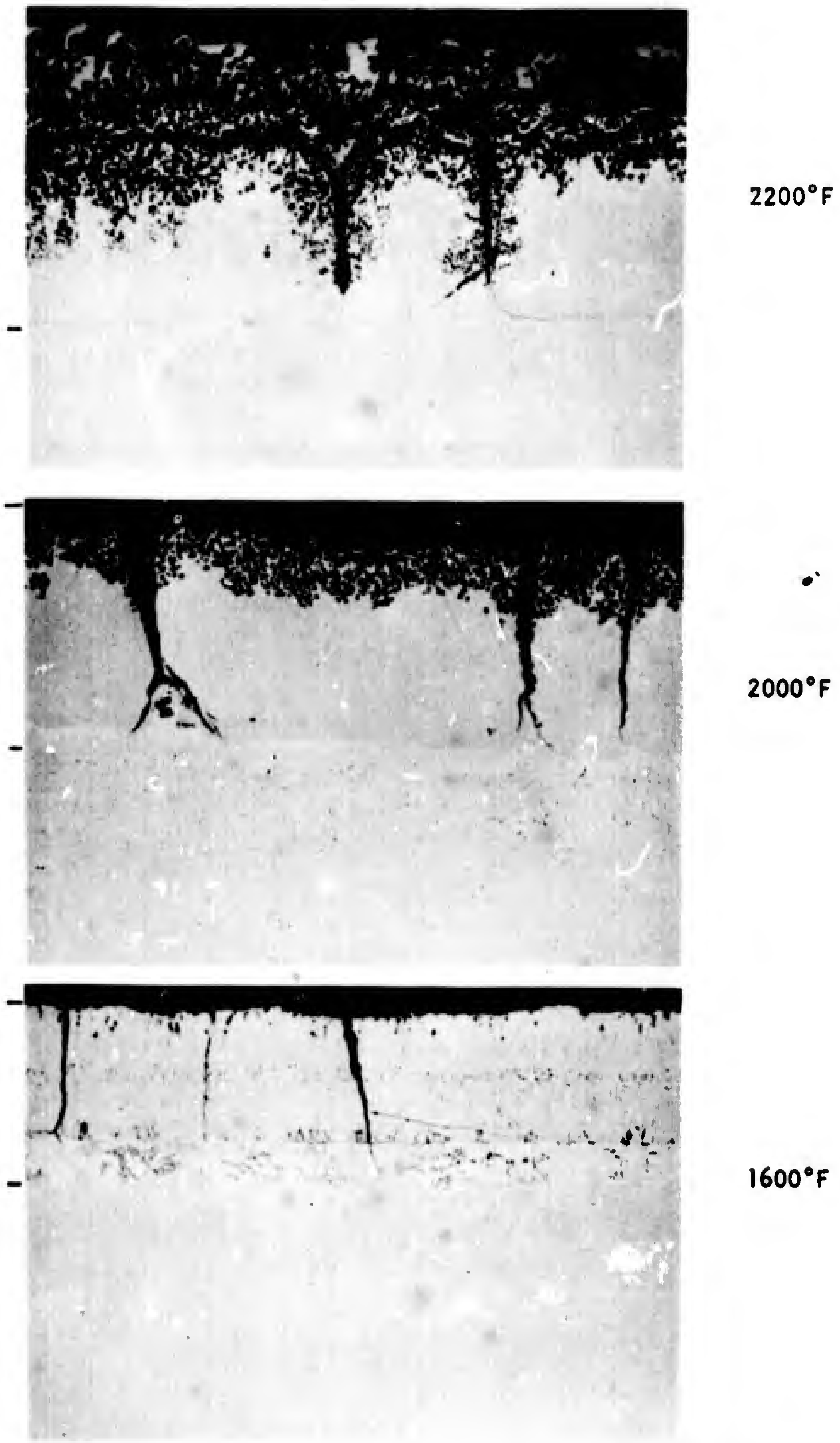


Figure 100 Microstructures of V-CrTi-Si Coated Columbium Alloy XB-88 after 1000 Hour Cyclic Exposure at the Indicated Temperatures. 250X

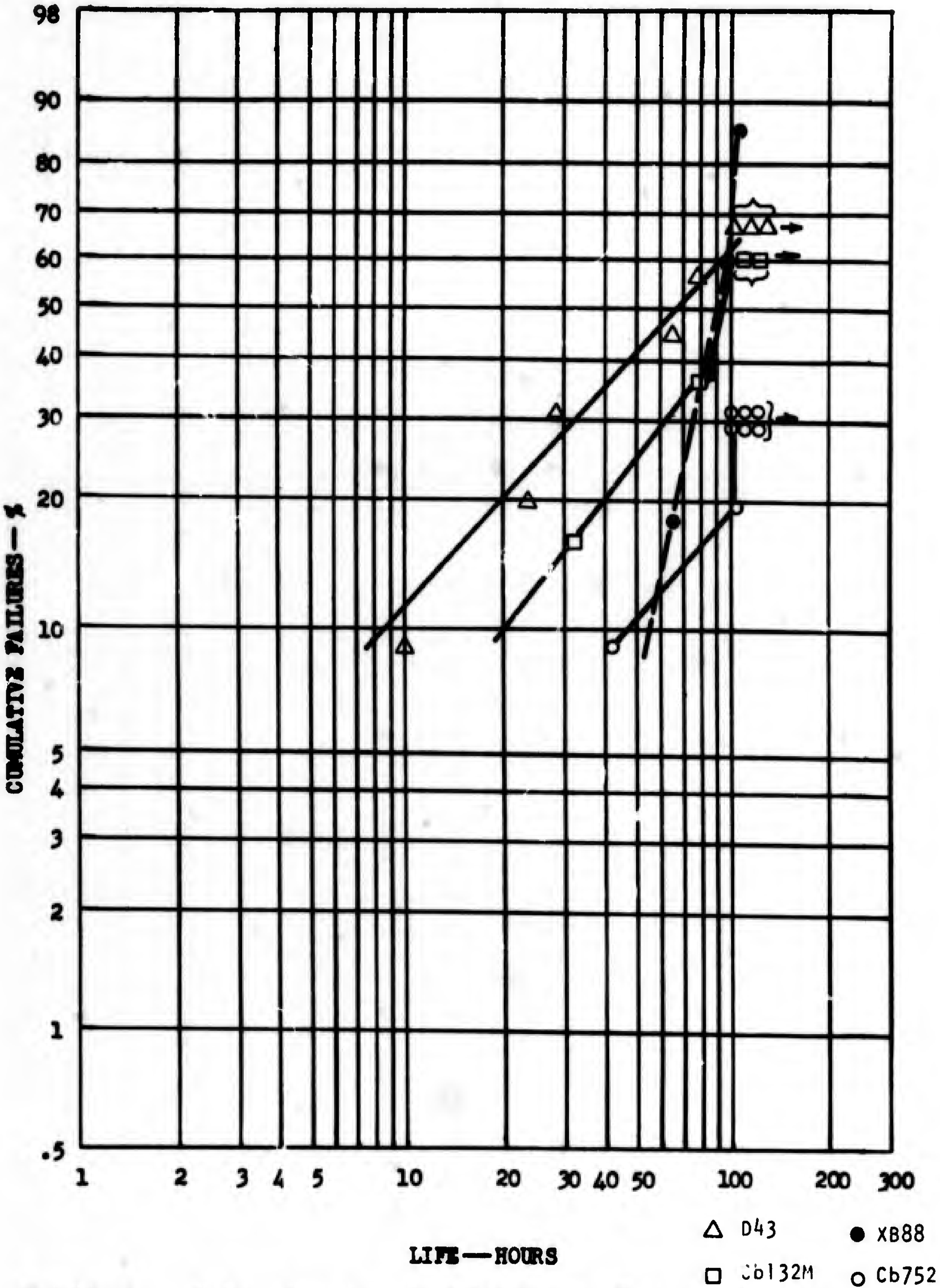


FIGURE 101. WEIBULL PLOT SHOWING PERCENT CUMULATIVE FAILURE VERSUS CYCLIC OXIDATION LIFE AT 1600°F FOR V-CrTi-Si COATED COLUMBIUM ALLOYS.

TABLE XXXVI

EXPECTED LIFE OF V-Cr Ti-Si COATING ON VARIOUS COLUMBIUM ALLOY SUBSTRATES AT 50 AND 90% RELIABILITY BASED ON WEIBULL ANALYSIS

Temperature °F	Alloy	Reliability - Life in Hr. 90%	50%
1600	D-43	90	700
	Cb 132M	200	850
	Cb-752	450	3000
	XB-88	600	850
2000	D-43	400	1600
	Cb 132M	50	800
	Cb-752	20	1000
	XB-88	400	1600
2200	D-43	600	1600
	Cb 132M	140	600
	Cb-752	850	1600
	XB-88	160	600
2400	D-43	200 +	200 +
	Cb 132M	200 +	200 +
	Cb-752	200 +	200 +
	XB-88	200 +	200 +

7.3 THERMAL PROFILE OXIDATION RESULTS

Thermal profile oxidation tests simulating a typical re-entry condition were conducted on the V-CrTi-Si coated columbium alloys. The test profile is shown in Figure 102.

The specimens were placed on pure alumina brick housed in a semicylindrical Inconel shell. The unit was moved in and out of the hot zone of a tube furnace by means of an assembly activated by a motor gear train which made approximately one revolution per hour. Results of the above test are summarized below (Table XXXVII).

TABLE XXXVII

RE-ENTRY SIMULATION TEST DATA

Base Alloy	2400°F Maximum Temperature Re-entry Simulation Life (No. of 1-hr Cycles to Failure)
Cb-752	25 +, 25 +, 25 +[a]
Cb-132M	6, 16[b], 25 +
D43	25, 25, 25
XB-88	25, 25 +, 25 +

---

a. + Plus sign indicates test stopped - no failure

b. Surface failure-otherwise edge failure

The results show that the Cb-132M and D43 coated materials were susceptible to failure in 25 thermal cycles or less by slow cyclic testing at atmospheric pressure. In contrast, the Cb-752 and XB-88 coated substrates appeared to be capable of 25 or more re-entry simulated exposures. No failures were experienced on any of the coated substrates when air cooled from 2400°F to room temperature during furnace cyclic oxidation testing in over 100 cycles.

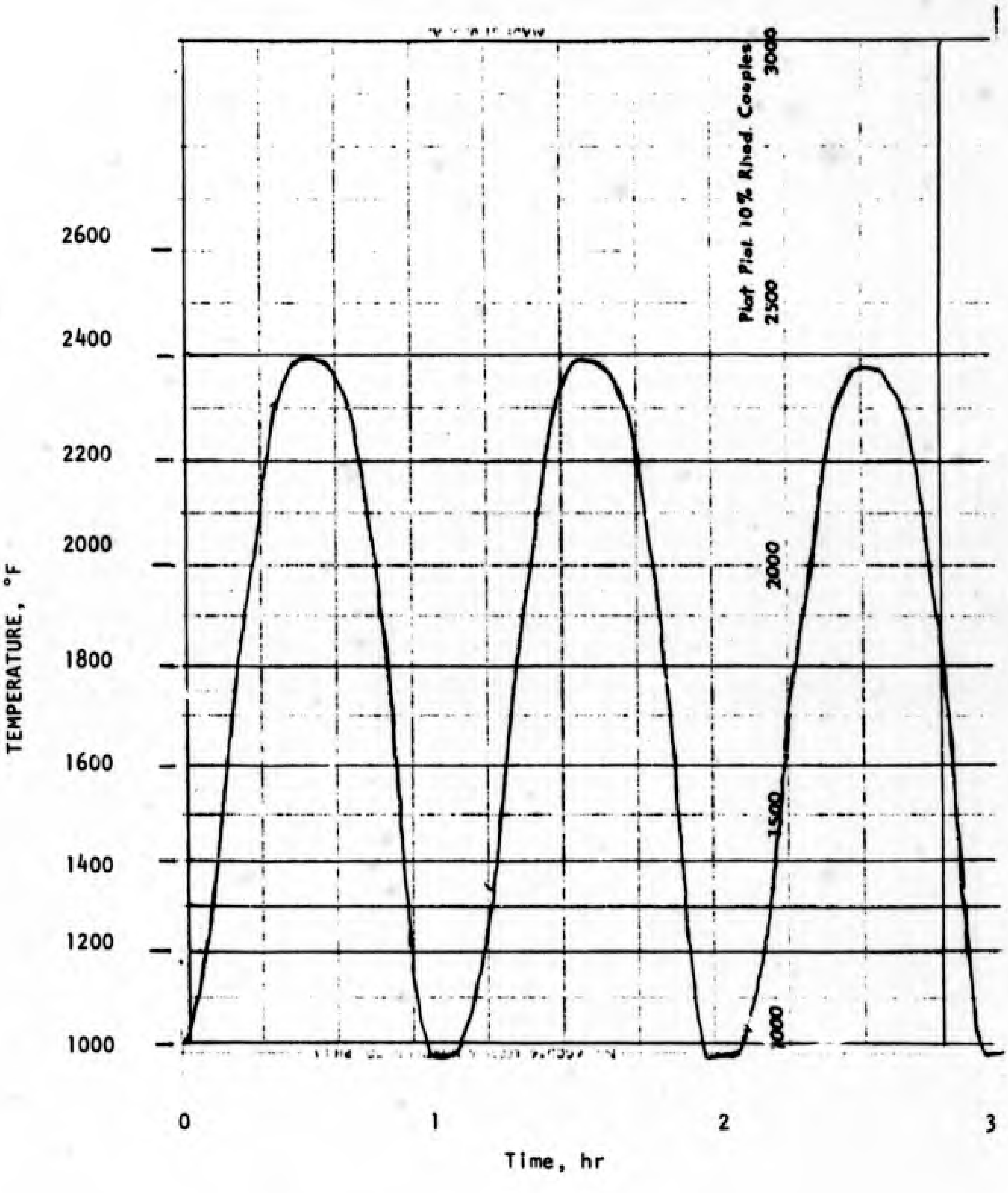


Figure 102 Temperature Profile for Reentry Simulation Test.

