ADVANCEMENT OF HIGH TEMPERATURE PROTECTIVE COATINGS FOR COLUMBIUM ALLOYS (II)

Technical Documentary Report No. ASD TDR-62-934 Part II

APRIL 1964

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7312, Task No. 731201

(Prepared under Contract No. AF 33(657)-7396
by Thompson Ramo Wooldridge Inc., Cleveland, Ohio,
D. B. Warmuth, J. D. Gadd and R. A. Jefferys, Authors)

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FOREWORD

This report was prepared by Materials Processing Department, TRW Electromechanical Division, Thompson Ramo Wooldridge Inc. under USAF Contract No. AF 33(657)-7396. . This contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 731201, "Surface Treatments and Coatings". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Mr. N. M. Geyer acting as project engineer.

This report describes the results of the program conducted during the period 1 March 1963 to 1 March 1964.

The project at TRW was managed and directed by R. A. Jefferys and D. B. Warmuth was in charge of conducting the technical effort.

ABSTRACT

The objective of this program was a) to advance and optimize the Cr-Ti-Si coating process for laboratory scale and pilot scale coating furnaces, b) to determine the protective reliability of the Cr-Ti-Si coating, and c) to investigate the effects of elevated temperature-reduced pressure (air) exposure upon the protective characteristics of the Cr-Ti-Si coating.

In a process optimization study the most protective Cr-Ti-Si coatings for cyclic oxidation in air at 1800, 2500 and 2700°F were formed utilizing the following process conditions. The Cr-Ti alloy layer was deposited in 8 hours at 2300°F in either a 50Cr-50Ti or a 60Cr-40Ti prealloyed powder pack. A system pressure of 1.5 mm was employed for the laboratory scale furnace and 10^{-2} mm for the pilot scale furnace. Siliconizing for 6 hours at 2100°F at a system pressure of 10^{-2} mm was considered optimum for both furnace sizes.

In a reproducibility and reliability study a statistical analysis was conducted to determine the oxidation protective reliability of the Cr-Ti-Si coating on B-66 and D-43 alloys at 2000, 2500 and 2700°F. A high degree of reliability for the two Cr-Ti-Si coated alloys was established for 150 hours protective life at 2000°F, 28 to 32 hours protective life at 2500°F and 1 to 2 hours protective life at 2700°F. The protective reliability of the Cr-Ti-Si coating at either 2500 or 2700°F was found to be strongly dependent upon coating composition.

An investigation to evaluate a completely vapor phase process for silicon deposition was conducted employing a gas flow process. Coatings potentially equal to those deposited in the vacuum pack process were formed by this technique.

Extensive testing of the Cr-Ti-Si coating at pressures as low as 10^{-2} mm and temperatures to 2600°F was accomplished. The Cr-Ti-Si coating prevented visible columbium oxide growth for low pressure exposures up to 4 hours in duration. Post oxidation protective life at 1800 and 2500°F was unaffected by low pressure exposure at pressures greater than 1 mm. Exposure to pressures less than 1 mm caused varying degrees of loss of one atmosphere oxidation resistance at 1800 and 2500°F.

The relationship of joint fabrication and coating process procedures was investigated relative to cyclic oxidation life.

A detailed analysis of the work of the program and conclusions are presented.

This technical documentary report has been reviewed and is approved.

I. Perlmutter

I. PERLMUTTER
Chief, Physical Metallurgy Branch
Metals and Ceramics Division
AF Materials Laboratory

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1. INTRODUCTION

The advent of space exploration has introduced a tremendous challenge to both design and materials engineers. The need for high temperature engineering materials in the design and fabrication of flight structures, such as hypersonic aircraft and re-entry glide vehicles, has been the major stimulus in the accelerated development of refractory metals. Columbium base alloys are leading candidates in this category of high temperature materials of construction. However, it is well recognized that the inherently poor oxidation resistance of columbium base materials, as well as all the refractory metals, precludes their utilization in oxidizing environments without surface protection. Independent coating development programs are being conducted by many industrial organizations and several useful protective coating-columbium alloy systems have reached the advanced development stage.

In two previous programs at TRW, sponsored by Materials and Processes ASD under Contracts AF 33(616)-7215 and AF 33(657)-7396, the Cr-Ti-Si vacuum pack coating process for columbium materials was advanced from the laboratory stage to its current status as a pilot scale process. The protective capabilities of the Cr-Ti-Si coating and the level of process reproducibility has made possible the utilization of the Cr-Ti-Si coating on components of space research vehicles such as ASSET. Cr-Ti-Si coated columbium alloy fasteners, heat shield and leading edge structures will be evaluated on several ASSET vehicles in various re-entry flight profiles.

The two previous coating development programs were successful in advancing and scaling up the Cr-Ti-Si process, however, further efforts were required to optimize the processing conditions for the various size coating furnaces and to assess the protective reliability of the coatings produced. In order to pursue these objectives, Air Force support of the Cr-Ti-Si coating process development was continued under Contract AF 33(657)-7396 S2. This extension of previous efforts involved essentially three phases: (I) coating process optimization for the various coating furnaces, (II) coating protective reliability and (III) protection of joined configurations. In Phase I the coating process variables were investigated in coating furnaces of three distinctly different sizes. This phase was extended to include an investigation of the effects of reduced pressure oxidation exposure upon the protective life afforded by the Cr-Ti-Si coating. In Phase II a large number of columbium alloy specimens, coated in two different size furnaces were evaluated to determine the protective reliability of the Cr-Ti-Si coating. A limited number of joint designs were selected for an evaluation of the protective performance of the Cr-Ti-Si coating on simple joint configurations. This program also included a limited investigation of a completely vapor phase deposition technique, to the extent of alloying silicon with the Cr-Ti layer in a system not requiring the use of vacuum.

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2. SUMMARY

Previous advances in the Cr-Ti-Si coating process reduced time, temperature and pressure requirements for formation of the Cr-Ti-Si coating. The next logical step in process advancement was a determination of the optimum combination of process parameters for a given size coating furnace and retort. The influence of the various process parameters is discussed and correlated with protective characteristics and an analysis of coating formation.

The optimum Cr-Ti pack compositions were determined as either 50Cr-50Ti or 60Cr-40Ti. Optimum system pressures changed for changes in retort sizes. For the laboratory scale furnace (3" diameter x 8" high retort) 1.5 mm was preferred and for the pilot scale furnace (7-1/2" diameter x 18" high retort) 10 microns (10^{-2} mm) was optimum.

Titanium precoating non-titanium bearing columbium alloys prior to application of the Cr-Ti alloy coating had previously been found to be beneficial. An attempt to incorporate the titanium precoat with the Cr-Ti application was generally unsuccessful. A low temperature hold treatment prior to heating to the Cr-Ti application temperature promised some benefit, particularly with respect to large retort sizes, owing to reduction of thermal gradients within the retort.

An investigation to optimize silicon coating process parameters resulted in establishing a set of parameters for application of coatings having useful protective life over the temperature range 1800-2700°F. Silicon coating at 2100°F for 6 hours at a system pressure of 10^{-2} mm was considered optimum for both 3" diameter x 8" high and 7-1/2" diameter x 18" high retorts.

A vapor phase technique for deposition of silicon was investigated by employing a gas flow process. The feasibility of this type of deposition process was demonstrated.

An investigation of the effects of fabrication and coating sequence on the protection of welded and riveted joints was conducted.

The protective performance of the Cr-Ti-Si coating on 2940 D-43 and B-66 alloy specimens was investigated at 2000, 2500 and 2700°F and the relationship of retort size, specimen retort position, Cr-Ti and silicon coating process parameters and base alloy to coating thickness and protective life was determined. A statistical analysis of the cyclic oxidation test data was conducted on 1080 specimens and a 98.5 ± 0.5% probability at a 99% confidence level was established for a 150 hour protective life at 2000°F for the two alloys. At 2500°F for mean life values of 67 to 83 hours (671) specimens) a 95 ± 1% probability at a 99% confidence level was indicated for a 28 to 32 hour protective life for D-43 and B-66 alloys, respectively. At 2700°F a 95 ± 2% probability for a 2 hour life (mean life 7 hours) and 95 ± 3.5% probability for a 1 hour life (mean life 4 hours) was determined for D-43 and B-66 alloys, respectively. Protective life at 2500 and

2700° F was significantly affected by retort position with the top region of the retort giving rise to generally poorer quality coatings. Coating composition appears to be the determining factor for protective life of coatings within the 1.5-3.0 mils thickness range.

A detailed investigation of the reduced pressure oxidation protective characteristics of the Cr-Ti-Si coating was made at 2500 and 2600° F. Air pressures above 1 mm did not significantly alter the protective characteristics of the coating; lower pressures caused various degrees of coating degradation. However, in no case was coating failure observed during reduced pressure testing for a maximum of 4 hours. Coating degradation at reduced pressures results from volatilization of coating constituents and diffusion of atomic oxygen into the substrate.

3. MATERIALS

Three columbium alloy sheet materials were utilized for this program: (a) D-14, (b) D-43 and (c) B-66 alloys. The chemical analysis of the sheet materials, reported by the suppliers, and associated sheet thicknesses are listed in Table 1. The D-14 alloy was used in the optimization studies and low pressure oxidation studies. The B-66 and D-43 alloys were used primarily for the reliability study.

Approximately 100 inch^2 of 40 mil D-14 alloy (Heat No. 14-080) was transferred from Contract No. AF 33(657)-7396 to the present Contract No. AF 33(657)-7396 S2. An additional ten square feet of 40 mil D-14 alloy sheet was purchased from Du Pont for the fabrication of coating pack retorts. Surplus material from this lot was also utilized in the coating development work.

Four square feet of 30 mil B-66 alloy sheet was purchased from Westinghouse Electric Corporation.

Approximately seven square feet of 30 mil D-43 alloy sheet was transferred to the coating development program from the Air Force sponsored columbium alloy sheet rolling program at Du Pont, under Contract AF 33(600)-39942.

4. ADVANCEMENT OF THE Cr-Ti-Si COATING PROCESS

The development stages of the Cr-Ti-Si coating process were discussed in detail in two final summary reports on previous Air Force sponsored programs(1,2). The original work with this process involved placing the material to be coated in a refractory metal can which contained an all metallic particle pack of the coating elements. The pack was evacuated to a pressure of less than 0.1 micron (10^{-4} mm) in a cold wall resistance heated vacuum furnace and subsequently heated to the coating temperature. Cr-Ti-Si diffusion alloy coatings were formed on columbium substrates by a vapor-solid interface reaction which was dependent on both the diffusion rates of the coating elements in the columbium substrates and on the characteristic vapor pressures of the metallic coating elements. Cr-Ti alloy coatings were formed in a first cycle of 16-24 hours at 2350° F. Silicon was alloyed with the Cr-Ti coating in a second cycle of 8-16 hours at 2100-2200° F. The detrimen-

TABLE 1

Chemical Analysis of Columbium Alloy Sheet Materials
Reported by the Producers

Alloy	Heat No.	Sheet Thickness Mils	Element							
			W (%)	Mo (%)	V (%)	Zr (%)	O (ppm)	N (ppm)	C (ppm)	H (ppm)
D-14 (1)	14-080	40	-	-	-	4.80	162	15	28	4
D-14 (1)	14-222	40	-	-	-	5.00	314	19	43	1
D-14 (1)	14-366	40	-	-	-	4.90	177	31	66	3
D-43 (2)	43-283	30	10.2	-	-	0.94	82	38	1040	2
D-43 (2)	43-387	30	9.3	-	-	1.10	141	40	1090	3
B-66 (3)	DX-603	30	-	4.6	4.8	0.90	92	82	33	-

(1) Purchased from Du Pont

(2) Acquired from Air Force sponsored sheet rolling program at Du Pont

(3) Purchased from Westinghouse

tal effect of these process conditions on the mechanical properties of temperature sensitive columbium alloys, as well as the poor scale up potential of a high vacuum process, directed further development efforts toward a reduction in processing requirements.

Halide activators were added to the metallic coating packs which substantially increased the rate of formation of Cr-Ti-Si coatings on columbium base metals. Small quantities of halide salts such as potassium fluoride and sodium fluoride reduced the processing requirements for the Cr-Ti coating cycle to 8 hours at 2200-2300°F and for the silicon coating cycle to 2-4 hours at 2000-2050°F. A similar reduction in the process vacuum requirement was also brought about by the activator addition, permitting the coatings to be applied at furnace pressures of 1.5-150 mm in comparison to the previous requirement of less than 10^{-4} mm. Coincident with these less demanding processing requirements of the activated pack process was a tremendous improvement in the protective properties of the Cr-Ti-Si alloy coating. Average oxidation protective lives for the coating were elevated from a few hours to several hundred hours at temperatures up to 2300°F, in excess of 100 hours at 2500°F and for useful periods of time at temperatures up to 3000°F.