7.4 REDUCED PRESSURE CYCLIC OXIDATION RESULTS

Coated specimens were exposed at two reduced pressures, (0.1 - 0.5 and 1-5 mm) for 1 and 4 hours at 2400°F and for 1 hour at 2600°F, to determine performance under low pressure-high temperature conditions which are encountered during the flight of a re-entry vehicle. Post oxidation at one atmosphere after low pressure exposure was also employed to determine the degree of coating degradation. The cyclic post oxidation exposure was conducted at 2400°F. Test results are summarized in Table XXXVIII, and microstructures after low pressure exposure are presented in Figures 103 through 106.

The photomicrographs show that some coating changes occurred as a consequence of exposure. These changes, which are manifested as probable oxide precipitates in the silicide layer, are not only a direct function of time, but also of temperature. On the other hand, pressure apparently had a reverse effect, with more precipitate being visible for the lower pressure exposures. Vaporization loss of silicon via SiO formation undoubtedly occurred under these conditions causing some loss of coating reservoir.

Cyclic oxidation exposure indicates that little coating degradation occurred as a result of low pressure exposure at 2400°F for the four columbium alloys coated. On the other hand, low pressure exposure at 2600°F appeared to be detrimental to the oxidation life of the Cb-132M and D43 materials, whereas the Cb-752 and XB-88 materials were not adversely affected. Thus, an important conclusion is the probability that the V-CrTi-Si system will provide multiple usage capability for hypersonic and re-entry vehicles.

7.5 THERMAL SHOCK TESTS

Thermal shock tests were performed on coated Cb-752 and D43 1 inch x 2 inch sheet specimens formed into a "V", and on Cb-132M and XB-88 wedge specimens with a configuration identical to an erosion bar. Testing at 2000, 2200 and 2400°F consisted of heating to the desired peak temperature with an oxyacetylene flame, and cooling to approximately 200°F with an ambient temperature air blast. Each thermal cycle consisted of 15 seconds to temperature followed by a 15 second cooling period.

Photographs of specimens after 1000 cycles are presented in Figures 107 and 108. Failure of two Cb-132M specimens and one XB-88 specimen occurred at 2200°F after 240, 760 and 570 cycles respectively, Table XXIX. Failure, as judged by the appearance of substrate oxide, occurred as small localized tubercles on specimen edges. The growth rate of these failure areas for the remainder of the exposure time was generally low. Coating flaking was noted for the Cb-752 and D43

TABLE XXXVIII

CYCLIC EXPOSURE LIFE AT 2400°F OF V-CrTi-Si COATED COLUMBIUM ALLOYS AFTER LOW PRESSURE EXPOSURE

Low Pressure Pre-Exposure Conditions			2400°F Post-Exposure Life of Coated Columbium Alloys, Hr.			
Temperature °F	Time Hr.	Pressure mm	Cb-752	Cb 132M	D-43	XB-88
2400	1	0.1-0.5	575+,575+[a]	55,575+	215,575+	575+,575+
2400	1	1-5	55,575+	575+,575+	575+,575+	9,575+
2400	4	0.1-0. 5	32,575+	359,575+	575+,575+	575+,575+
2400	4	1-5	551,575+	575+,575+	527,575+	575+,575+
2600	1	0.1-0.5	527,551	55,359	32,32	551,575+
2600	1	1-5	575+,575+	32,32	9,32	575+,575+

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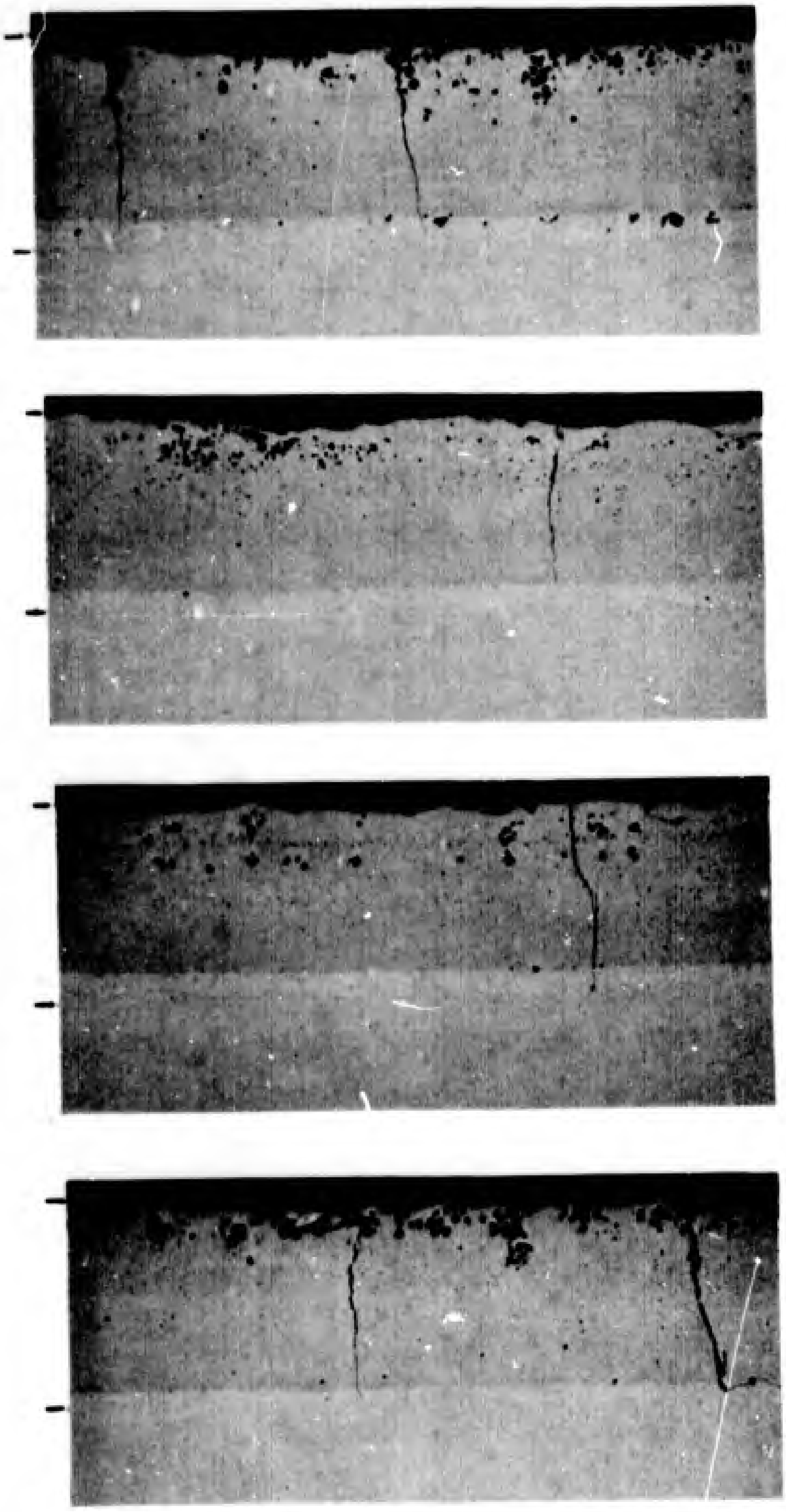
a. Plus sign indicates no failure - test terminated.



CB-752

Cb-132M

D-43

XB 88

Figure 103 Microstructures of V-CrTi-Si Coated Columbium Alloys after a 4 hour Low-Pressure (1-5 mm) Exposure at 2400°F. 250X

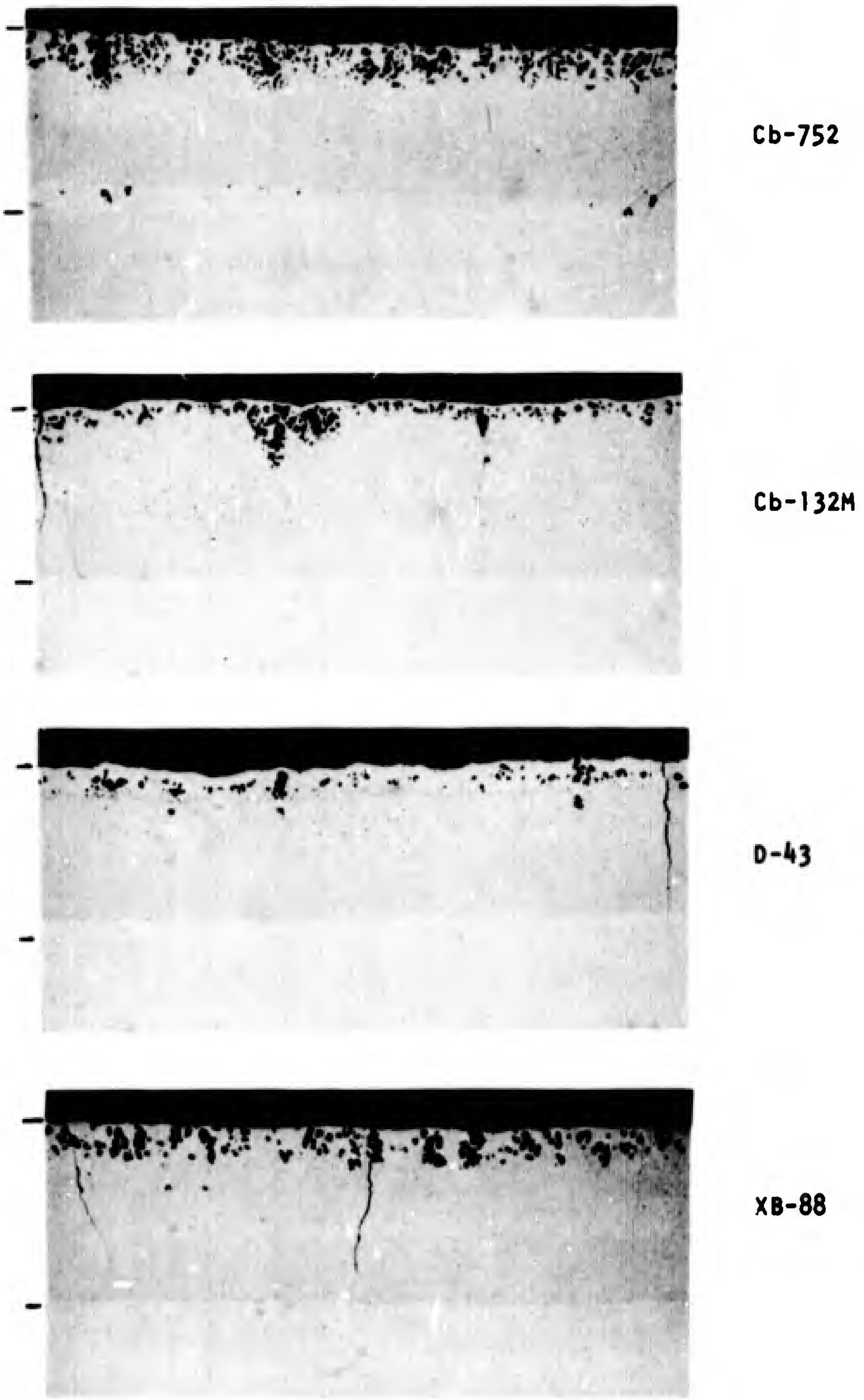
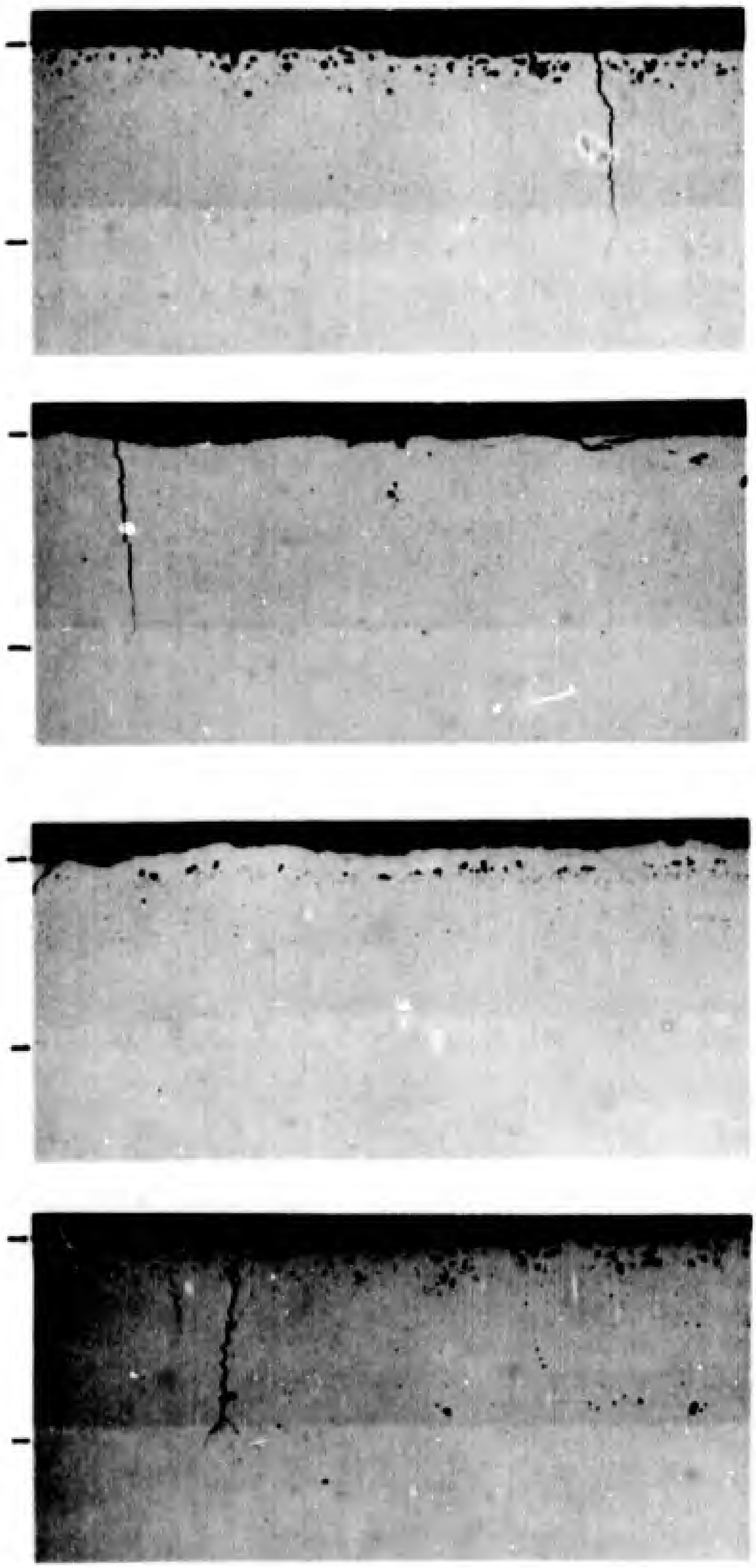


Figure 104 Microstructures of V-CrTi-Si Coated Columbium Alloys after a 4 hour Low Pressure (0.1-0.5mm) Exposure at 2400°F. 250X



Cb-752

Cb-132M

D-43

Xb88

Figure 105 Microstructures of V-CrTi-Si Coated Columbium Alloys after a one Hour Low-Pressure (1-5mm) Exposure at 2600°F. 250X

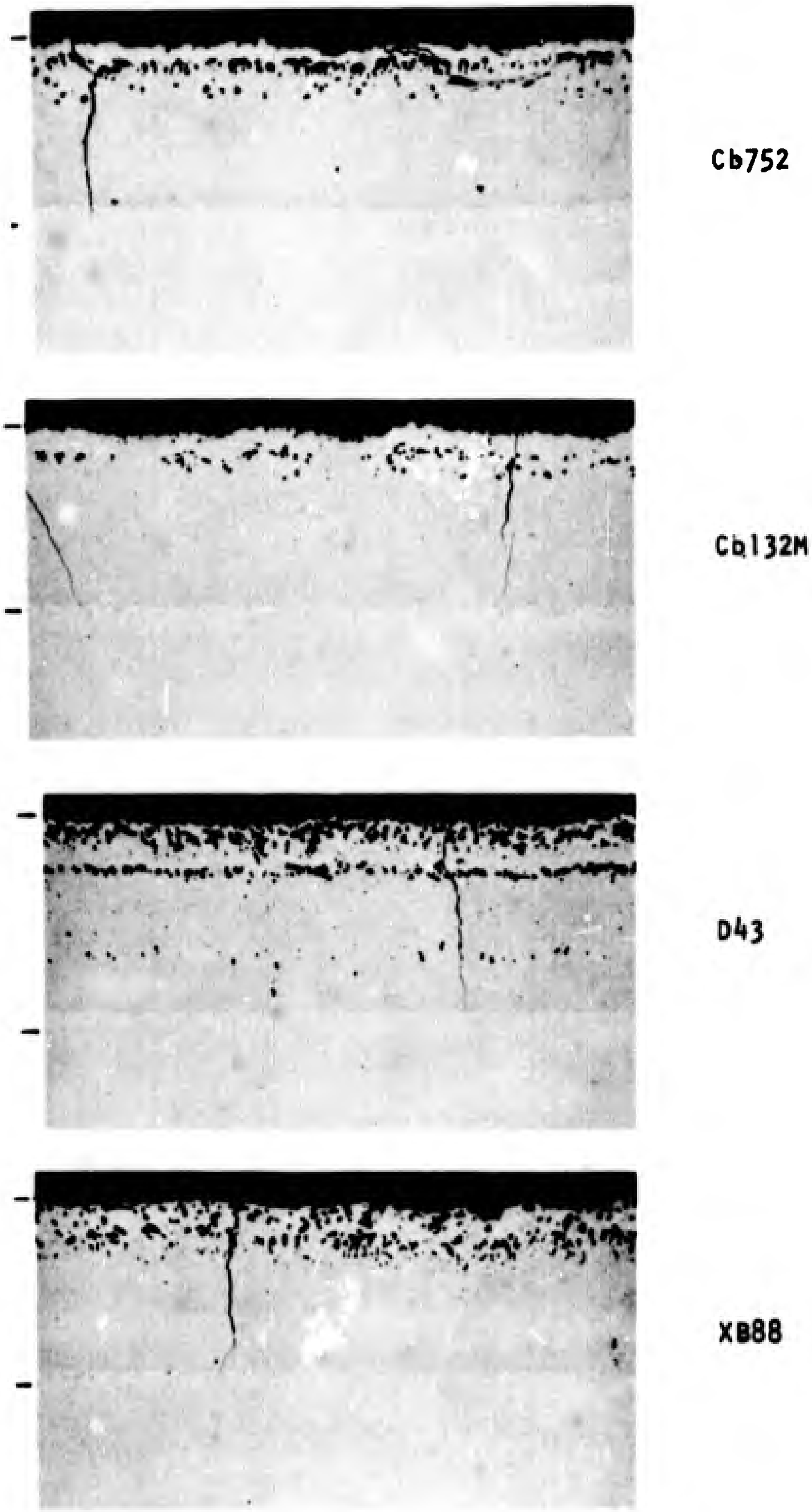
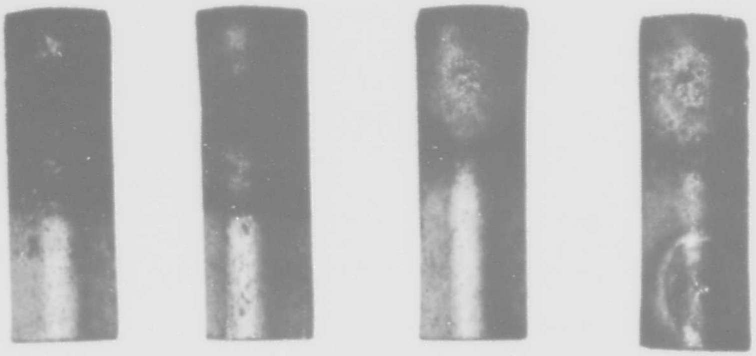
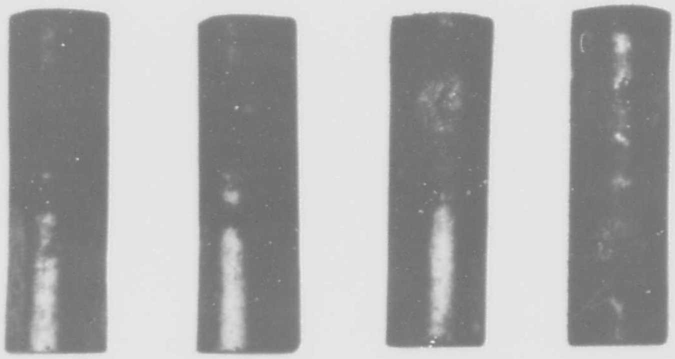


Figure 106 Microstructures of V-CrTi-Si Coated Columbium Alloys after a One Hour Low Pressure (0.1-0.5 mm) Exposure at 2600°F. 250X



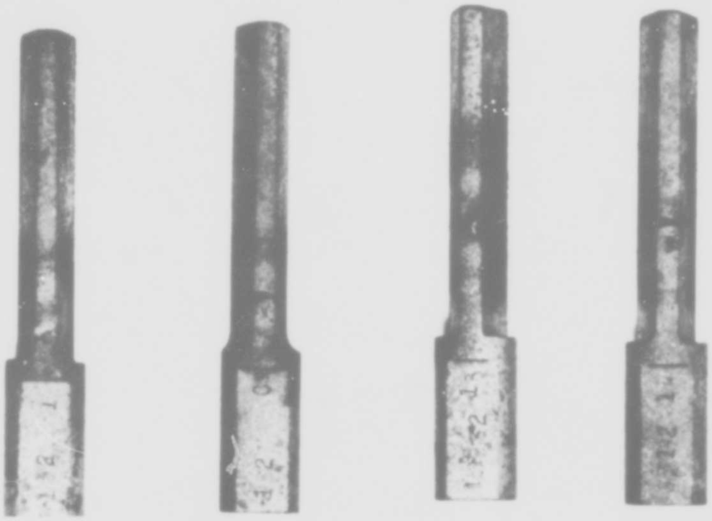
Cb752

2200°F 2400°F

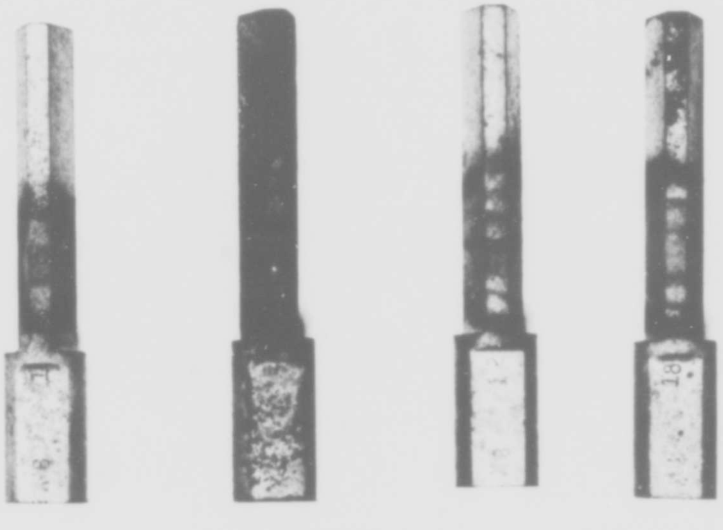


2200°F D43 2400°F

Figure 107 Thermal Fatigue Cb-752 and D-43 Columbium Alloy Specimens with V-CrTi-Si Coating after 1000 cycles at 2200°F and 2400°F.



2000°F Cb132M 2200°F



2000°F XB88 2200°F

f

Figure 108 Thermal Fatigue Cb-132M and Xb-88 Columbium Alloy Specimens with V-CrTi-Si Coating after 1000 cycles at 2000 and 2200°F.

TABLE XXXIX

THERMAL SHOCK TEST DATA

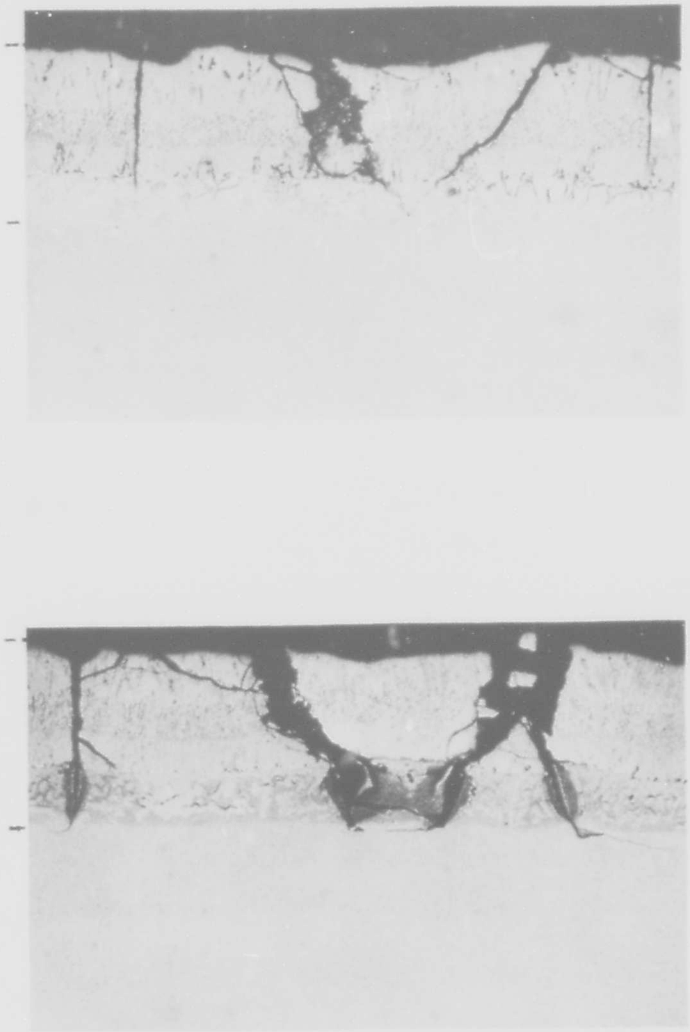
Alloy	Number of Cycles[a] at Peak Temperature 2000°F	2200°F	2400°F
Cb-752	-	1000+,1000+[b]	1000+,1000+
Cb 132M	1000+,1000+	240,760[c]	-
D-43	-	1000+,1000+	1000+,1000+
XB-88	1000+,1000+	570[c] ,1000+	-

---

[a] 15-second heating to peak temperature followed by 15-second cooling.