The emphasis during the second development program was directed toward both determining minimum processing requirements along with establishing the feasibility of process scale up. This program was successful in providing further insight into the factors which influence the performance of the Cr-Ti-Si coating and also in establishing certain limitations on the flexibility of the coating process.

The program just completed was intended to further develop techniques for application of the Cr-Ti-Si coating with primary emphasis being placed on: (a) optimizing processing conditions in existing scaled up coating furnaces and (b) statistically analysing protective reliability. In addition, a detailed analysis of the protective characteristics of the Cr-Ti-Si coating under high temperature-reduced pressure (air) environments was conducted. A limited effort was directed toward demonstrating the feasibility of forming the Cr-Ti-Si coating on columbium alloys by a gas flow process.

5. PHASE I - COATING PROCESS OPTIMIZATION STUDY

Since the elimination of the high vacuum requirement of the Cr-Ti-Si coating process, three reduced pressure versions of the coating process have been investigated:

(a) continuous mechanical pump evacuation of the furnace - 10^{-2} mm of Hg

(b) initial mechanical pump evacuation followed by sealing off the furnace from the vacuum system producing an operating pressure of approximately 1.0-1.5 mm of Hg

(c) initial mechanical pump evacuation followed by sealing off and back filling the furnace with argon - 150 mm of Hg

Furnace operating pressure (relative evacuation rate) has been found to strongly interact with other process variables such as pack composition, quantity of pack activator and type of activator. Utilizing the results of previous coating development programs, the objective of Phase I was then to optimize the principal variables in the coating process.

Three furnace sizes were employed in this work, two of which represent present levels of process scale up:

(a) laboratory scale furnace - 3" diameter x 8" high retort induction heated

(b) pilot scale furnace - 7-1/2" diameter x 18" high retort - induction heated

(c) bell furnace - 8" x 24" x 24" retort - resistance element heated

The major effort in the process optimization study was devoted to coating in the two induction heated furnaces, with only a limited coating investigation conducted in the larger resistance element heated bell furnace. The initial studies were carried out in the laboratory scale retort, and the optimized processing conditions for this size furnace were subsequently employed as base line parameters for coating in the pilot scale furnace. Correlation of the processing conditions for the two variations of furnace size then provided relative variable relationships which could be extrapolated to a larger coating furnace. This study also provided information necessary for selection of the coatings which were evaluated in Phase II of the program, i.e., the coating reliability study.

5.1 Coating Studies in the Laboratory Scale Furnace

The majority of the basic Cr-Ti-Si coating development effort in previous programs was performed in the laboratory scale induction heated furnace utilizing a pack container approximately 2" diameter x 4" high. The maximum retort size this furnace will accommodate is 3" diameter x 8" high. The following discussion presents the results of Cr-Ti-Si coating studies in this larger container, aimed at optimizing the coating process variables for this particular furnace.

5.1.1 Cr-Ti Coating Cycle

Four Cr-Ti alloy pack compositions were investigated: 50Cr-50Ti, 60Cr-40Ti, 65Cr-35Ti and 70Cr-30Ti. The pack material consisted of -8+30 metallic particles of prealloyed chromium and titanium. Based on previous results, a processing cycle of 8 hours at 2300°F and an activator pack addition of 0.5 w/o KF were selected for all coating runs in this series. D-14 columbium alloy coupons (0.040" x 1/2" x 1/2") were coated in each of the four pack compositions, employing the three previously discussed operating pressure levels: 10^{-2}, 1.5 and 150 mm. Specimens from each run were examined metallographically, and eight additional specimens from each process combination were siliconized for cyclic oxidation evaluation at 1800 and 2500°F.

The silicon coating cycle involved 4 hours at 2050°F, using 1.0 w/o KF and a pressure of 10^{-2} mm. Cyclic oxidation consisted of cooling the specimens to room temperature once each hour for 8 hours, followed by 16 hours of static exposure in each 24 hour period. This procedure was followed in all one atmosphere cyclic oxidation studies in this program. The criteria for failure was visual observation of a rupture in the coating and the protrusion of columbium oxide.

Table 2 presents both the metallographic and oxidation data from the full factorial analysis of the twelve variable combinations. Photomicrographs of the Cr-Ti alloy coatings produced in these runs are shown in Figures 1, 2 and 3. A study of these microstructures will aid in the interpretation of the metallographic measurements listed in Table 2. As shown in the sketch at the bottom of Table 2 the coating overlay consists of the chromium rich alloy layer formed on the substrate surface. The measured depth of coating element diffusion corresponds to the metallographically observed titanium enriched region directly beneath the Cr-Ti alloy overlay. The chromium rich intermetallic phase observed in prior substrate grain boundaries and dispersed in the diffusion zone has been identified as having a FCC $MgCu_2$ type structure(3), with a lattice parameter corresponding closely to $CbCr_2$ and $TiCr_2$. It has also been found that the diffusion of titanium into the columbium substrate further enhances the diffusion rate of chromium in this region. This phenomenon is associated with the lowering of the alloy melting point by the dissolution of titanium and a corresponding decrease in the activation energy requirement for chromium diffusion.

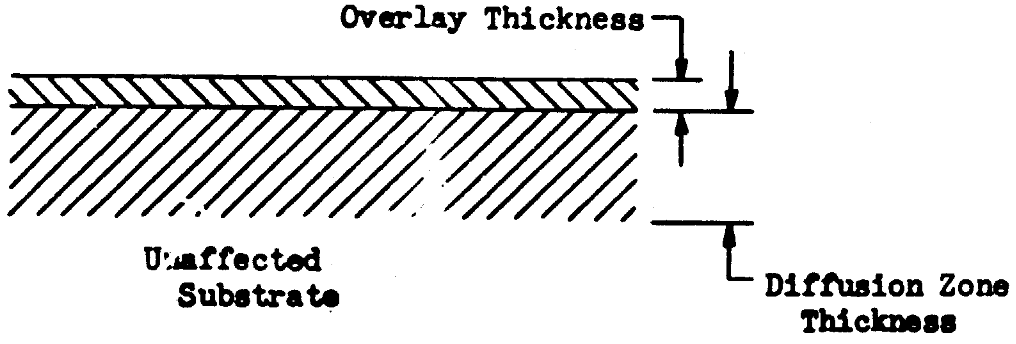
The metallographic measurements are plotted in Figures 4 and 5 showing graphically the influence of coating pack composition and furnace pressure on the Cr-Ti coating microstructure. For a constant pack composition, as the operating pressure increases the depth of coating element diffusion also increases, whereas the average overlay thickness is a maximum for the 1.5 mm intermediate coating pressure. For a constant operating pressure, as shown in Figure 5, as the chromium content of the pack increases the coating overlay thickness also increases and the depth of diffusion correspondingly decreases. It is apparent from these data that the halide activator reacts preferentially with the titanium constituent in the pack alloy, whereas the chromium contribution to the coating occurs by both halide activation and by metallic vaporization. At the lowest pressure (10^{-2} mm) the furnace is continuously evacuated (mechanical pump) throughout the coating cycle and the residence time of the activated species in the coating pack is a minimum. Cr-Ti coatings formed at this pressure display the least depth of titanium diffusion. In the blanked off system (1.5 mm) the residence time of the halide activated species in the pack is significantly increased, whereas the furnace pressure is still low enough to permit vaporization of appreciable chromium. The result is a greater depth of titanium diffusion, a slightly thicker overlay and considerably more inward diffusion of chromium, owing to titanium enrichment of the substrate. Backfilling the furnace with argon (150 mm) then reduced the pressure differential in the furnace which was produced by the thermal gradient, thereby further increasing the residence time of the activator in the pack. A considerable portion of the evacuated furnace chamber is water cooled, which creates an effective internal vacuum system by the condensation of vapors evolved from the hot portion of the furnace

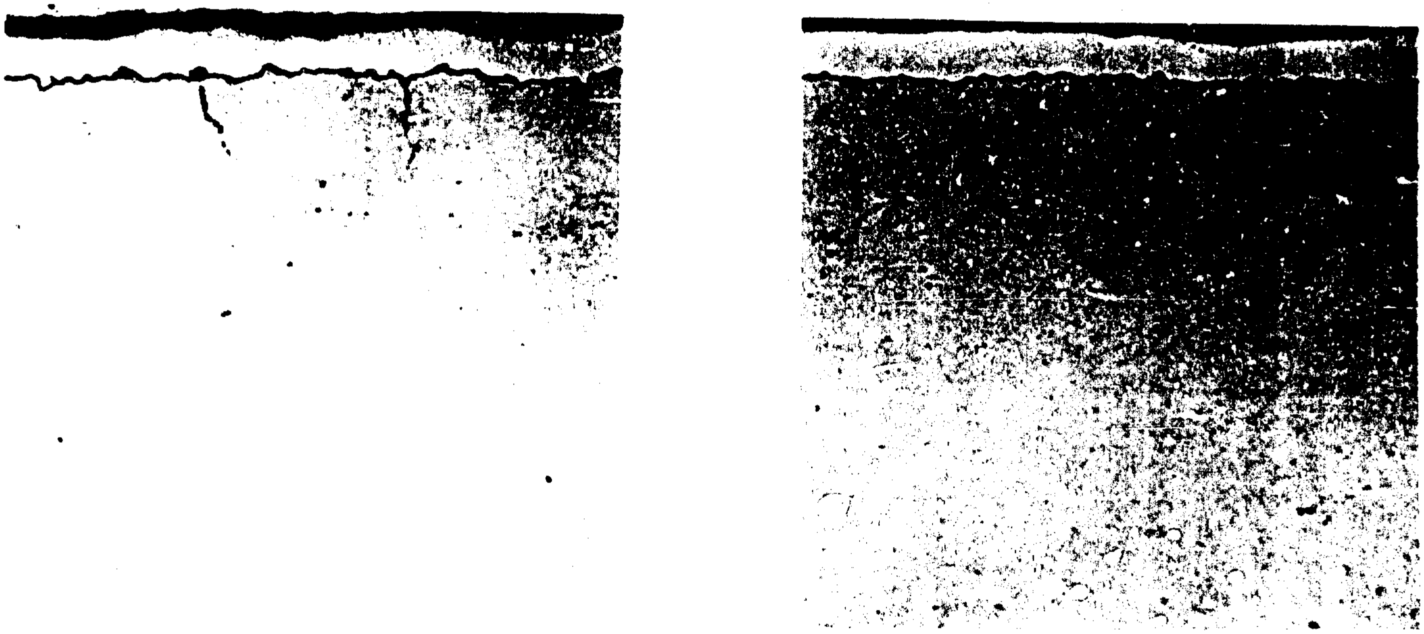
TABLE 2

Metallographic and Cyclic Oxidation Results for Coatings Formed on D-14 Alloy Using Various Cr-Ti Alloy Pack Compositions and Furnace Operating Pressures

Cr-Ti Coating Conditions(1)		Cr-Ti Alloy Coating Measurements		Cr-Ti-Si(2) Oxidation Protective Life - Hours	
Pack Composition	Pressure mm	Overlay Thickness Mils	Diffusion Zone Depth - Mils	1800°F	2500°F
50Cr-50Ti	10^{-2}	0.3-0.5	1.0-1.2	28,57,200*,200*(3)	75,80,99,99
50Cr-50Ti	1.5	0.4-0.6	1.5-1.8	200*,200*,200*,200*	99,124,146,146
60Cr-40Ti	10^{-2}	0.3-0.5	0.8	24,31,38,57	57,75,75,83
60Cr-40Ti	1.5	0.5-0.8	1.0-1.2	200*,200*,200*,200*	83,99,146,146
60Cr-40Ti	150	0-0.1	1.8-2.8	24, 200*,200*,200*	30,35,35,38
65Cr-35Ti	10^{-2}	0.2-0.4	0.6-0.7	23,23,24,27	28,28,28,28
65Cr-35Ti	1.5	0.2-0.4	0.8-1.0	38,83,130,200*	59,75,75,80
65Cr-35Ti	150	0-0.1	1.0-1.2	23,200*,200*,200*	30,30,35,35
70Cr-30Ti	10^{-2}	0.4-0.6	0.4-0.5	6,6,24,25	31,35,54,57
70Cr-30Ti	1.5	0.6-0.8	0.5	57,59,200*,200*	35,54,59,80
70Cr-30Ti	150	0.1-0.3	0.5	200*,200*,200*,200*	25,27,30,31