[b] Plus sign indicates no failure.

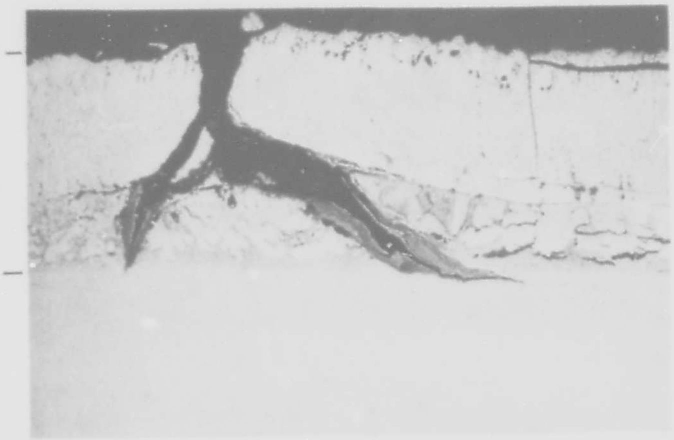
[c] Failure areas manifested as localized small tubercles which grew slowly in size with continued testing.



2000°F

2200°F

Figure 109 Microstructures of V-CrTi-Si Coated XB-88 Columbium Alloy Thermal Shock Specimens after 1000 Cycles at the Indicated Temperatures.
250X



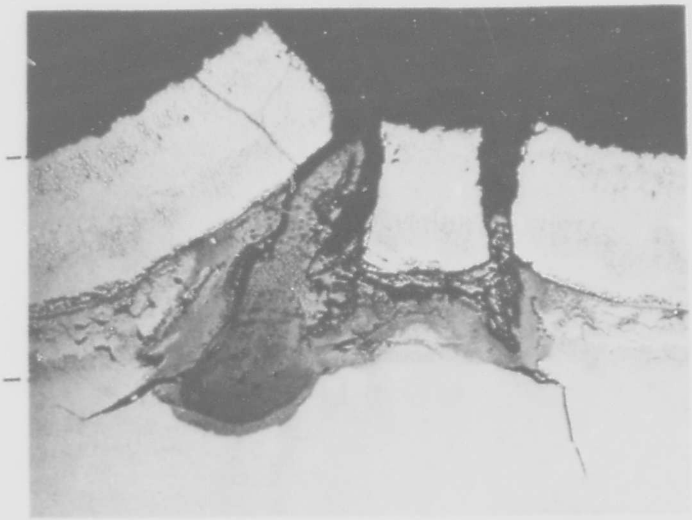


Figure 110 Microstructures of V-CrTi-Si Coated Cb752 Columbium Alloy Thermal Shock Specimens after 1000 Cycles at the Indicated Temperatures. 250X

specimens tested at 2400°F.

Microscopic examination of specimens exposed for 1000 cycles showed, in general, the formation of cracks in the coating with oxide formation in the cracks, Figures 109 and 110. At a peak temperature of 2000°F, the Cb-132M and XB-88, Figure 109, substrates were protected from internal oxidation. At the peak temperature of 2200°F, the oxide build-up in the fissures was greater than at the lower test temperature. Although the coating was penetrated, no serious oxygen contamination of the Cb-752, D43 and XB-88 materials was noted, with exception of the Cb-132M material where oxygen penetration of the substrate occurred. At a peak temperature of 2400°F, the oxide formation in the coating cracks was heavy, and oxide growth laterally at the silicide-substrate interface was evident, Figure 110. In addition, crack growth into the substrate was observed for the Cb-752 and D43 materials. Based on the above results, the V-CrTi-Si coating appeared to have a capacity for protecting various columbium alloy substrates in a thermal shock environment for up to 1000 cycles at peak temperatures to 2400°F before severe coating degradation occurred.

7.6 BALLISTIC IMPACT TEST RESULTS

Ballistic impact tests results at room temperature, 1600 and 2200°F, are summarized in Table XL. The energy of impact was 4.6 - 4.7 ft-lb. as in previous tests. The data show that the Cb-752 and XB-88 substrates were cracked or fractured at room temperature only; whereas, the Cb-132M substrate was fractured at all test temperatures. Generally, impact resulted in coating spalling adjacent to the impact area on both the impact and reverse sides. Photographs showing the ballistic impacted and reverse surfaces are presented in Figures 111 through 113 for typical samples of the various V-CrTi-Si coated alloys.

Cyclic oxidation life at 2200°F of the ballistic impact tested coupons is summarized in Table XLI. The specimens were cycled to room temperature every hour until failure. Other than the fractured or cracked specimens, which were not exposed, all coated materials demonstrated a capacity for operation for 16 hours or more after impact.

7.7 EROSION-OXIDATION RIG TEST RESULTS

Erosion-oxidation rig data are presented in Table XLII, and photographs of the tested bars are shown in Figures 114 through 116. Coated specimens were tested in a burner rig utilizing a mixture of jet type A fuel and air. The sulfur content of the fuel was adjusted to 0.4 w/o by the addition of ditertiary butyl disulfide. Temperature

TABLE XL

BALLISTIC IMPACT TEST RESULTS
V-CrTi-Si COATED COLUMBIUM ALLOY SUBSTRATES

Alloy	Specimen Temperature at Impact, °F	Remarks
Cb-752	R.T.	Cracked (2)
	1600	Spalling on opposite side adjacent to depression (1)
	2000	Spalling adjacent to depression - both sides (2)
Cb 132M	R.T.	Fractured (2)
	1600	Cracked (2)
	2000	Cracked (1); edge hit (1)
D-43	R.T.	Spalling on both sides (2)
	1600	Spalling on both sides adjacent to depression
	2000	Spalling on opposite side (1) Spalling on both sides (1)
XB-88	R.T.	Cracked (1); Fractured (1)
	1600	Spalling on both sides (1); edge hit (1)
	2000	Depression on one side, no spalling (2)

Thickness of substrate: Cb-752 and D-43 - 0.030 in.; Cb 132M - 0.063 in.; XB-88 - 0.049 in.

Velocity: 340 ft/sec.

Impact Energy: 4.6 - 4.7 ft-lb.

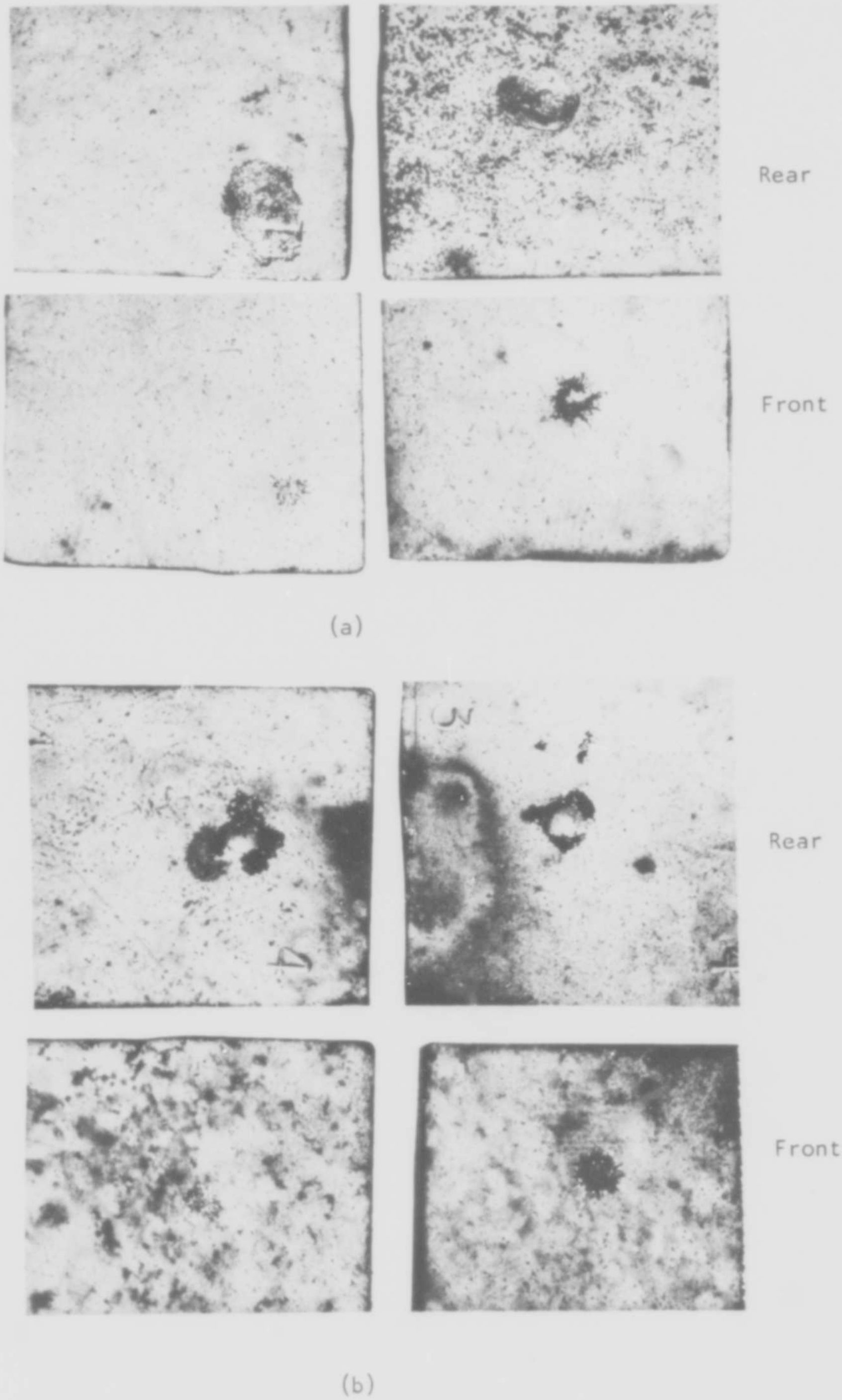


Figure 111 Ballistic Impact Tested V-CrTi-Si System on Columbium Alloy D-43 at (a) Room Temperature and (b) 1600°F. 2-1/2 X

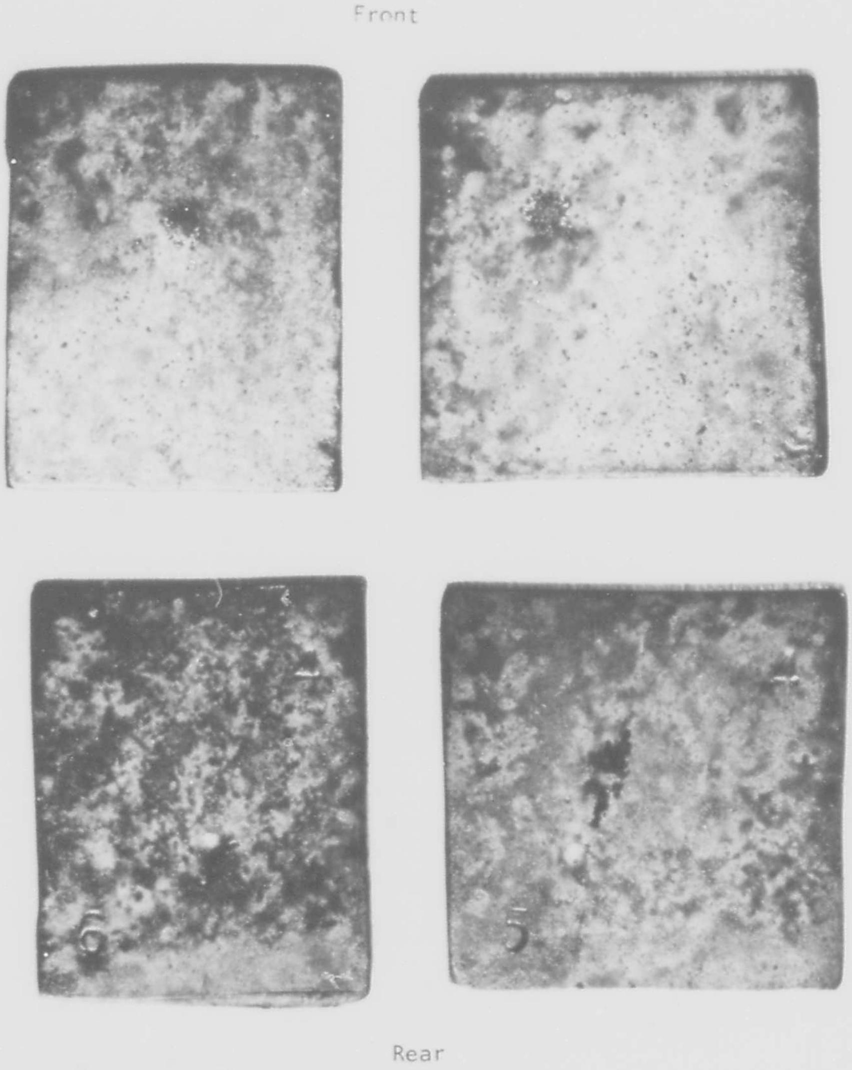
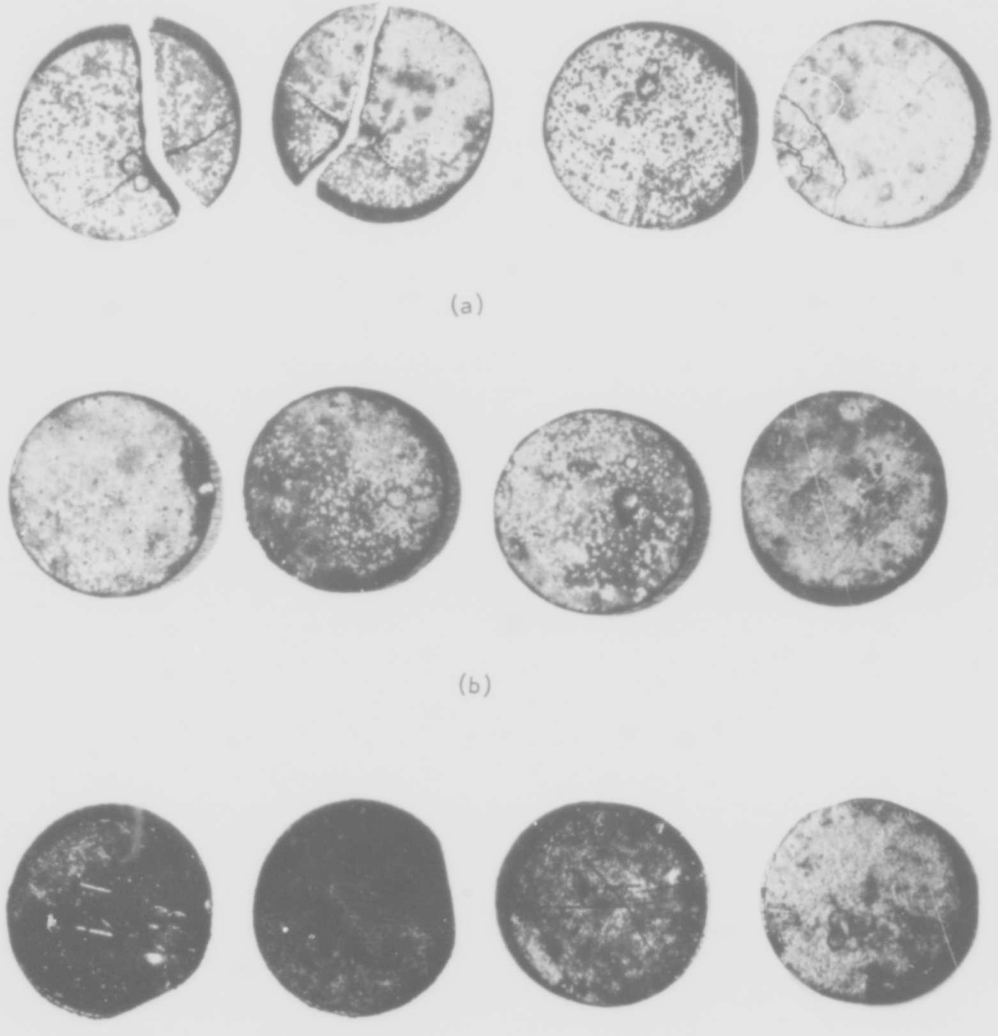


Figure 112 Ballistic Impact Tested V-CrTi-Si System on Columbium Alloy D-43 at 2000°F. 2-1/2 X.



(a)

(b)

Figure 113 Ballistic Impact Tested V-CrTi-Si System on Columbium Alloy XB-88 at (a) Room Temperature, b) 1600°F and c) 2000°F. 2-1/2X

TABLE XLI

BALLISTIC IMPACT TEST RESULTS AFTER EXPOSURE AT 2200°F FOR THE V-CrTi-Si SYSTEM ON VARIOUS COLUMBIUM ALLOY SUBSTRATES

Alloy	Specimen Temperature at Impact, °F	Oxidation Life at 2200°F after Impact, Hr.	Observed Condition after Oxidation Exposure: Surface at Impact Point	Observed Condition after Oxidation Exposure: Surface Behind Impact Point
Cb-752	75	[a]		
	1600	16	oxide adjacent to depression	oxide
	2000	16,16	oxide adjacent to depression	oxide
Cb 132M	75	[a]		
	1600	[a]		
	2000	16,16[b]	oxide adjacent to depression	no oxide
D-43	75	16,16	oxide	oxide
	1600	16,16	oxide adjacent to depression	oxide
	2000	16,16	oxide adjacent to depression	oxide
XB-88	75	[a]		
	1600	16,16[b]	oxide adjacent to depression	no oxide
	2000	16, 16[b]	oxide adjacent to depression	no oxide

---

[a] Specimen cracked or broken - not tested.

[b] Edge hit.

TABLE XLII

EROSION-OXIDATION RIG TEST RESULTS OF V-CrTi-Si COATED COLUMBIUM ALLOYS

Temperature °F	Alloy	Time to Failure Hr.	Remarks
2000	Cb 132M	104+,104+	O.K.
2000	XB-88	104,104	Spot failure on edge
2200	Cb-752	103,103	Spot failures
2200	Cb 132M	103+,208+	O.K.
2200	D-43	103+,208+	O.K.
2200	XB-88	208+,208	One spot failure on edge
2400	Cb-752	106,106	Spot failures on edge in 54 hours
2400	D-43	106,106	Spot failures on edge in 54 hours

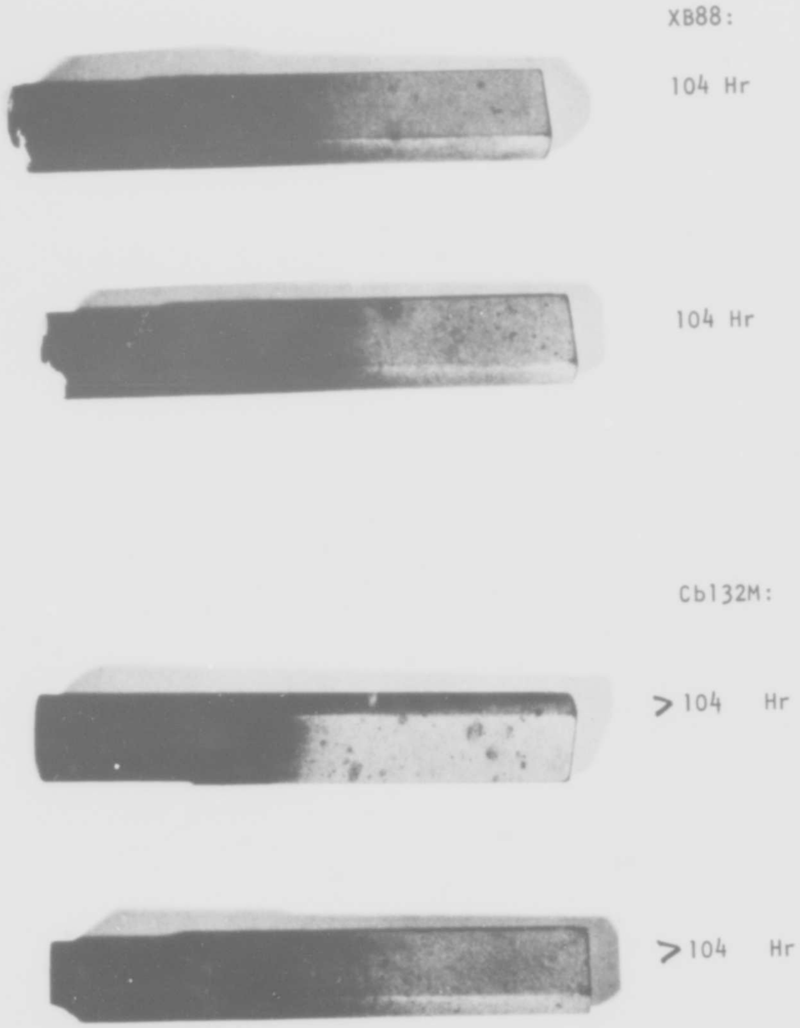


Figure 114 V-CrTi-Si Coated Columbium Alloy Bars after Oxidation-Erosion Testing at 2000°F for the Indicated Times. 1X

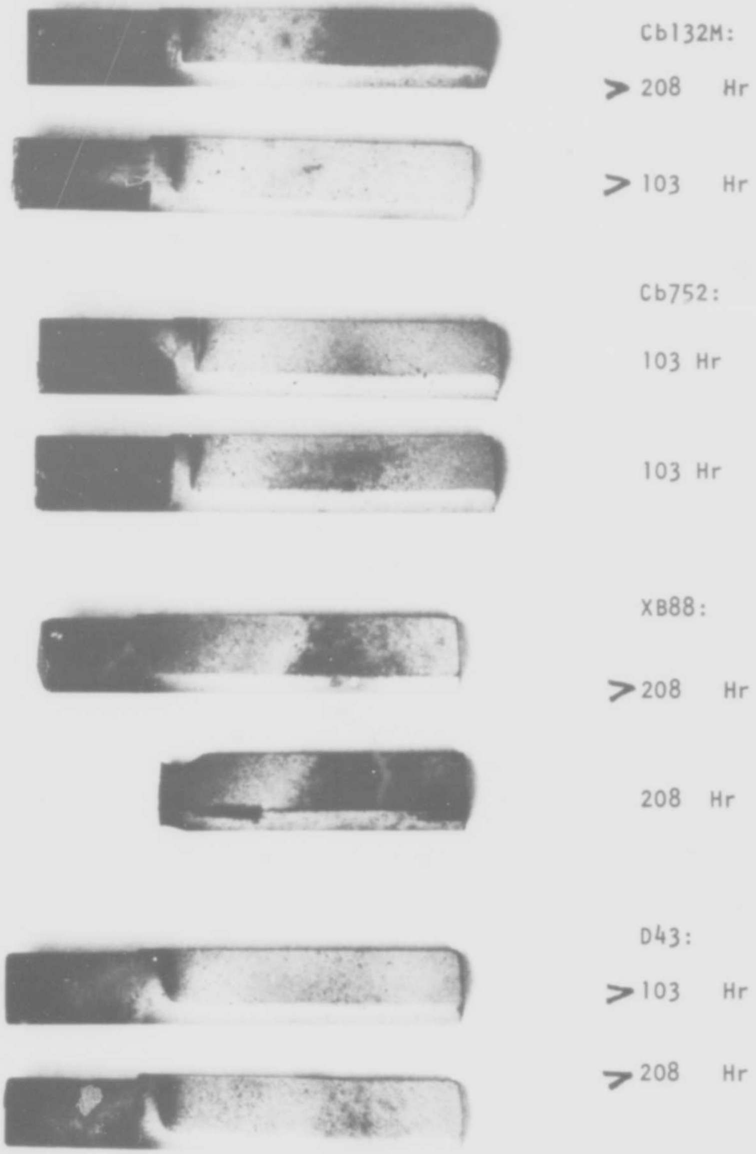


Figure 115 V-CrTi-Si Coated Columbium Alloy Bars after Oxidation-Erosion Testing at 2200°F for the Indicated Times. 1X

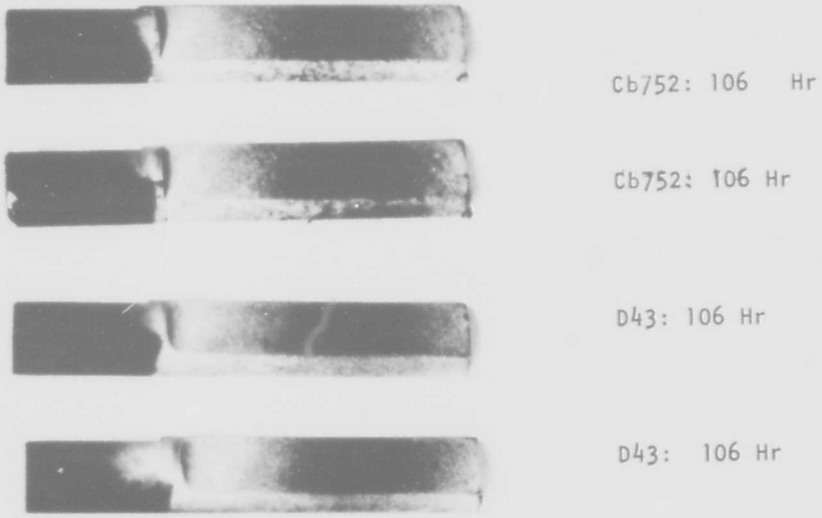


Figure 116 V-CrTi-Si Coated Columbium Alloy Bars after Oxidation-Erosion Testing at 2400°F for the Indicated Times. 1X

uniformity was maintained by rotation at 1750 rpm. Failure was defined as the first appearance of substrate oxide on the specimen airfoil surface.

The V-CrTi-Si coating system demonstrated a protective life ranging from over 100 to 200 hours at 2000°F to 2200°F, and up to 100 hours at 2400°F. The 2400°F tested bars developed spot failures or tubercles after 54 hours of exposure; however, the localized growth was insignificant for the remainder of the test period. All failures resulted from localized oxidation at specimen edges.