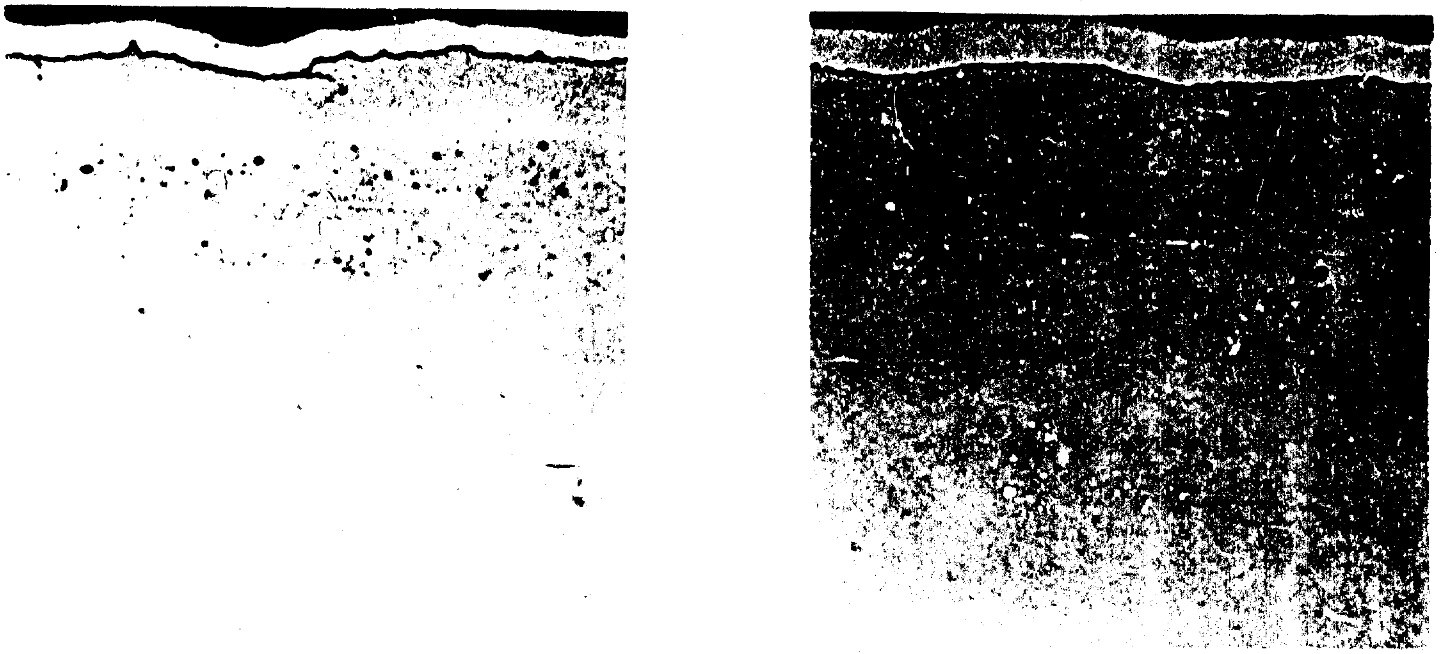
(1) All Cr-Ti coating cycles 8 hours at 2300°F with 0.5 w/o KF activation
(2) All specimens silicon coated in 4 hours at 2050°F and 10^{-2} mm using 1.0 w/o KF activation
(3) * - Oxidation tests discontinued with no visible failure





50Cr-50Ti

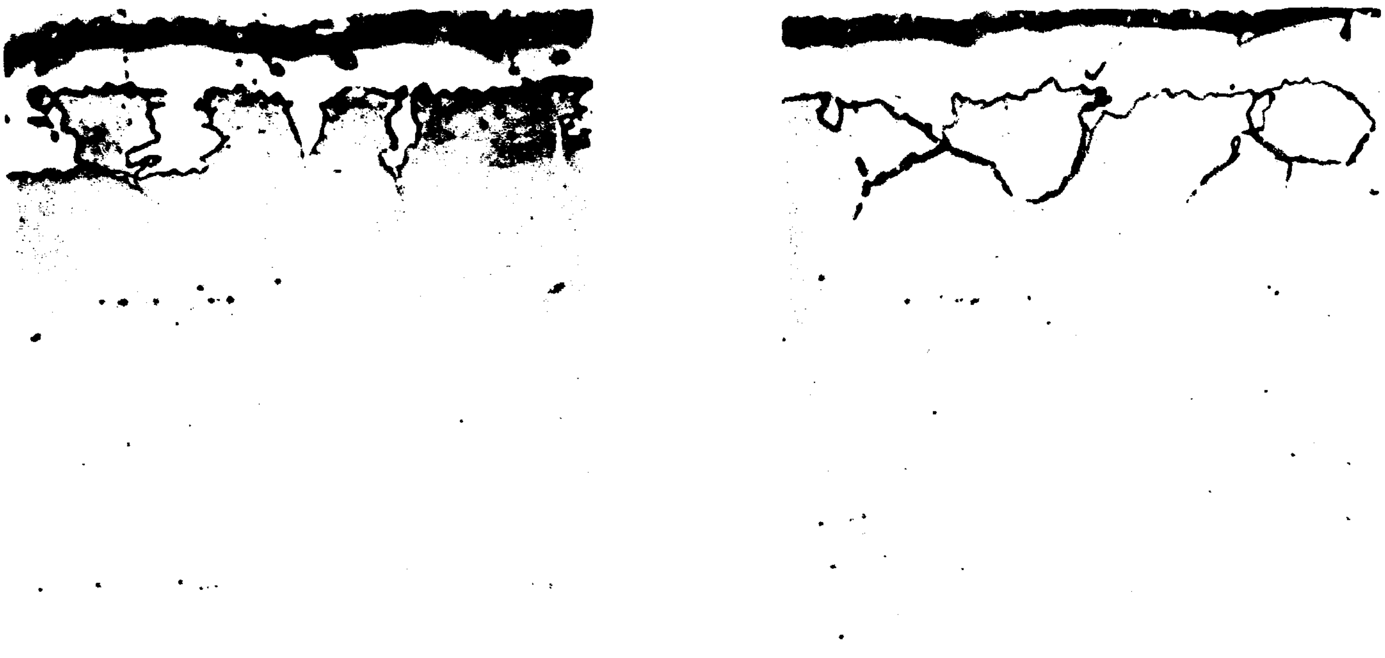
60Cr-40Ti



65Cr-35Ti

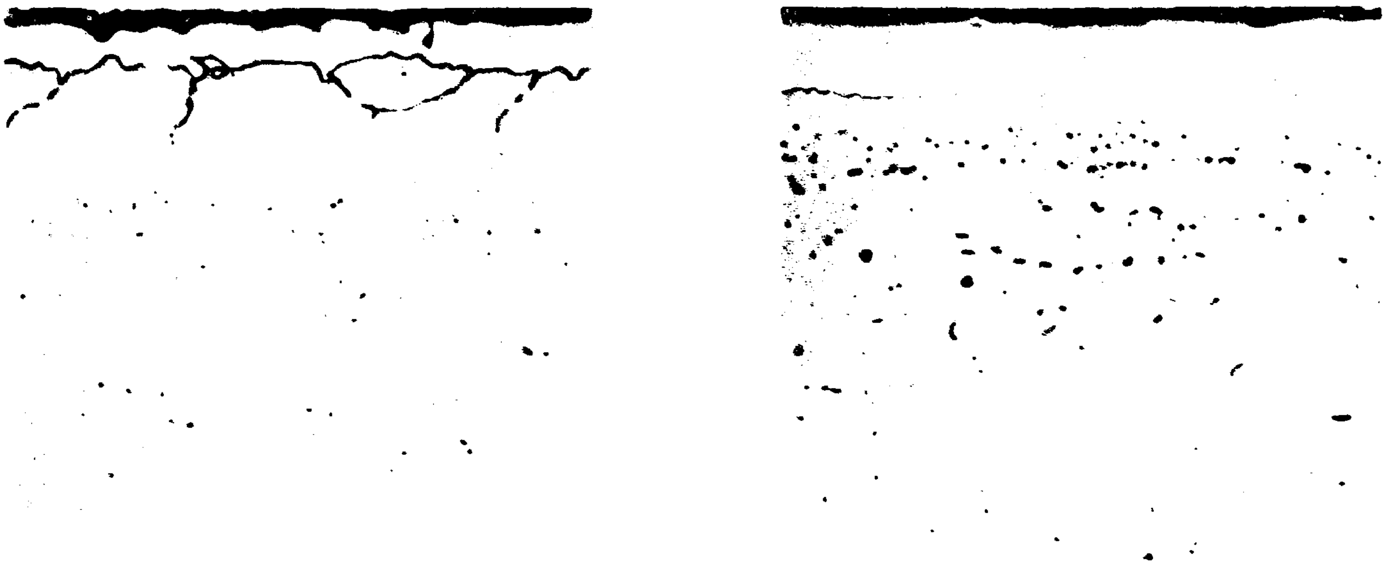
70Cr-30Ti

Figure 1 Cr-Ti Coated D-14 Alloy Specimens Coated in 8 Hours at 2300° F and a Pressure of 10-2 mm Using Various Cr-Ti Pack Compositions 500X



50Cr-50Ti

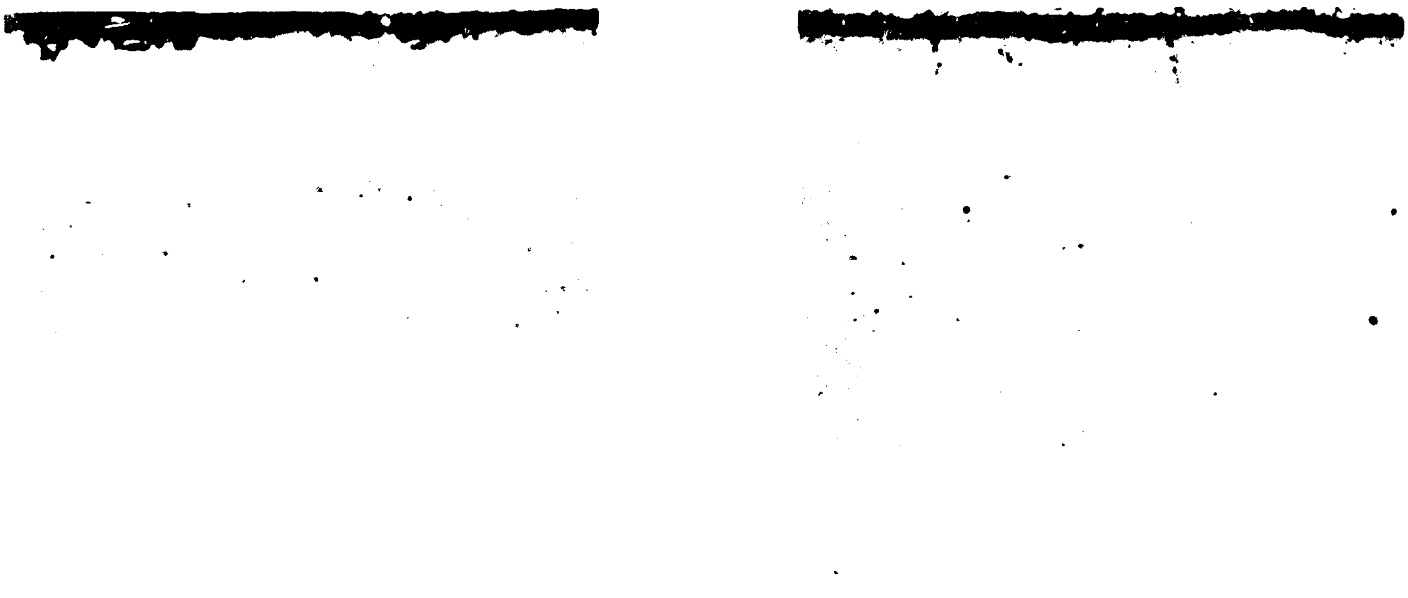
60Cr-40Ti



65Cr-35Ti

70Cr-30Ti

Figure 2 Cr-Ti Coated D-14 Alloy Specimens Coated in 8 Hours at 2300°F and a Pressure of 1.5 mm Using Various Pack Composition 500X



60Cr-40Ti 65Cr-35Ti

70Cr-30Ti

Figure 3 Cr-Ti Coated D-14 Alloy Specimens Coated in 8 Hours at 2300°F and a Pressure of 140 mm Using Various Pack Compositions 500X

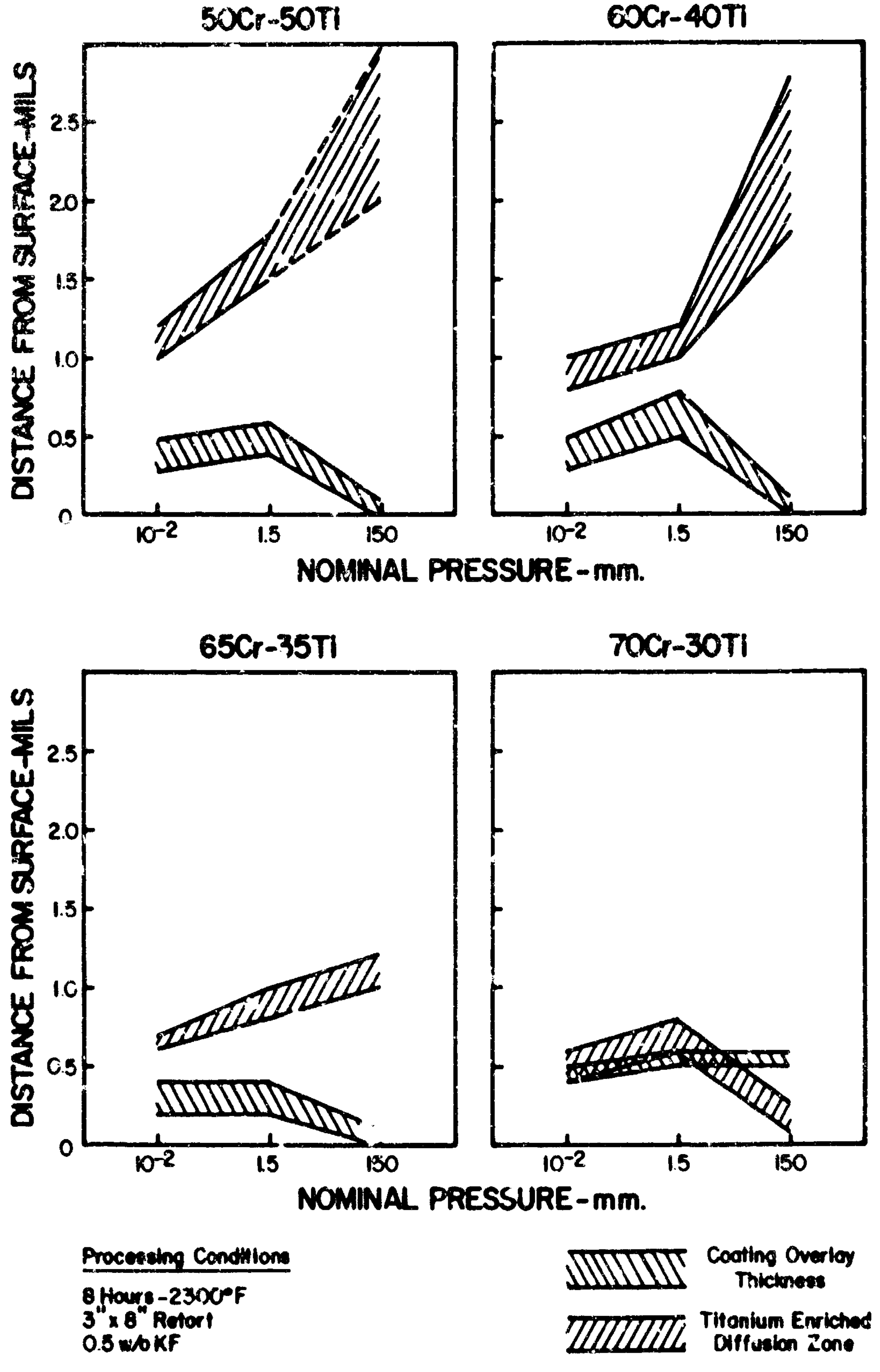
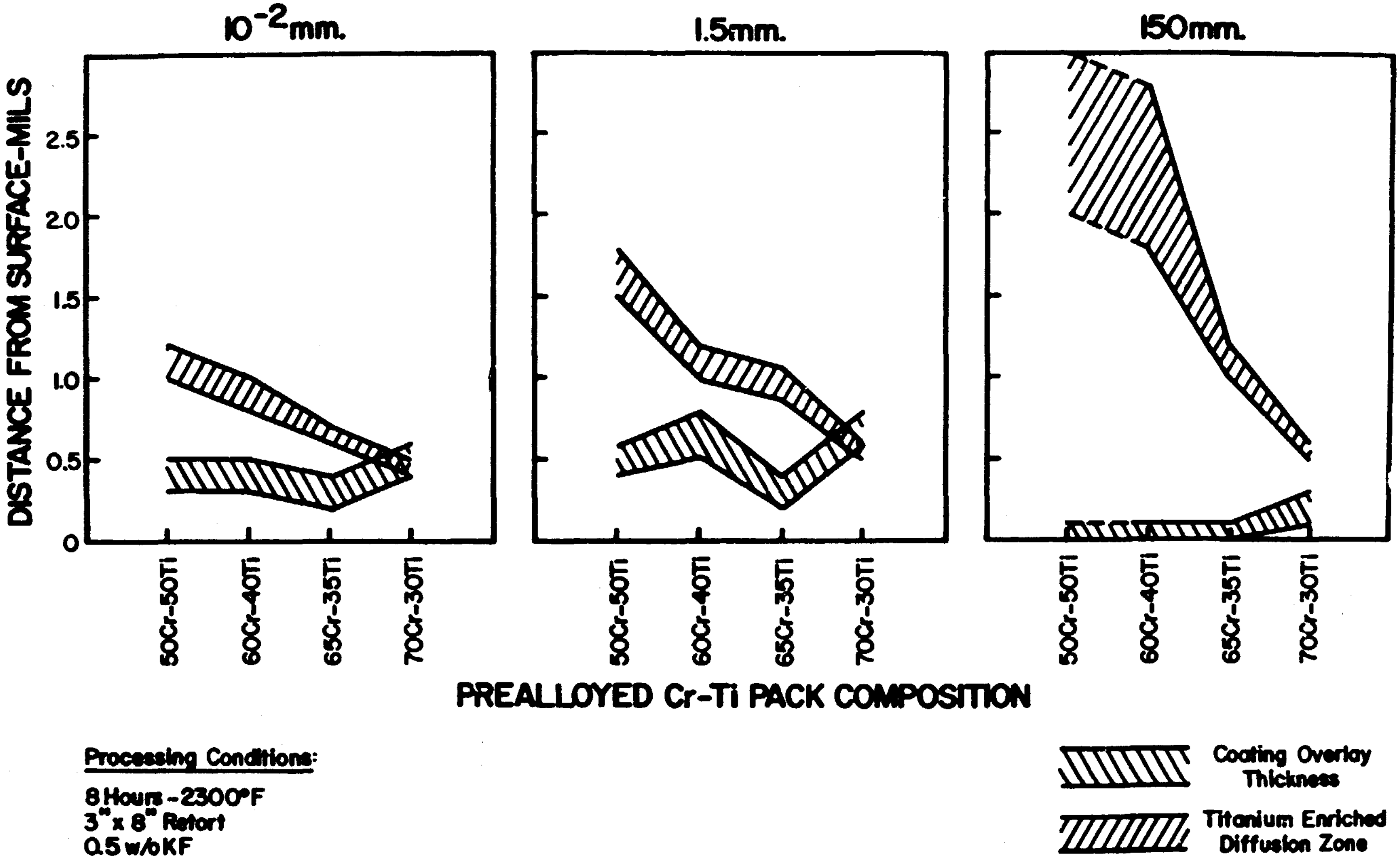


Figure 4 Relationship of Coating Thickness and Depth of Diffusion to Processing Pressure for Formation of Cr-Ti Alloy Coatings in Four Cr-Ti Pack Compositions



Processing Conditions:

8 Hours - 2300°F
3" x 8" Retort
0.5 w/o KF

Figure 5 Relationship of Coating Thickness and Depth of Diffusion to Cr-Ti Pack Composition for Formation of Cr-Ti Alloy Coatings at Three System Pressures

Increasing the overall system pressure apparently reduced the chromium-halide reaction kinetics and suppressed the vaporization of metallic chromium. The resulting Cr-Ti alloy coatings consisted of essentially a titanium enriched surface layer with only localized chromium deposits associated with intimate contact between the columbium surface and the pack particles. Only in the 70Cr-30Ti alloy pack was there formed a continuous Cr-Ti alloy overlay. The combination of 50Cr-50Ti and 150 mm pressure was not run after observing the metallographic results from the 60Cr-40Ti alloy pack.

The reason for the anomalously thin overlay and diffusion depth of coatings formed in the 65Cr-35Ti pack composition is not clear. It may, however, be associated with the relative activities of chromium and titanium constituents in this alloy; since 65Cr-35Ti is approximately the composition of the stable intermetallic compound $TiCr_2$.

The utility of the metallographic observations is only realized by their comparison with the cyclic oxidation results after siliconizing. These data are also shown in Table 2. For cyclic oxidation in air at 1800 and 2500°F, the most protective Cr-Ti-Si coatings were produced by formation of the Cr-Ti alloy coating in either a 50Cr-50Ti or 60Cr-40Ti alloy pack at a furnace pressure of 1.5 mm. It is observed from a comparison of the oxidation data with the coating microstructures that the depth of titanium diffusion and the corresponding diffusion of chromium into the columbium substrate play an essential role in the 1800°F protective life of the coatings. Three basic characteristics of the Cr-Ti alloy coatings are evident in all reliably protective Cr-Ti-Si coatings: (1) a distinct titanium enriched diffusion zone of 0.5-1.0 mil thickness, (2) sufficient chromium diffusion into this titanium enriched region to form the chromium rich intermetallic phase as a continuous interface layer between the overlay and the substrate, (3) a continuous 0.3-0.5 mil Cr-Ti overlay coating, diffusion alloyed with the columbium substrate. The two processing combinations mentioned above were successful in forming Cr-Ti diffusion alloy layers displaying these microstructures.

The key role played by the diffusion of titanium into the columbium substrate is by no means a recent observation. Titanium precoating has been used effectively in the past, particularly with non-titanium bearing columbium alloys, to produce more reliably protective Cr-Ti-Si coatings. However, precoating requires a third processing cycle and is for this reason undesirable. Formation of the Cr-Ti alloy coatings in the blanked-off system, on the other hand, has produced coatings with adequate titanium diffusion. This technique, however, has the lone disadvantage of poor control over vacuum leaks and outgassing in the system. Thus it would be desirable to perform the coating operation in a continuously mechanical pump evacuated system, if coatings of comparable protective properties could be obtained.

A technique was investigated to attempt incorporating the titanium precoat cycle into the normal Cr-Ti processing cycle. This involved blanking-off the furnace from the vacuum system for short periods of time (2-4 hours) at intermediate temperatures, during the heat up portion of the Cr-Ti processing cycle. It was considered that retaining the activated titanium species in the blanked-off pack might effect a titanium precoat. At the conclusion of the isothermal hold (1.5 mm) the furnace was evacuated and the cycle continued at 10^{-2} mm pressure.

The metallographic and oxidation results from these runs are shown in Table 3. Data are presented for coatings formed in both 50Cr-50Ti and 60Cr-40Ti alloy pack compositions and comparative data are shown for coatings formed without the isothermal hold. No improvement in oxidation properties was obtained by employing this technique with the 60Cr-40Ti alloy pack. Improvement was produced in the 1800°F protective life of coatings formed in the 50Cr-50Ti alloy pack; and there was also some improvement indicated in the 2500°F protective life as a result of holding the pack 4 hours at 2000°F. Although the overall improvement in protective life as a result of the isothermal hold was not great, there are some indications of a titanium precoat effect. This technique was thus investigated on a very limited basis in the larger resistance element heated bell furnace.