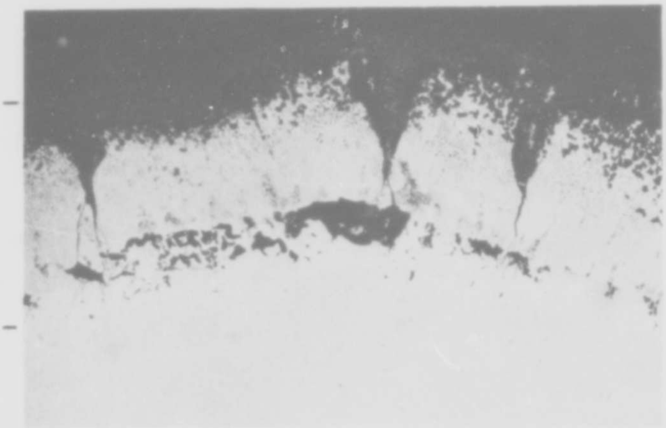
Typical coating microstructures after testing are presented in Figures 117 through 120. Oxide filled cracks or fissures are apparent in the silicide layers in addition to an oxide surface layer. Oxygen penetration of the substrate is visible in the Cb 132M specimen tested at 2000°F. No oxygen penetration was observed for the XB88 material at 2000 or 2200°F. The D-43 material was protected by the coating at 2400°F, whereas the Cb752 substrate showed oxygen penetration.

The V-CrTi-Si coating system shows protective capabilities for the various columbium alloy substrates up to 200 hours at 2000 to 2400°F. However, the coating system appeared to be somewhat prone to edge failures. Oxygen leakage into the substrate through cracks in the silicide also appears to be characteristic. These cracks have the typical appearance of thermal fatigue cracks. This system evaluated by other investigators(1) also showed similar behavior in erosion-oxidation rig tests.

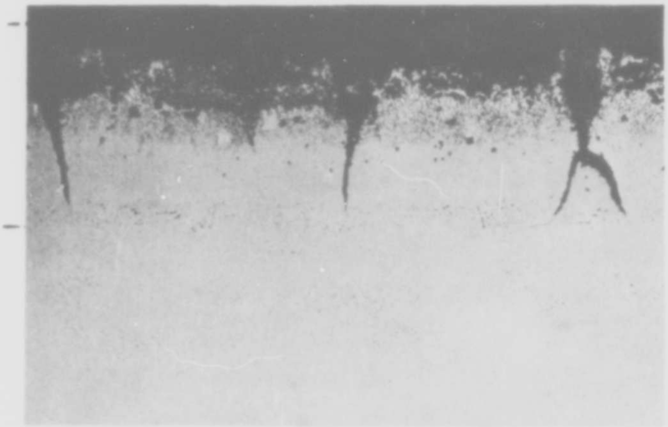
7.8 TENSILE TEST RESULTS

Tensile tests were performed on V-CrTi-Si coated Cb-752, D43 and XB-88 at room temperature, 1600, 2000, 2200 and 2400°F in air, and on uncoated specimens in vacuum. The test specimen configuration is shown in Figure 121, and the gage length was in the direction of working. Testing was conducted with an Instron tensile machine employing a constant crosshead speed of 0.02 in/in/min. until fracture. Elevated temperature tests on coated sheet specimens were conducted in an infrared radiant heated furnace, and on coated bar specimens in a Marshall furnace. Temperatures were controlled with a Pt vs. Pt-10% Rh thermocouple wired to the gage section (shielded for radiation). Stress calculations were based on the original substrate cross-section prior to coating. The tensile data are summarized in Table XLIII for the coated specimens tested in air, and in Table XLIV for the uncoated specimens tested in vacuum (10^{-5} microns).

Compared to the uncoated substrate, the coated Cb-752 showed an insignificant loss in yield and ultimate strength (5% reduction) at room temperature, while the elongation was reduced by about 30%. At elevated temperatures, the yield and ultimate strengths were reduced by approximately 20%, while the elongation wasa minimum at 1600°F (90% reduction).



Cb-752



Cb-132M

Figure 117 Microstructures of V-CrTi-Si Coated Columbium Alloy Erosion Bars after 100 Hours Exposure at 2200°F

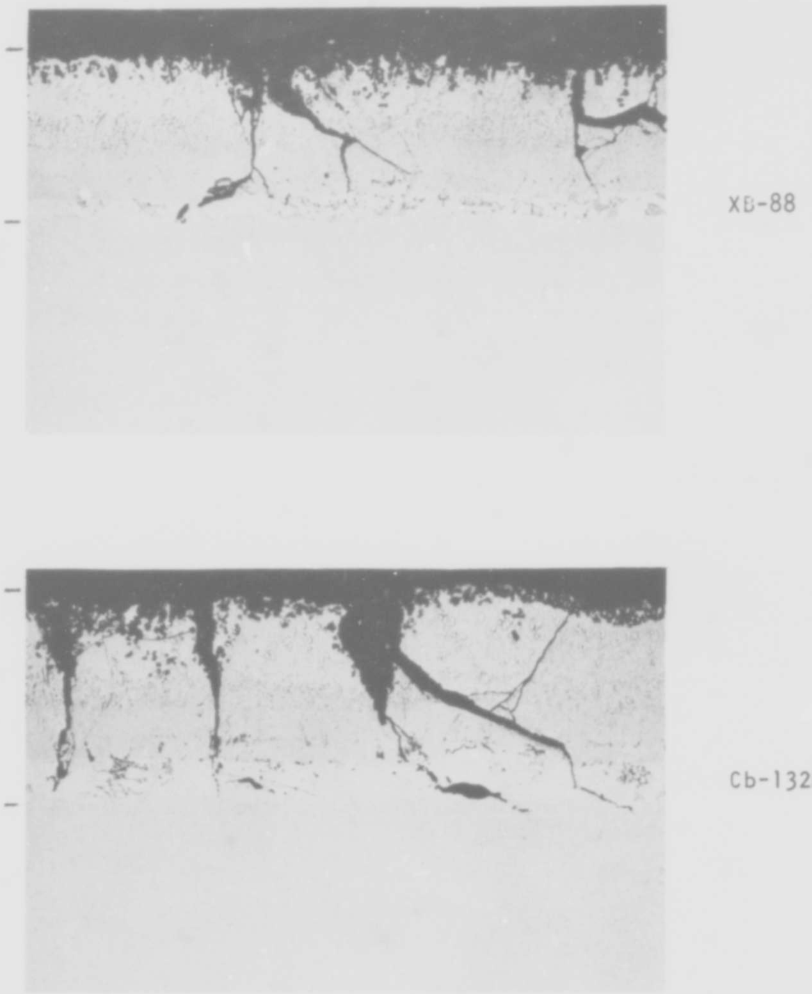
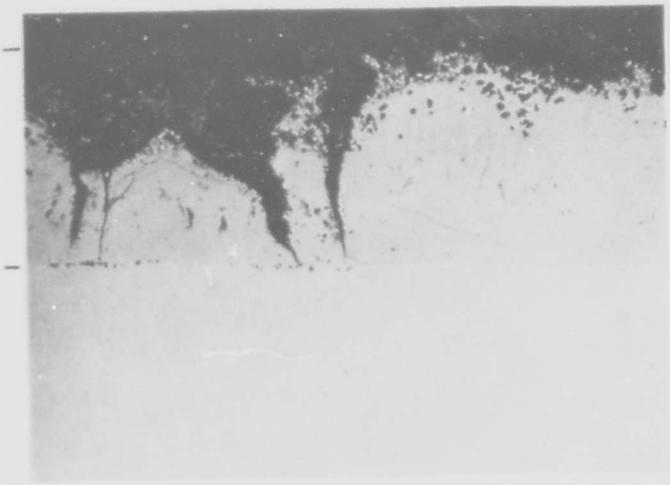


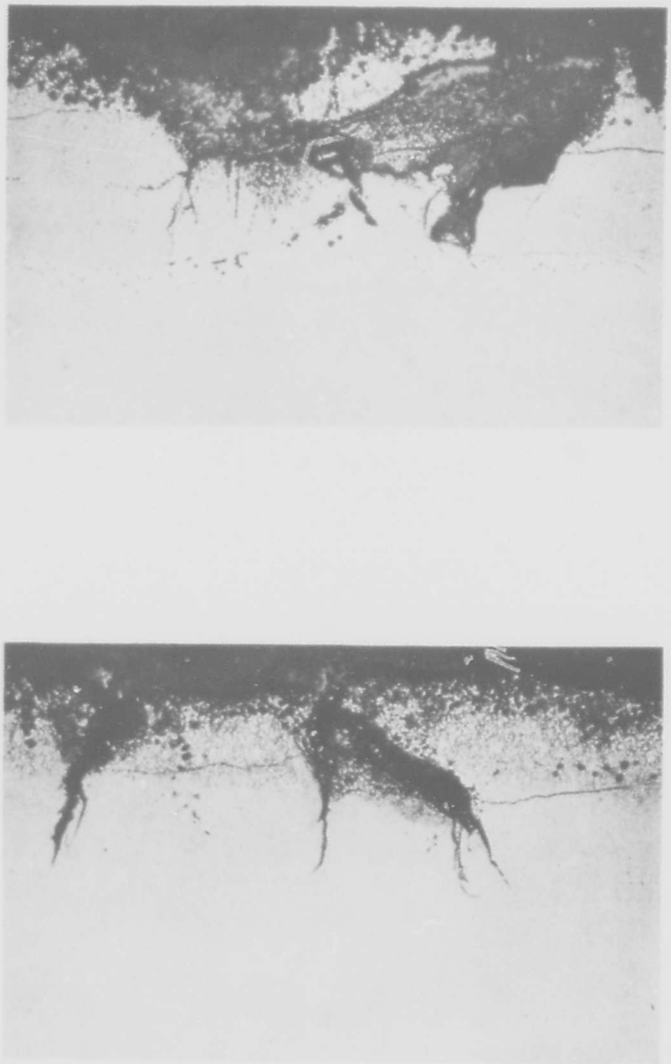
Figure 118 Microstructures of V-CrTi-Si Coating on Columbium Alloy Erosion Bars after 100 Hours Exposure at 2000°F. 250X

D-43



XB-88

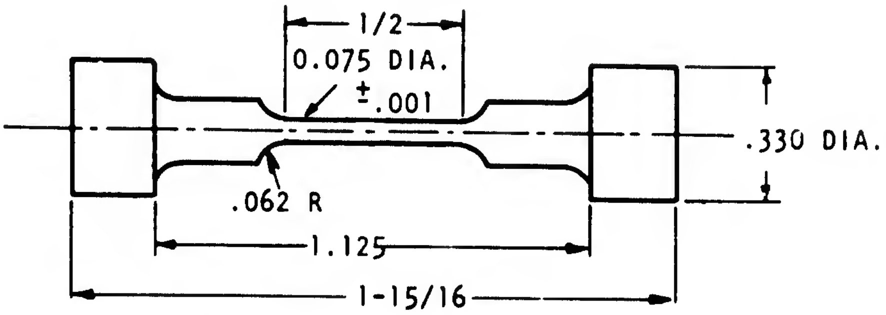
Figure 119 Microstructures of V-CrTi-Si Coated Columbium Alloy Erosion Bars after 100 Hours Exposure at 2200°F. 250X



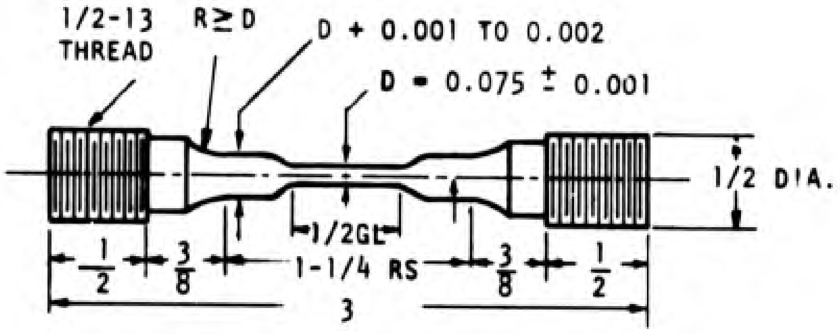
Cb-752

D-43

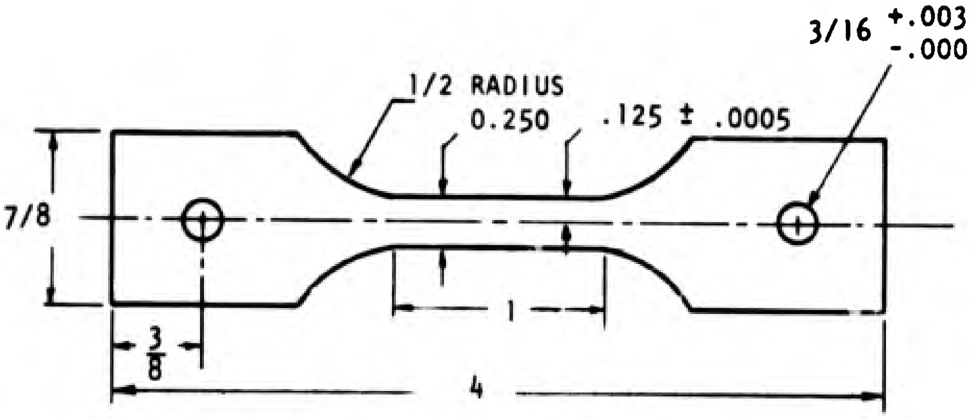
Figure 120 Microstructures of V-CrTi-Si Columbium Alloy Erosion Bars after 100 Hour Exposure at 2400°F. 250X