Several miscellaneous Cr-Ti coating runs were made to survey other possible factors associated with process optimization. One frequent area of concern is the questionable influence of activator carry over during a series of runs with the same pack materials. This situation was investigated utilizing a 50Cr-50Ti alloy pack and two furnace pressures, 10^{-2} and 1.5 mm. A series of three runs were made at each pressure in which the activator addition was omitted from a previously used pack for two consecutive runs, and then increased by a factor of four (2.0 w/o KF) over that normally added to the pack (0.5 w/o KF) in a third run. The metallographic measurements on these specimens and cyclic oxidation results after siliconizing are shown in Table 4. Photomicrographs of representative microstructures are shown in Figures 6 and 7.

Absence of the pack activator markedly reduced the titanium enriched diffusion zone thickness, particularly on coatings formed in the second consecutive run without activator addition. However, activator omission had little influence on the overlay coating thickness. Increasing the quantity of activator to four times the normal addition correspondingly increased the concentration of both titanium and chromium in the substrate diffusion zone, whereas, the overlay thickness was again virtually unaffected. These data further substantiate the previous observation that the activator reacts primarily with the titanium component of the pack alloy, whereas chromium is supplied to the coating by both reaction with the halide and by metallic vaporization. Conclusive evidence of the need for titanium enrichment of the substrate surface is indicated by the poor 1800°F protective life of coatings formed in non-activated packs. It is desirable to minimize the quantity of activator added to the coating pack. However, the excellent protective lives exhibited by coatings formed using four times the normal activator quantity, indicate there is a need for further optimization of this particular processing variable.

5.1.2 Silicon Coating Cycle

Previous coating development studies have shown that the four principal variables associated with the silicon coating cycle are: (a) time, (b) temperature, (c) furnace pressure and (d) quantity of pack activator. The series of silicon coating runs discussed in this section involved an investigation of the following

TABLE 3

Metallographic and Cyclic Oxidation Results for Coatings Formed on D-14 Alloy Using Various Temperature Step-Cycles for the Cr-Ti Alloy Coating Formation

Cr-Ti Coating Processing Parameters(1)				Cr-Ti Alloy Coating Measurements		Cr-Ti-Si Coating Oxidation Protective Life - Hours	
Pack Composition	Temperature °F	Pressure mm	Time Hours	Overlay Thickness Mils	Diffusion Zone Depth Mils	1800°F	2500°F
50Cr-50Ti	2000 +2300	1.5 10^{-2}	2 8	0.4-0.6	1.4	200*,200*,200*(2)	96,96,96
50Cr-50Ti	2000 +2300	1.5 10^{-2}	4 8	0.4-0.6	1.4	200*,200*,200*	120,144,144
50Cr-50Ti	2100 +2300	1.5 10^{-2}	4 8	0.2-0.6	1.3-1.5	200*,200*,200*,200*	96,96,96,96
50Cr-50Ti	2200 +2300	1.5 10^{-2}	4 8	0.2-0.6	1.3-1.6	200*,200*,200*,200*	77,96,96,96
50Cr-50Ti	2300 +2300	1.5 10^{-2}	4 8	0.2-0.8	1.5-1.8	200*,200*,200*,200*	51,104,120,120
50Cr-50Ti	2300	10^{-2}	8	0.3-0.5	1.0-1.2	28,57,200*,200*	75,80,99,99
60Cr-40Ti	2100 +2300	1.5 10^{-2}	4 8	0.3-0.7	0.8-1.0	24,28,28,53	53,70,70,77
60Cr-40Ti	2200 +2300	1.5 10^{-2}	4 8	0.35-0.55	0.9-1.1	26,51,53,124	70,77,77,77
60Cr-40Ti	2300 +2300	1.5 10^{-2}	4 8	0.6	0.8-1.0	48,51,96,195	96,96,104,104
60Cr-40Ti	2300	10^{-2}	8	0.3-0.5	0.8	24,31,38,57	57,75,75,83

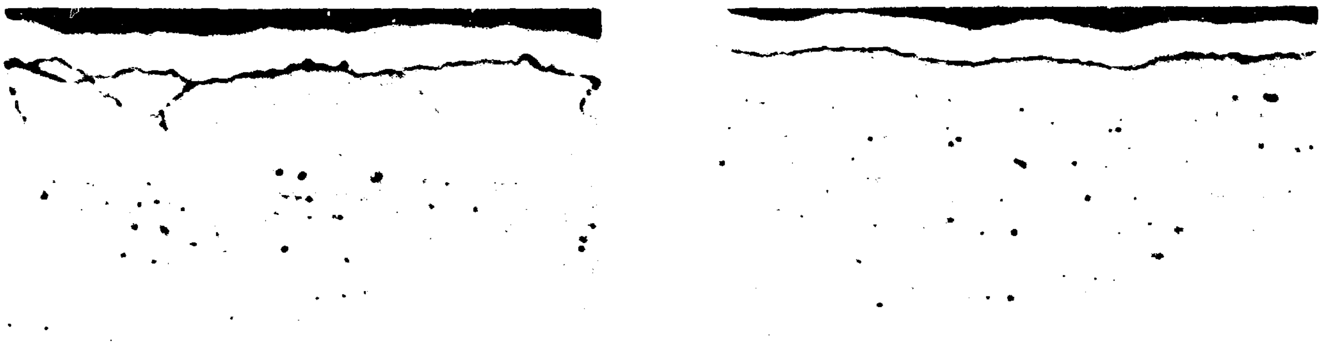
(1) All coating cycles utilized 0.5 w/o KF activation
(2) * Denotes tests discontinued with no visible failure

TABLE 4

Metallographic and Cyclic Oxidation Results for Coatings Formed on D-14 Alloy Utilizing Both Activated and Non-Activated Cr-Ti Alloy Packs

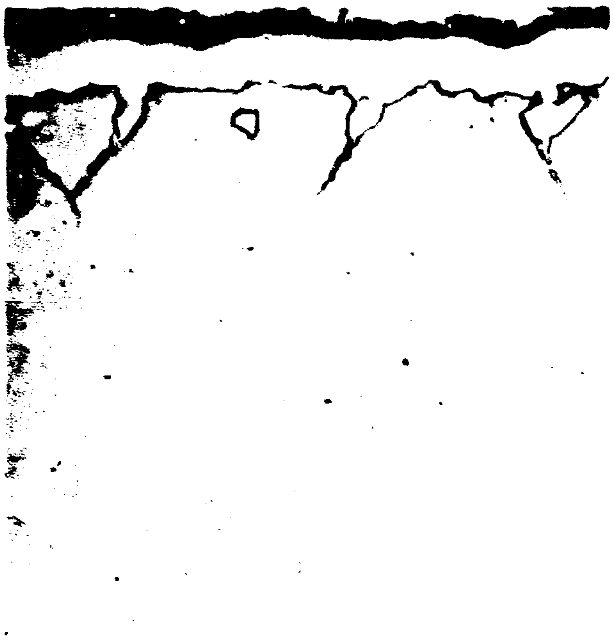
Cr-Ti Coating Cycle Parameters(1)			Cr-Ti Alloy Coating Measurements		Cr-Ti-Si(3) Coating Oxidation Protective Life - Hours	
Pack Composition	Activator	Pressure mm	Overlay Thickness Mils	Diffusion Zone Depth Mils	1800°F	2500°F
50Cr-50Ti	None	10^{-2}	0.3-0.5	1.0	75,104	54,56
50Cr-50Ti	None	10^{-2}	0.2-0.4	0.4-0.5	38,107	30,32
50Cr-50Ti	40 gm KF	10^{-2}	0.4-0.6	1.3	200*(4),200*	104,106
50Cr-50Ti	10 gm KF	10^{-2}	0.3-0.5	1.0-1.2	28,57,200*,200*	75,80,99,99
50Cr-50Ti	None	1.5	0.5-0.6	1.0	28,29,51,200*	96,96,96,104
50Cr-50Ti(2)	None	1.5	0.05-0.1	0.5	3,5,5,6	24,24,24,28
50Cr-50Ti	40 gm KF	1.5	0.2-0.6	2.0	5,200*,200*,200*	120,165,172,188
50Cr-50Ti	10 gm KF	1.5	0.4-0.6	1.5-1.8	200*,200*,200*,200*	99,124,146,146

(1) All Cr-Ti coating cycles 8 hours at 2300°F except (2)
(2) Discontinued at 1.5 hours - mechanical failure
(3) All specimens silicon coated in 4 hours at 2050°F and 10^{-2} mm using KF activation
(4) * Oxidation tests discontinued with no visible coating failure



No Activator Addition
Run No. 1

No Activator Addition
Run No. 2



2.5 w/o HF Activator

Figure 6 Cr-Ti Alloy Coatings Formed on D-14 Alloy at 10-2 mm Furnace Pressure in a 50Cr-50Ti Alloy Pack 500X

No Activator Addition
Run No. 1

2.0 w/o KF Activator

Figure 7 Cr-Ti Alloy Coatings Formed on D-14 Alloy at 1.5 mm Furnace Pressure in a 50Cr-50Ti Alloy Pack 500X levels of each of these variables:

(a) temperature - 1900, 2000 and 2100°F

(b) time - 3 and 6 hours

(c) furnace pressure - 10^{-2}, 1.5 and 150 mm

(d) pack activator - 0.5 and 1.0 w/o KF

A one-third sample of the full factorial analysis (36 runs) was conducted, with the levels of the four variables completely randomized throughout a sequence of twelve runs. Table 5 shows a layout of the Random Balance experiment. A large number of D-14 alloy coupons were Cr-Ti coated for this study, utilizing the best processing conditions derived from the investigation discussed in the previous section. These coating parameters were: (a) 8 hours at 2300°F, (b) a 50Cr-50Ti alloy pack, (c) 0.5 w/o KF and (d) a furnace pressure of 1.5 mm (blanked-off). Specimens coated in each run of the Random Balance series were then evaluated by metallographic examination and by cyclic oxidation at 1800 and 2500°F. The results of these are given in Table 6.

A comparison should be made of the metallographic measurements with the photomicrographs of these coatings shown in Figures 8 through 10. The sketch shown in Section 5.1.1 also applies to the coating which results after the silicon coating cycle. In this case the overlay consists of a Cr-Ti-Si alloy layer formed by alloying the Cr-Ti overlay layer with Si. The apparent interface between the overlay and the diffusion zone advances inward during the silicon cycle, thus consuming a portion of the chromium rich intermetallic and the titanium enriched diffusion zone. The Cr-Ti-Si alloy overlay measurement pertains to the distance from the surface to the sharp interface at the substrate diffusion zone. The diffusion zone measurement is actually that of the retained titanium enriched substrate layer (including the precipitated intermetallic phase) which was not alloyed with the diffusing silicon. In Figure 11 are two photomicrographs which depict the diffusion alloying of the Cr-Ti alloy coating with silicon at a processing pressure of 10^{-2} mm. With the aid of oblique lighting and the hardness differential associated with localized variations in coating composition, a silhouette of the prior Cr-Ti alloy coating and precipitated intermetallic phase can be observed behind the advancing silicon diffusion front. As the coating pressure increased silicon is observed to have diffused completely through the titanium enriched substrate layer. At the higher system pressures (blanked-off furnace) where the residence time of the activated species in the pack was increased, the rate of formation of the Cr-Ti-Si coating was also increased. Correspondingly, there was a decrease in the thickness of the retained substrate diffusion layer.

Figure 12 is a scatter diagram showing graphically the variation in coating thickness and diffusion zone thickness for the various levels of each process variable. Based on the median differentials which are noted on the diagram, Cr-Ti-Si coating thickness was influenced by all four process variables, with system pressure

TABLE 5

Randomized Sequence of Silicon Processing Variables

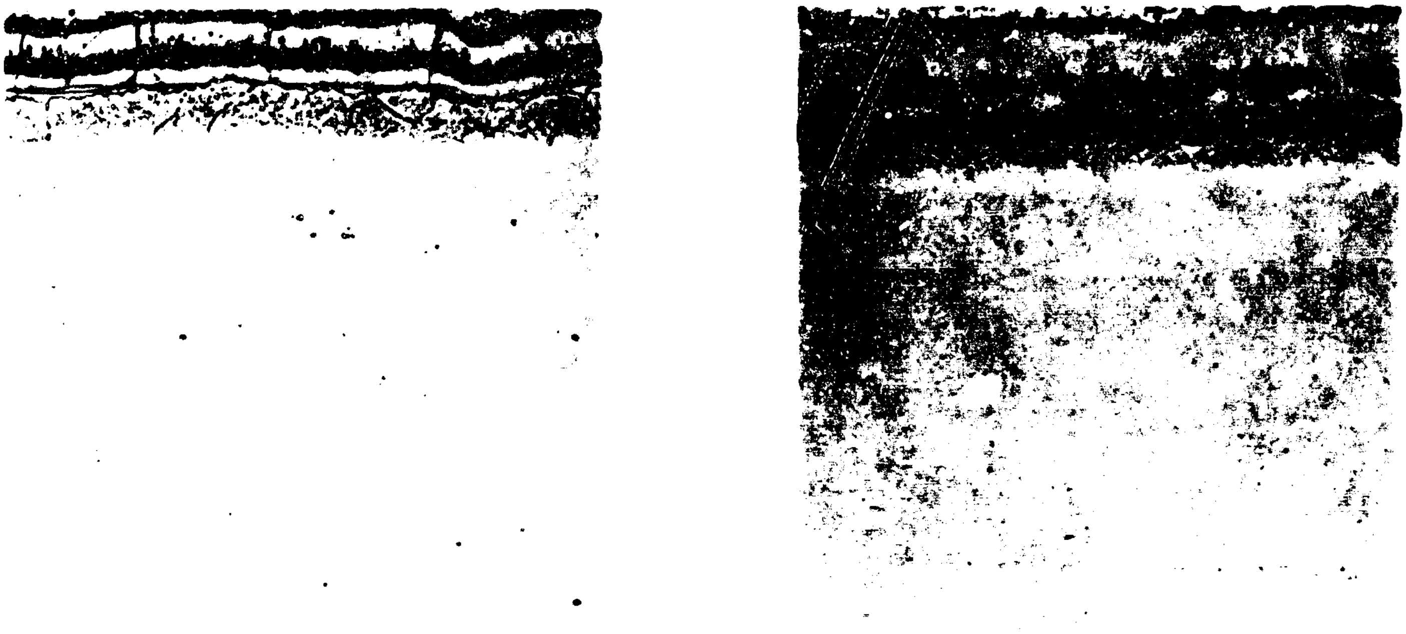
Run No.	w/o KF	Pressure mm	Temperature °F	Time Hours
1	1.0	1.5	1900	3
2	1.0	150	2000	3
3	0.5	150	1900	3
4	0.5	10^{-2}	2100	6
5	0.5	150	1900	6
6	1.0	150	2100	6
7	1.0	1.5	2100	3
8	1.0	10^{-2}	2100	6
9	0.5	10^{-2}	1900	3
10	1.0	10^{-2}	2000	6
11	0.5	1.5	2000	6
12	0.5	1.5	2000	3

TABLE 6

Metallographic and Cyclic Oxidation Results From Random Balance Investigation of Silicon Processing Variables

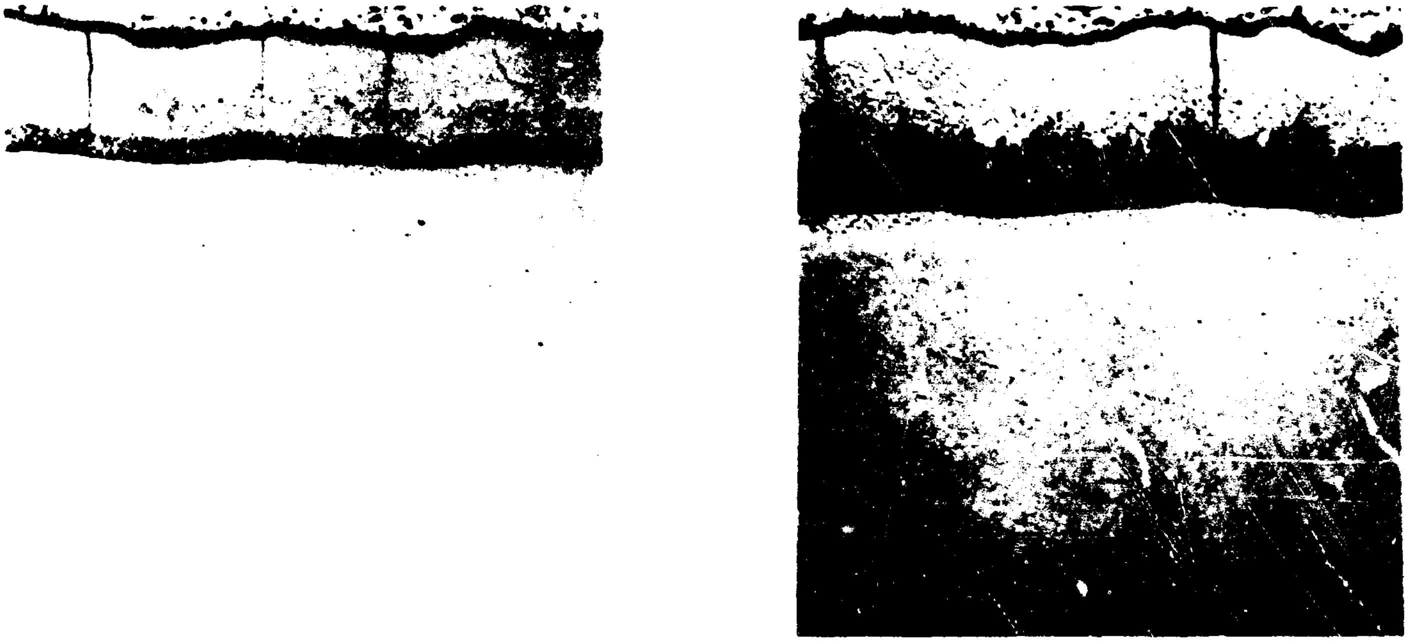
Si Coating Conditions				Cr-Ti-Si Metallographic Measurements		Cr-Ti-Si Coating Oxidation Protective Life - Hours	
Activator w/o	Temperature °F	Pressure mm	Time Hours	Overlay Thickness Mils	Diffusion Zone Depth Mils	1800°F	2500°F
0.5 KF	1900	10^{-2}	3	0.9-1.3	1.0-1.2	200*,200*,200*,200*(1)	56,77,96,96
1.0 KF	1900	1.5	3	1.8-2.2	0.5-0.7	56,72,80,200*	56,56,56,96
0.5 KF	1900	150	3	2.0-2.5	0.4-0.6	56,72,96,96	96,104,120,124
0.5 KF	1900	150	6	3.0-3.6	0.4-0.6	8,8,24,32	96,120,124,128
1.0 KF	2000	10^{-2}	6	1.5-1.8	1.0-1.2	200*,200*,200*,200*	80,120,124,128
0.5 KF	2000	1.5	3	1.9-2.1	1.0-1.2	128, 200*,200*,200*	72,80,104,124
0.5 KF	2000	1.5	6	2.5-2.8	0.4-0.8	200*,200*,200*,200*	29,72,96,96
1.0 KF	2000	150	3	2.9-3.2	0.2-0.5	24,32,32,32	101,120,120,144
0.5 KF	2100	10^{-2}	6	1.8-2.2	0.5-0.8	200*,200*,200*,200*	72,72,120,120
1.0 KF	2100	10^{-2}	6	1.8-2.2	0.8-1.2	200*,200*,200*,200*	101,104,120,124
1.0 KF	2100	1.5	3	3.0-3.7	0.4-0.6	27,27,49,56	124,128,144,144
1.0 KF	2100	150	6	4.6-5.0	0	6,6,6,26	8,8,32,48

(1) * Denotes test discontinued - no coating failure



0.5 w/o KF at
10-2 mm - 3 Hours

1.0 w/o KF at
1.5 mm - 3 Hours



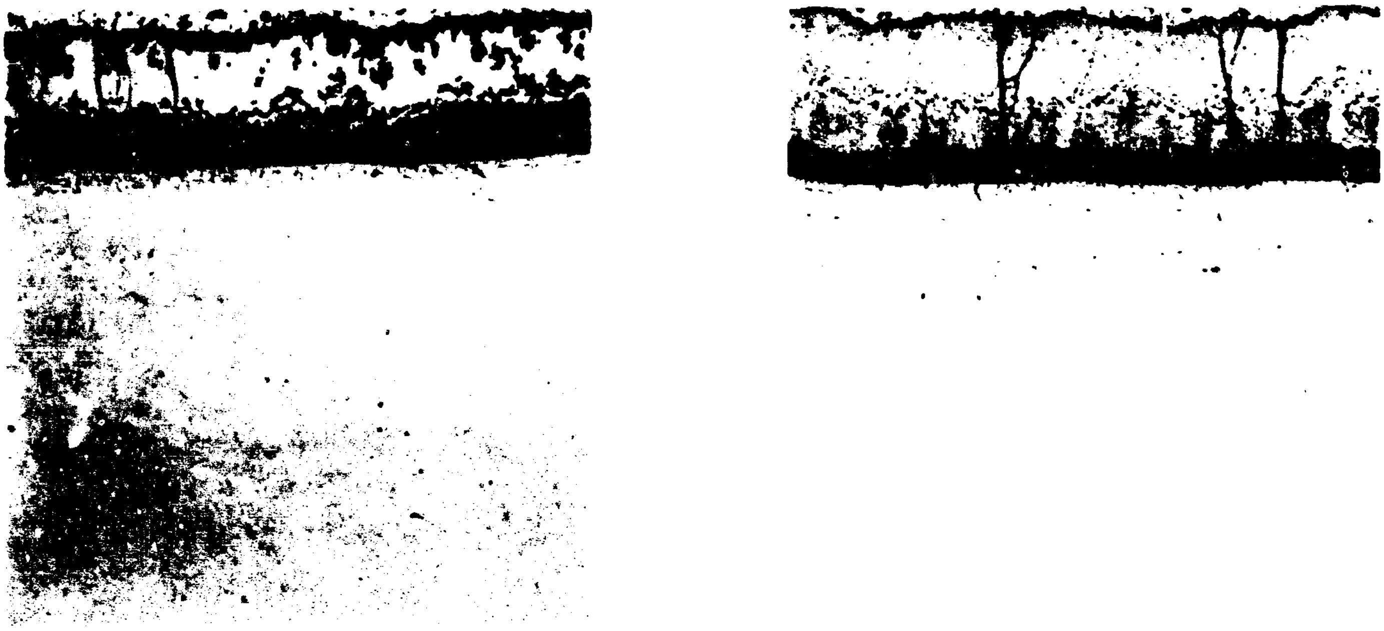
0.5 w/o KF at
150 mm - 3 Hours

0.5 w/o KF at
150 mm - 6 Hours

Figure 8 Cr-Ti-Si Alloy Coatings Formed on D-14 Alloy Comparing Silicon Coating Process Variables at a Constant Coating Temperature of 1900° F 250X

1.0 w/o KF at
10^{-2} mm - 6 Hours

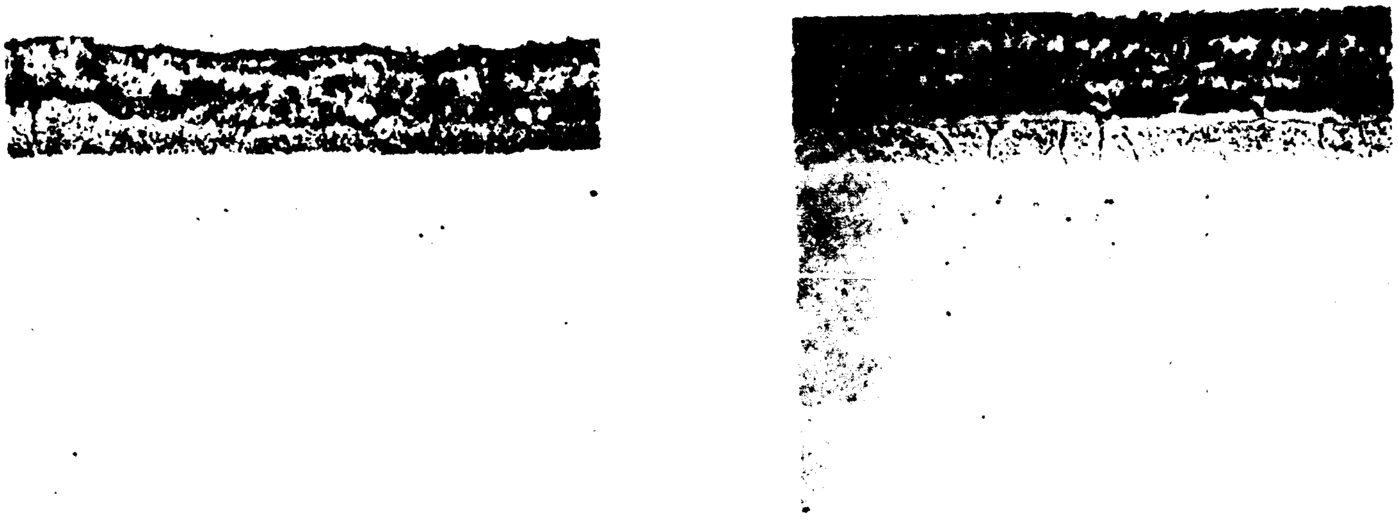
0.5 w/o KF at
1.5 mm - 3 Hours



.5 w/o KF at
1.5 mm - 6 Hours

1.0 w/o KF at
150 mm - 3 Hours

Figure 9 Cr-Ti Coatings Formed on D-14 Alloy Comparing Silicon Coating Process Variables at a Constant Coating Temperature of 2000°F 250X