BAR TENSILE, VACUUM



BAR TENSILE AND STRESS RUPTURE - AIR



SHEET TENSILE AND STRESS RUPTURE - AIR & VACUUM

FIGURE 121 TENSILE AND STRESS-RUPTURE SPECIMEN CONFIGURATION

TABLE XLIII

TENSILE TEST RESULTS OF V-CrTi-Si COATED Cb-752 D-43, and XB-88 COLUMBIUM ALLOYS IN AIR

Alloy	Temperature °F	0.2% Offset Yield, 1000 psi	Ultimate Tensile, 1000 psi	Elongation % in 1.0 inch
Cb-752	RT	63.4 63.7	83.2 83.3	15.9 17.5
	1600	35.2 36.0	41.0 41.6	1.4 2.2
	2000	30.6 26.8	39.1 33.5	8.1 15.4
	2200	22.2 23.4	28.4 30.1	33.5 16.4
	2400	16.7 18.9	23.2 24.7	51.0 38.9
D-43	RT	48.8 49.3	72.6 72.0	17.2 19.6
	1600	36.7 34.1	38.9 39.1	2.2 2.4
	2000	29.4 28.2	32.6 31.9	10.0 11.5
	2200	20.7 20.9	26.5 26.8	36.9 23.2
	2400	15.7 15.7	20.9 20.4	41.8 48.2
XB-88	RT	- -	62.9 81.9	0.4[a,b] 0.3[b]
	1600	77.5 78.1	78.2 80.8	3.8 2.7
	2000	65.9 65.0	77.4 72.6	3.7 4.7

---

a. Gage length 1/2 in. for XB-88 specimens
b. Shoulder break

TABLE XLIV

TENSILE TEST RESULTS OF UNCOATED Cb-752, D-43, AND XB-88 COLUMBIUM ALLOYS IN VACUUM (10^{-5} microns)

Alloy	Temperature °F	0.2% Offset Yield, 1000 psi	Ultimate Tensile, 1000 psi	Elongation % in 1.0 inch
CB-752	RT	66.2	86.7	25.4
		66.3	85.8	24.2
	1600	40.2	57.3	12.6
		41.4	57.3	12.4
	2000	35.9	41.7	23.9
		35.9	41.1	22.8
	2400	22.2	23.6	56.0
		21.8	24.1	50.8
D-43	RT	63.4	85.8	26.7
		58.0	83.3	23.9
	1600	48.1	55.4	9.0
		47.4	55.1	9.1
	2000	40.1	42.2	17.5
		39.6	41.6	17.3
	2400	22.7	24.0	32.9
		21.3	23.7	33.8
XB-88	RT	140.2	146.2	1.7[a,b]
		-	126.1	0.9[b]
	1600	104.9	105.5	6.5
		100.3	101.9	12.0
	2000	76.7	79.2	14.8
		86.1	88.6	12.5

---

a. Gage length 1/2 in. for XB-88 specimens
b. Shoulder break

However, the elongation improved with temperature showing only a 20% reduction at 2400°F. The 1600°F minimum in elongation is a normal occurrence in columbium alloys, and is attributed to a strain aging phenomenon.

The coated D43 showed approximately a 30% loss in yield and ultimate strengths at room and elevated temperatures. The room temperature elongation was reduced 20% by coating, while at 1600°F, the elongation was a minimum (75% reduction) similar to the minimum observed for the coated Cb-752 specimens. Again the elongation improved with increasing temperature above 1600°F, providing an elongation about 30% greater than that of the uncoated material at 2400°F.

In the case of the coated XB-88 specimens, initially a 0.212 in. diameter standard reduced section was selected. However, at a stress level of 18,500 psi at 2200°F, the draw bars rather than the specimens yielded and broke during testing. Therefore, the specimens were stripped, remachined to a 0.075 in. diameter reduced section, and recoated. The coated XB-88 specimens showed approximately a 50% loss in ultimate strength at room temperature, and the yield strength was virtually identical to the ultimate strength. The room temperature elongation was reduced by about 70% by application of the coating. Both the coated and uncoated specimens broke in the shoulder in these tests, indicating that the XB-88 is a notch sensitive material at this temperature. At elevated temperatures, the yield strength was reduced by 20%, whereas the ultimate strength was reduced by approximately 20% at 1600°F and only 10% at 2000°F. The elongation at elevated temperatures was approximately 70% less than that of the uncoated material tested in vacuum.

In summary, the tensile test data on V-CrTi-Si coated and uncoated Cb-752, D43 and XB-88 substrates showed that the coating had an adverse effect upon the tensile properties of these alloys. The Cb-752 alloy was least affected by the coating, showing a significant reduction in strength and ductility only at the 1600°F test temperature. Columbium alloys exhibit strain aging upon deformation in the 1400 to 1800°F temperature range, and thereby experience a minimum in ductility and an attendant reduction in ultimate tensile strength. Coating of the D43 alloy produced a significant reduction in tensile properties at all test temperatures. Although D43 and Cb-752 have similar chemistries, the D43 alloy is quite thermally and chemically sensitive owing to a duplex heat treat condition and to a strong dependence upon carbide and oxide precipitation hardening. Cb-752 alloy, on the other hand, depends primarily upon solid solution strengthening. The coating thermal treatment (2300°F) and "interstitial sink" effects (Ti,V) were consequently more deleterious to the properties of D43 alloy. XB-88 alloy displayed a pronounced loss of room temperature strength as a result of coating, and exhibited a relatively high degree of notch sensitivity in the presence of the brittle silicide. As the test temperature increased above 1600°F, the influence of the coating on substrate properties was less pronounced with all alloys.

7.9 STRESS-OXIDATION TEST RESULTS

Stress-oxidation tests were performed in air on coated Cb-752, D43 and XB-88 material at 2000°, 2200° and 2400°F. The specimen configuration is shown in Figure 121. Initially, a 0.212 in. diameter reduced section was chosen for the XB-88. However, high loading (50,000 psi at 2000°F) resulted in failure of the superalloy grips. Therefore, these bars were stripped, remachined to an 0.075 in. diameter reduced section (1/2 in. long), and recoated. Heating of the sheet specimens was accomplished in a Globar element heated box furnace, and for the bar specimens in a Marshall furnace. Sheet specimens were loaded via a CrTi-Si coated columbium alloy strap and pin assembly. Original substrate dimensions prior to coating were employed in calculating the applied stress.

Stress oxidation results are summarized in Table XLV. In Figures 122 through 124, the rupture life for each alloy is plotted as a function of rupture time. Comparison of the coated data with uncoated values obtained from the literature shows that the V-CrTi-Si coating had no significant effect upon the rupture strength of columbium alloys D43 and Cb-752 at 2200 and 2400°F. In contrast, the rupture life of coated XB-88 was significantly reduced at stress levels over 50,000 psi, while at lower stress levels, the influence of the coating was nil.

Total elongations measured after specimen failure, where possible, showed that the coated materials, especially the Cb-752 and D43 alloys, suffered extensive creep prior to rupture. This indicates that the V-CrTi-Si system is able to tolerate considerable plastic flow at elevated temperatures and protect the substrate.

TABLE XLV

STRESS OXIDATION DATA FOR V-CrTi-Si COATED COLUMBIUM ALLOYS TESTED IN AIR

Spec. No.	Alloy	Temperature °F	Stress psi	Rupture Time, Hr.	Elongation % in 1.0 in.	Remarks
1	Cb-752	2400	11,000	47	87.5	
2			9,500	45.6	-	
3			8,000	158.6	103	
4			13,000	2.4	75	
5			12,000	4.8	87.5	
6		2200	18,000	4.4	62.5	
7			14,000	13.1	18.5	Pin oxidized, specimen twisted
8			14,000	34.9	112.0	
9			16,000	10.5	94	
11			12,000	56.4	-	
12			14,000	13.3	56	Pin oxidized, specimen twisted
13			12,000	62.9+	94	Pin oxidized, specimen twisted
75	D-43	2400	8,000	34.5	-	
76			7,000	132.9	31	
77			11,000	3.2	60	
78			10,000	5.6	100	
79		2200	14,000	23.7+	37.5	Hook broke, weights fell off
81			14,000	15.2	-	
83			11,000	66.2	-	
84			12,500	43.3	-	
88			16,000	9.1	17	
1	XB-88[a]	2000	55,000	5.0	-	
2			64,000	0.2	-	
3			30,000	~208	-	Reloaded to 43,000 psi
3			43,000	~240	-	" " 50,000
			50,000	31.8	14.8	