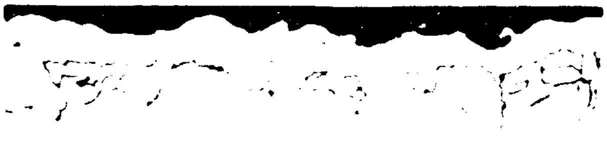
0.5 w/o KF at
10^{-2} mm - 6 Hours

1.0 w/o KF at
10^{-2} mm - 6 Hours

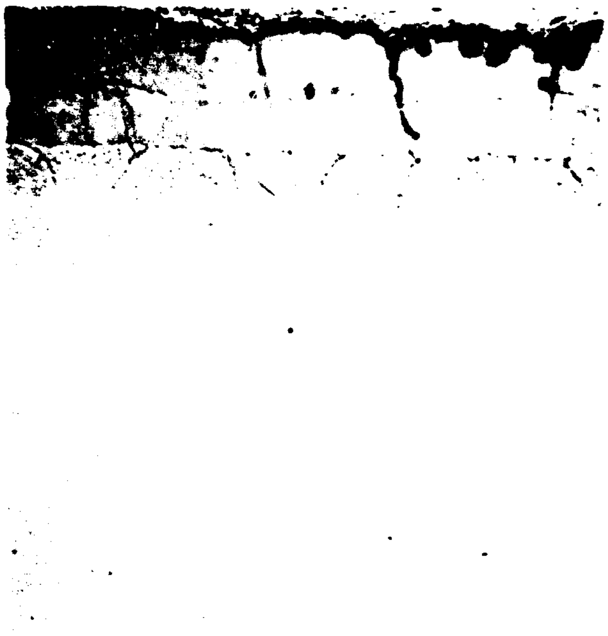
1.0 w/o KF at
1.5 mm - 3 Hours

1.0 w/o KF at
150 mm - 6 Hours

Figure 1[illegible] Cr-Ti-Si Alloy Coatings Formed on D-14 Alloy Comparing Silicon Coating Process Variables at a Constant Coating Temperature of 2100°F 250X



Cr-Ti Coated



Cr-Ti-Si Coated

Figure 11 Photomicrographs of Coated D-14 Alloy Showing a Silhouette of the Prior Cr-Ti Alloy Coating after Diffusion Alloying with Silicon 250X

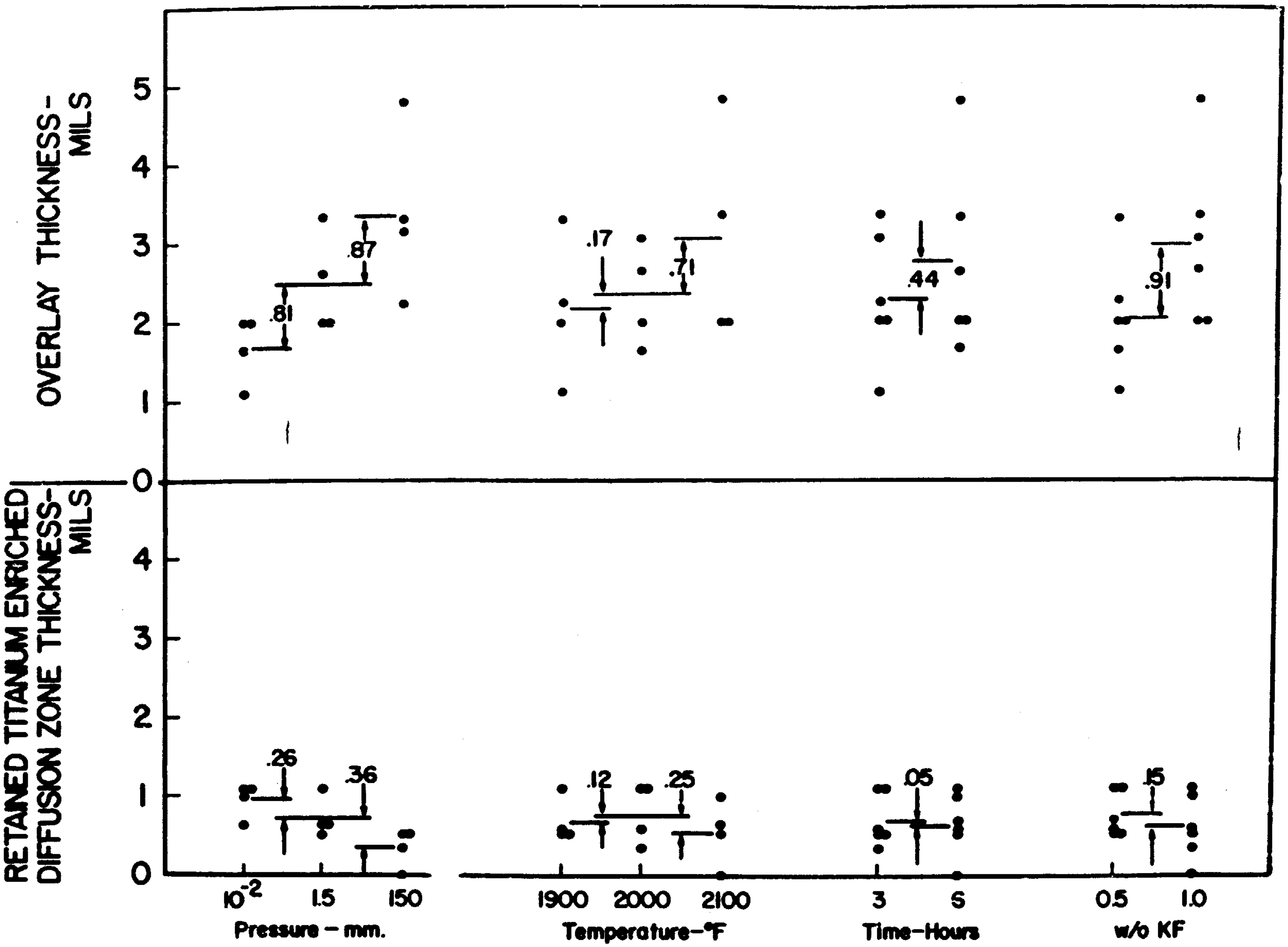


Figure 12 Scatter Diagram Showing Variation in the Cr-Ti-Si Alloy Coating Metallographic Characteristics for Various Levels of the Four Process Variables

being the most significant factor. In the case of retained diffusion zone, only system pressure appears to have had any real effect. The median differentials for the variation in diffusion zone thickness are significant with regard to furnace pressure, whereas these differentials are negligible when related to the other three variables. The apparent influence of system pressure is related to the residence time of the vapor phase in the retort. Increased pressure (decreased evacuation rate) increases residence time and thus deposition rate. The amount of activator used and the pressure maintained effects the concentration of the elements in the vapor phase. Time and temperature primarily control diffusion rate and to a certain degree, vapor phase composition. Again, however, residence time is apparently the significant factor, within the range of variables investigated.

The metallographic measurements are again useful in so far as they aid in interpreting the cyclic oxidation data. The cyclic oxidation protective lives, listed in Table 6, are plotted in scatter diagrams in Figure 13. Very small median differentials are noted for all variation in 2500°F oxidation protective life. Within the range of levels studied for the four variables, none of these variables significantly influenced the 2500°F protective life of the Cr-Ti-Si coatings. One exception is the 4.5-5.0 mil thick coating applied at 2100°F in 6 hours at 150 mm pressure. Splitting of the coating at the specimen edges accounts for the poor protective life of this coating.

For oxidation protection at 1800°F, however, a very pronounced influence of the system coating pressure is obvious from the scatter diagram. The significance of this variable is apparent from observing a correlation between the metallographic measurements and the oxidation protective lives, plotted in Figure 14. As the Cr-Ti-Si coating thickness increased the thickness of the titanium enriched substrate layer decreased and correspondingly the protective capabilities of the Cr-Ti-Si coating at 1800°F also decreased. Increasing the residence time of the activated species in the silicon coating pack substantially increased the rate of formation of the Cr-Ti-Si coating, however, at the expense of the titanium enriched substrate diffusion zone. Failure of these coatings at low temperature is analogous to the "pest" problem characteristic of silicide coatings, where there is no intermediate protective layer between the silicide and the unaffected substrate. The key factor for low temperature protection is the retention of a titanium enriched substrate layer and associated chromium rich intermetallic phase after alloying with silicon. Under the conditions of this series of runs, increasing the Cr-Ti-Si coating thickness necessarily decreased the retained diffusion zone. For oxidation protection at 2500°F, this plot indicates generally a slight increase in protective life with increase in coating thickness, and less dependence of the high temperature life on the diffusion zone characteristics.

An investigation of the effect of additional adjustments in temperature, coating time, and activator quantity was conducted in an effort to further optimize the processing parameters investigated in the random balance analyses. Temperature was increased to 2200°F (maximum feasible since higher temperatures cause excessive pack sintering), activator quantity was increased to 3.0 w/o KF, and time was increased to 9 hours. Not all possible combinations of these variables were investi-

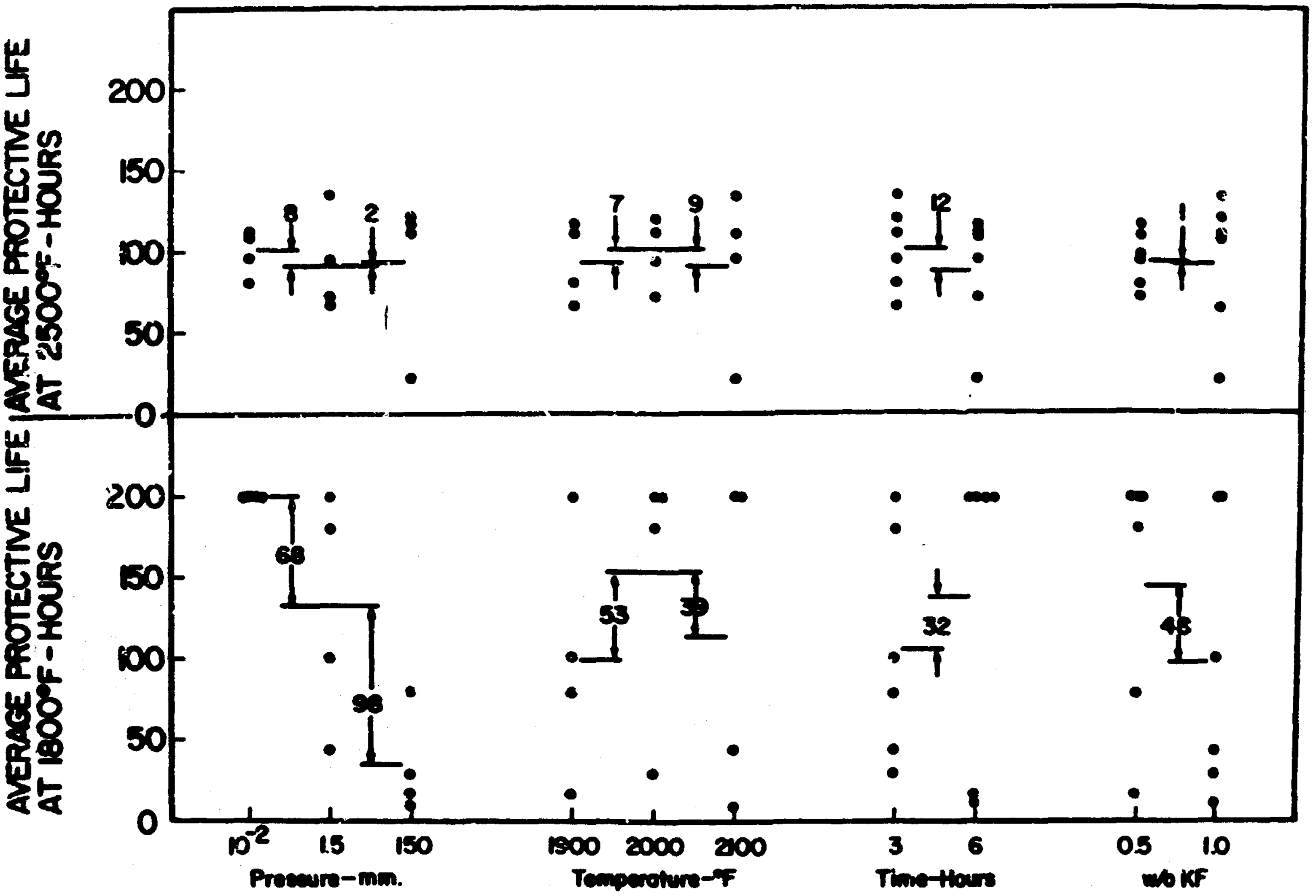


Figure 13 Scatter Diagrams Showing the Effect of Silicon Processing Variables on Variation in the Oxidation Protective Lives of Cr-Ti-Si Coatings at 1800 and 2500°F