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a. 1/2 in. gage length

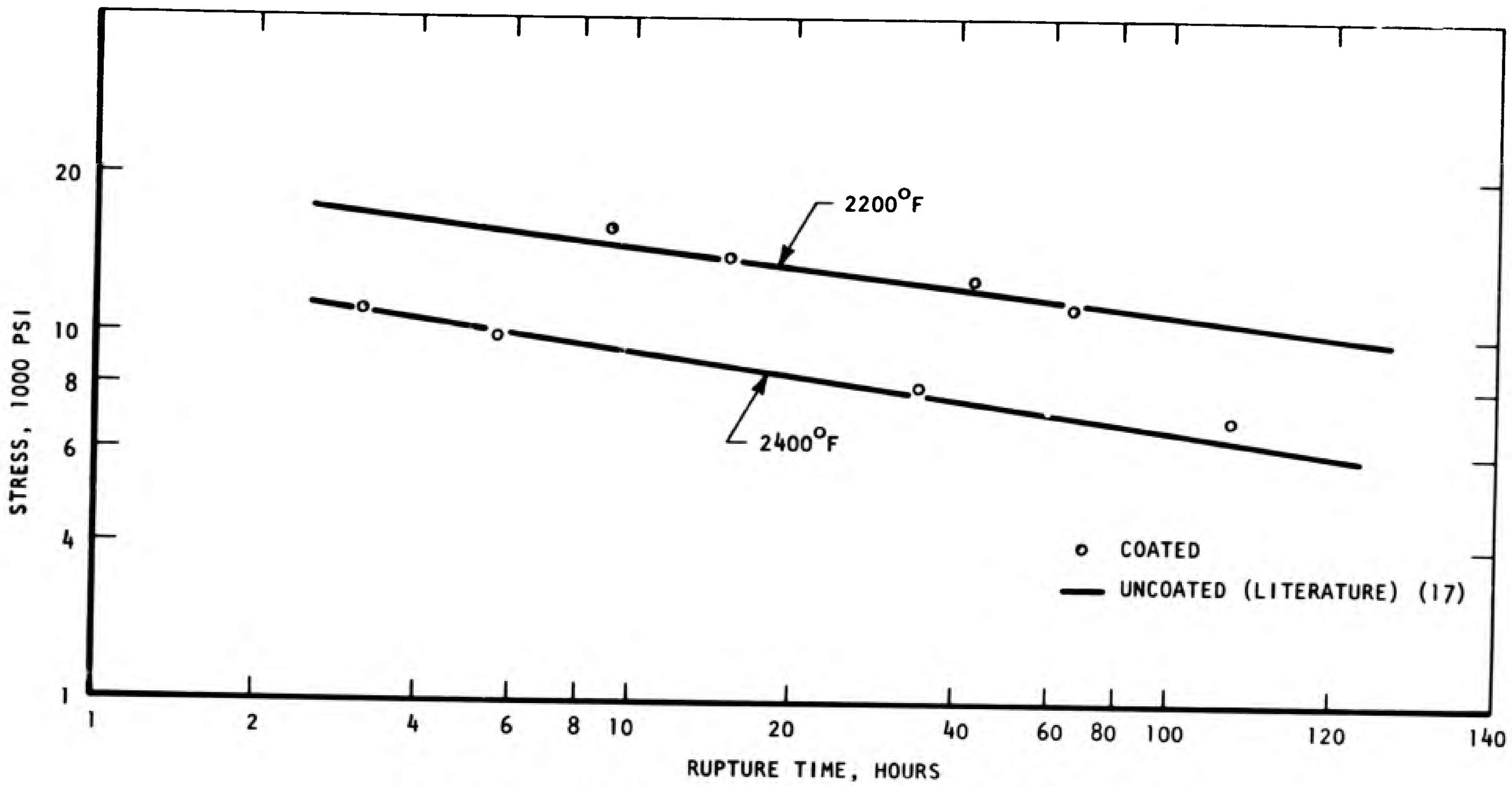

FIGURE 122 STRESS VS. RUPTURE TIME FOR V-Cr Ti-Si COATED D-43

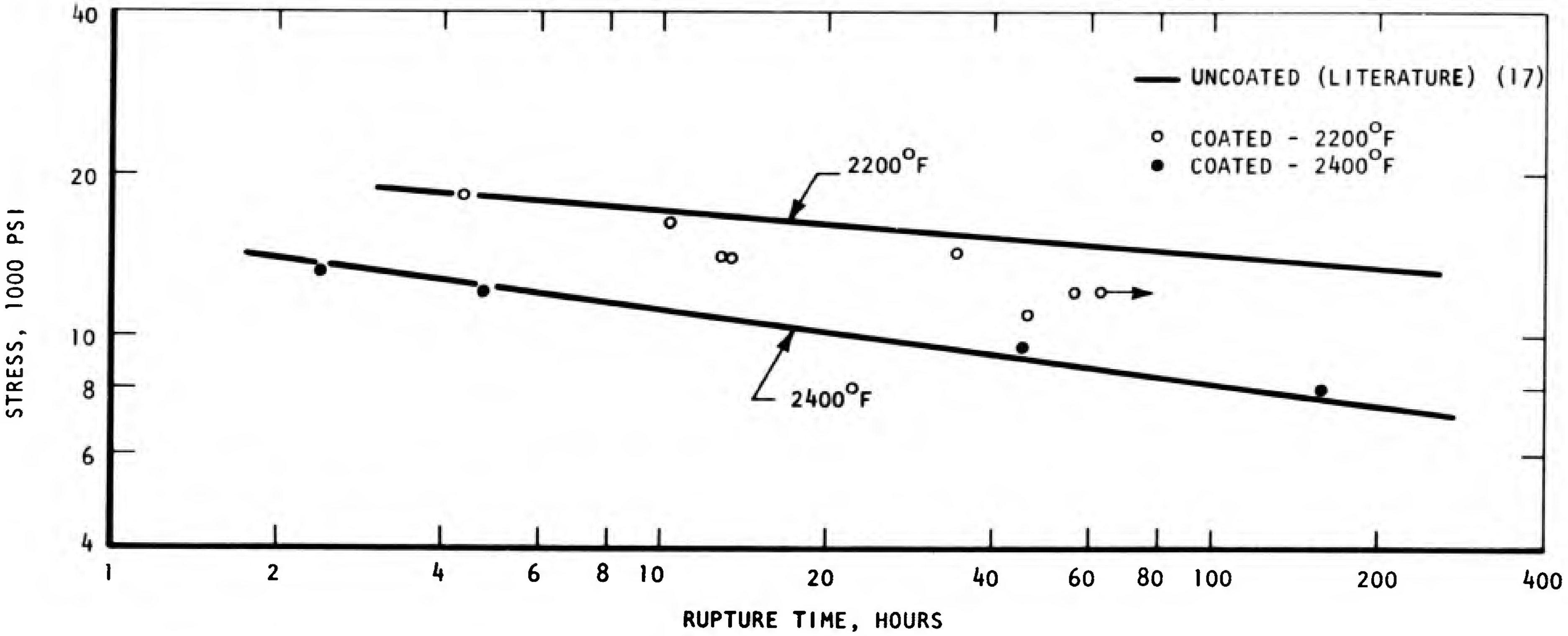

FIGURE 123 STRESS VS. RUPTURE TIME FOR V-Cr Ti-Si COATED Cb-752

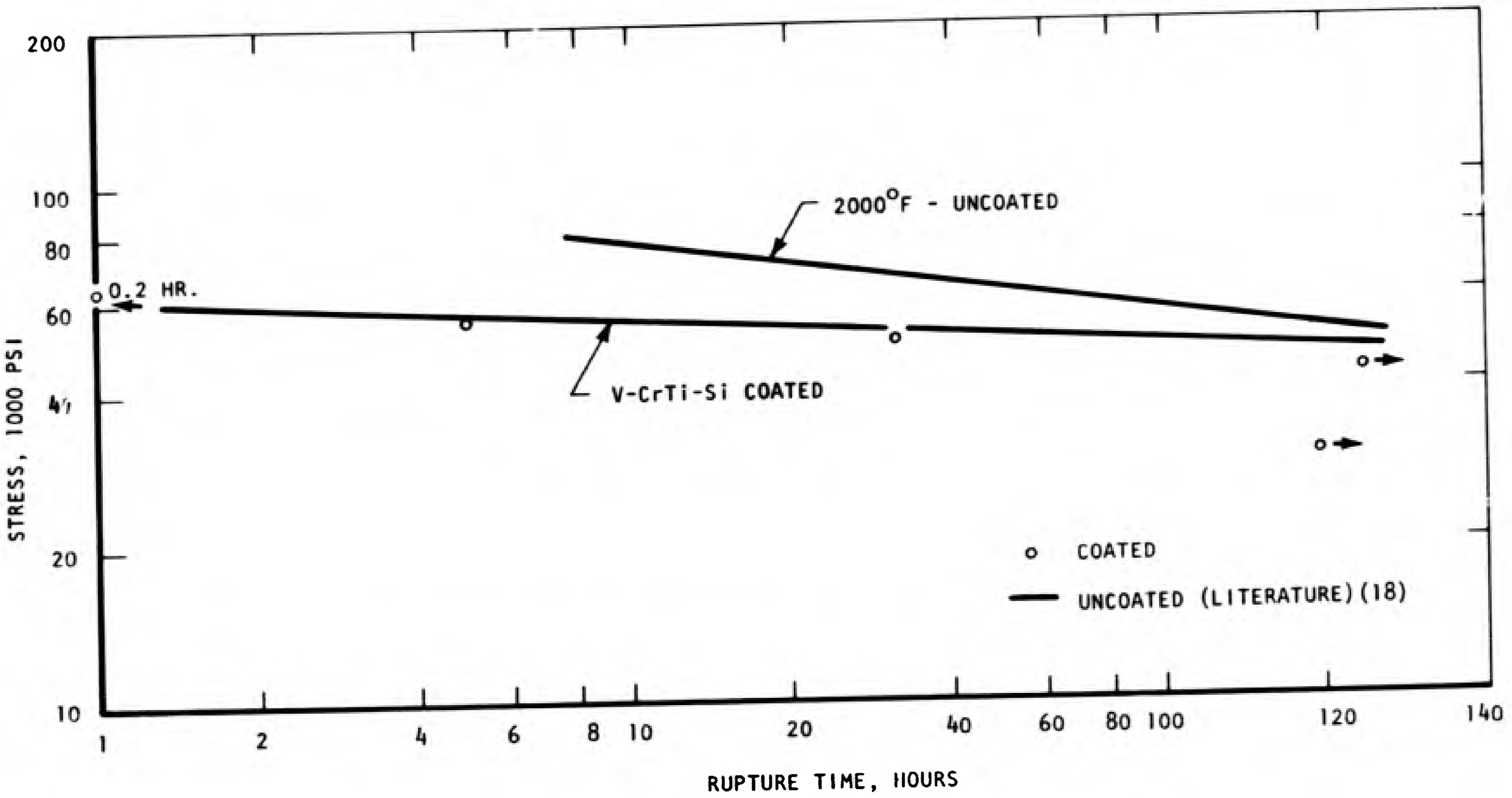

FIGURE 124 STRESS VS. RUPTURE TIME FOR V-Cr Ti-Si COATED XB-88 AT 2000°F

SECTION VIII

CONCLUSIONS

1. Vanadium may be deposited by the vacuum pack process on columbium alloys using a vanadium powder pack and a mixed sodium chloride-vanadium tetrachloride activator.

2. Molybdenum precoatings may be applied by the slurry method, using silver or titanium as liquid or solid state activators for sintering the particulate deposits. However, uniformity, thickness, porosity and adhesion are problems, even with the application of fine molybdenum powders (less than one micron).

3. Molybdenum cannot be satisfactorily deposited on columbium alloys by the vacuum pack method. Molybdenum deposition by the method of hydrogen reduction of molybdenum trioxide leads to serve substrate embrittlement and is thus not a useful method for coating application.

4. Molybdenum may be satisfactorily deposited on columbium alloys by the chemical vapor deposition method.

5. Silicide coating development studies showed that of the modified silicides investigated, only the following systems demonstrated potential to 2400°F: Mo-CrTi-Si, Mo-V-CrTi-Si, V-Al-CrTi-Si, V-CrTi-Si, and CrTi-Si. All other combinations were abandoned because of either poor performance or inability to be satisfactorily formed.. Of these systems, none displayed protective capabilities superior to those of the V-CrTi-Si system.

6. The preferred silicide compositions (by weight) were: 15Mo-18CrTi-12Si: 10 to 14Mo-8V-20CrTi-12Si: 7V-10Al-18CrTi-17 Si; and 7V-21CrTi-16Si; where the prefix numbers represent deposition levels in mg/cm^2.

7. Aluminide coating development studies showed that the 25Ti-5Al and 22Ti-4Al-1Si systems protected the columbium substrates at 1600°F, and may be considered as blade root coatings.

8. The 7V-21CrTi-16Si coating system showed a protective capability of up to 1000 hours in cyclic oxidation tests to 2200°F and greater than 200 hours at 2400°F. The coating may be used to peak temperatures of 2600°F. At 2800°F, the coating life is materially shortened. There was no significant effect of substrate on cyclic oxidation coating life for the alloys evaluated (D43, Cb752, C129Y, XB88 and Cb132M).

9. The V-CrTi-Si coating showed good resistance to damage by low pressure (0.5-5mm) exposure at 2400°F, as assessed by post cyclic oxidation tests at 2400°F on Cb752, D43, Cb132M and XB88 alloys. However, one hour reduced pressure exposure at 2600°F showed that the coating life on D43 and Cb132M alloys was adversely affected.

10. Thermal profile (reentry simulation) oxidation tests to a peak temperature of 2400°F showed that the V-CrTi-Si coating was capable of 25-one hour cycles on Cb752, XB88 and D-43 alloys.

11. The V-CrTi-Si coating displayed a tolerance for up to 1000 thermal shock cycles at peak temperatures to 2400°F.

12. The V-CrTi-Si system showed only a moderate capacity for protection in isothermal oxidation-erosion rig tests to 2400°F. A 200 hour life at 2200°F and a 100 hour life at 2400°F was approximately the limit of exposure before oxygen leakage into the substrate was observed.

13. Ballistic impacts of 4.6 foot-pounds at room temperature often resulted in cracking of V-CrTi-Si coated alloys, and usually produced spalling of the coating with significant loss of protective life, Impact damage decreases with increasing temperature and a minimum life of 16 hours at 2200°F may be expected after impact at either 1600 or 2000°F.

14. The V-CrTi-Si coating reduced the tensile properties (yield and ultimate strengths) of Cb752, D43 and XB88 by 10-30% at room and elevated temperatures.

15. The V-CrTi-Si coating had no deleterious effect upon the stress rupture strength of D43 and Cb752 at temperatures to 2400°F. The stress-rupture life of V-CrTi-Si coated XB88 alloy was significantly reduced at stress levels over 50,000 psi. At stress levels below 50,000 psi, the coating had no apparent influence on rupture life.

16. The oxidation protection afforded by the V-CrTi-Si coating system was due to the presence of an $MeSi_2$ silicide as indicated by electron microprobe analysis.

17. Coating deterioration of the V-CrTi-Si coating system was caused by conversion of coating elements to oxides, loss by vaporization of chromium and vanadium as oxides, and loss by diffusion of elements, notably silicon, into the columbium substrate.

18. The V-CrTi-Si coating system was clearly superior to the CrTi-Si system only in cyclic oxidation tests. In other tests, such as erosion-oxidation and ballistic impact, the systems performed similarly. Although lifetimes to initiation of coating failure were similar in many tests, propagation and growth of an oxidation site was notably slower for the vanadium modified coating; this behavior suggests a self-healing tendency to be the principal advantage of the V-CrTi-Si system.

SECTION IX

RECOMMENDATIONS

A comprehensive evaluation of the V-CrTi-Si coating on several columbium alloys generally indicated that its properties may not be sufficiently superior to those of the Cr-Ti-Si system to justify the additional vanadizing cycle. Only in one atmosphere-cyclic oxidation exposure did the vanadium modification significantly improve upon the performance of the Cr-Ti-Si composition. However, optimization of the processing techniques and chemistry of the V-CrTi-Si coating is required if the full potential of the vanadium addition is to be conclusively demonstrated. If additional development efforts are directed to this system, the following areas should be pursued relative to their influence on coating performance:

(a) coating morphology after each coating cycle, with particular attention directed to the V-CrTi microstructure,

(b) coating facility type and size,

(c) chromium-titanium powder composition and the attendant concentrations of these elements in the coating,

(d) reliability and reproducibility of the system based on large specimen groupings and multi-lot evaluation,

(e) parametric changes such as time, temperature and pressure for the Cr-Ti and silicon coating cycles, and

(f) an analytical study to define the contribution of the vanadium to the corrosion resistance, ductility, crack tolerance, and other characteristics of the V-Cr-Ti-Si system.

SECTION X

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13. ABSTRACT

The program objective was to develop protective coatings for columbium alloys that would provide hundreds of hours of protection at temperatures to 2500°F for application in gas turbine engines and aerospace environments. This work was intended to advance the research findings developed previously under contract AF33(615)-1598.

The coating systems under consideration were basically silicides and aluminides, with improvements to be achieved by modification with elements such as V, Al, Mo, Cr and Ti. Specifically, a ductile coating was sought that would improve upon the Cr-Ti-Si coating system, the standard of comparison for this program. Coating systems which evolved from the studies included Mo-CrTi-Si, Mo-V-CrTi-Si, V-Al-CrTi-Si and V-CrTi-Si for low to high-temperature applications, and Ti-Al and Ti-Al-Si for low-temperature applications.

The V-CrTi-Si system was extensively evaluated on various columbium alloy substrates. It exhibited a potential for 1000 hours of protection at 1600-2200°F in cyclic oxidation tests and over 200 hours at 2400°F. In oxidation-erosion rig tests the coating system protected various columbium alloy substrates for up to 200 hours at 2200°F and 100 hours at 2400°F. The V-CrTi-Si system was superior to the CrTi-Si system only in cyclic oxidation tests. In other tests, such as oxidation-erosion, ballistic impact, and slow thermal cyclic exposure, the two systems performed similarly.

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