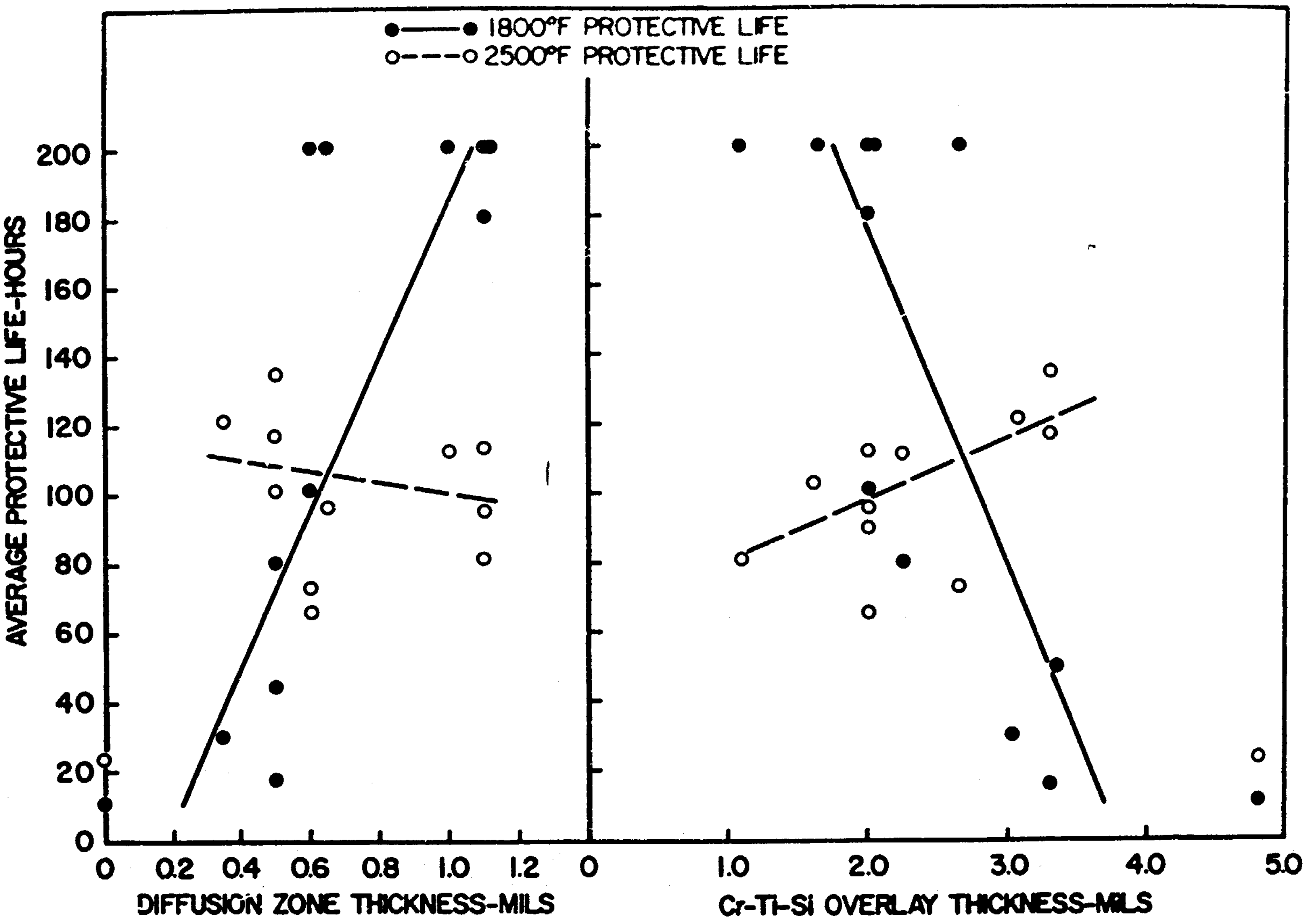


Figure 14 Protective Life of the Cr-Ti-Si Coating on D-14 Alloy as a Function of the Coating Diffusion Zone and Overlay Thickness

gated since it was felt that as few as five combinations would be sufficient to indicate significant trends. The actual process variable combinations investigated, resultant metallographic measurements, and cyclic oxidation test results are listed in Table 7.

For comparative purposes the Cr-Ti alloy layer was formed on these specimens by utilizing the process parameters previously employed in the random balance analysis.

In general, the test results further substantiated the findings of the random balance analysis. Increased silicide layer thickness decreased the retained intermetallic and diffusion zone thickness and accordingly the low temperature protective life was decreased. The protective life at 2500°F increased with increasing coating thickness. Note that with furnace operating pressure held constant at 10^{-2} mm, the greatest influence on coating thickness was derived from the processing temperature.

Some of the inconsistent test results for 1800°F oxidation protective life could have originated in the Cr-Ti coating cycle. In some instances particles of the 50Cr-50Ti alloy pack adhered to the columbium alloy coupons. Even though extreme care was exercised in removing these particles, minute coating damage may have resulted causing decreased protective life. This problem can be alleviated through the substitution of the 60Cr-40Ti alloy pack for deposition of the Cr-Ti alloy layer, since little if any particle sintering to the coupons is ever encountered with this pack composition.

The optimum set of process parameters for the silicon coating cycle in the 3" diameter x 8" high retort, based on the study just completed are:

a. temperature - 2100°F

b. time - 6 hours

c. activator - 1.0 w/o KF

d. system pressure - 10^{-2} mm

Figure 15 is a photomicrograph of the Cr-Ti-Si coating produced utilizing the above conditions.

5.2 Coating Studies in the Pilot Scale Furnace

A pilot scale induction heated coating furnace, similar to that used extensively in the Cr-Ti-Si coating of aerospace hardware components, was constructed for utilization in this phase of the program. Although a great deal of coating experience had been gained in this size furnace, no extensive effort had been made to optimize the coating process conditions. The cylindrical furnace retort, fabricated from 40 mil D-14 columbium alloy sheet, is 7-1/2" diameter x 18" high. This represents a volume increase of sixteen times and an increase in heat transfer distance (edge

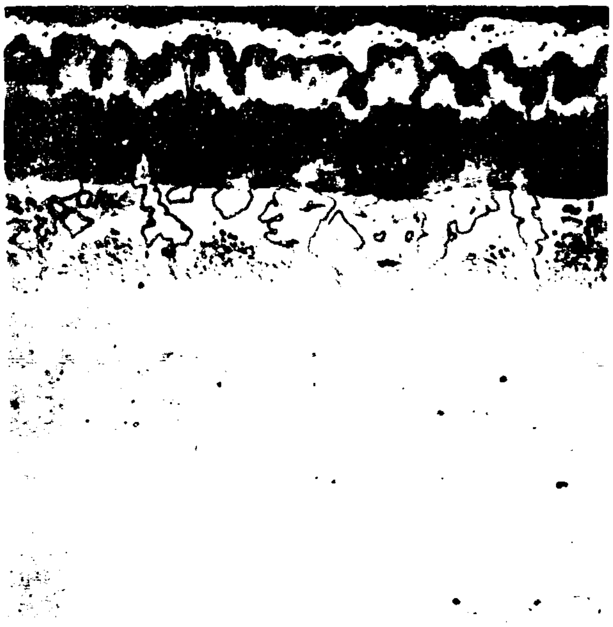
TABLE 7

Metallographic and Cyclic Oxidation Results from Silicon Process Variable Investigation - Cr-Ti-Si Coated D-14 Alloy

Si Coating Conditions				Cr-Ti-Si Metallographic Measurements(1)		Cr-Ti-Si Coating Oxidation Protective Life - Hours		
Activator w/o	Temp. °F	Pressure mm	Time Hours	Overlay Thickness Mils	Diffusion Zone Depth Mils	1800°F(2)	2500°F	2700°F
1.0 KF	2000	10^{-2}	6	1.5-1.8	1.5-1.8	30,30,200*	96,96,104	1,1
3.0 KF	2000	10^{-2}	6	2.0-2.2	2.0-2.3	200*,200*,200*	6,120,152	2,2
1.0 KF	2000	10^{-2}	9	2.0-2.5	1.5-2.0	26,200*,200*	78,96,168	2,6
1.0 KF	2100	10^{-2}	6	2.2-2.8	1.9-2.0	200*,200*,200*	168,192,192	2,6
1.0 KF	2200	10^{-2}	6	3.2-3.6	1.2-1.8	24,200*,200*	104,120,127	3,4

(1) Cr-Ti coating conditions: 50Cr-50Ti alloy pack, 8 hours at 2300°F, 1.5 mm pressure and 0.5 w/o KF activation

(2) * Denotes test discontinued - no coating failure



Cr-Ti-Si Coated D-14 Alloy

Figure 15 Cr-Ti-Si Alloy Coating Formed in Laboratory Scale Furnace - Silicon Cycle - 6 Hours at 2100°F - 10^{-2} mm of pack to center) of 2-1/2 times over that of the laboratory scale furnace. The retort to furnace volume ratios for the two systems are approximately equivalent. Both systems are induction heated and are virtually identical in design.

5.2.1 Cr-Ti Coating Cycle

Information acquired regarding the Cr-Ti alloy coating cycle in the laboratory scale furnace was utilized for the selection of process parameters to be investigated for deposition of the Cr-Ti alloy layer in the pilot scale furnace. Six coating runs were used to investigate the variables: (a) pack composition, (b) system pressure and (c) activator quantity. Pack compositions were limited to 50Cr-50Ti and 60Cr-40Ti based on the results obtained in the smaller furnace. System pressures of 10^{-2} and 1.5 mm and activator quantities of 0.15 and 0.30 w/o KF constituted the other variables. The two levels of pack activator (0.3 and 0.15 w/o KF) were somewhat lower than that used in the laboratory scale retort (0.5 w/o KF). Selection of these activator quantities for the initial runs in this furnace was dictated primarily by the results of previous experience in the other pilot scale furnace. In all cases the activator was mixed throughout the metallic coating pack.

Coupons of both D-14 and D-43 alloys were placed in six locations throughout the retort to investigate differences in coating morphology associated with possible temperature gradients within the pack. Coating cycle duration and temperatures were kept constant at 8 hours and 2300°F, respectively. The metallographic data pertaining to the 50Cr-50Ti alloy pack composition are tabulated in Table 8 and the data pertaining to the 60Cr-40Ti alloy pack composition in Table 9. A sketch showing the various retort positions is included with the tables.

A summary of the average metallographically measured coating thickness associated with the six coating runs is given in Table 10. These values obviously do not reflect differences in coating thickness obtained in a single run which are associated with retort position or substrate material. However, a general statement which applies to all six coating runs can be made as follows: 1) an increase in Cr-Ti alloy overlay thickness was obtained from center to edge at a given retort position, 2) Cr-Ti alloy overlay thickness increased from retort top to bottom, and 3) the Cr-Ti coating overlay produced on D-14 alloy was significantly thinner than that produced on D-43 alloy (the reverse was true of the titanium enriched diffusion zone).

The Cr-Ti overlay layer formed using a 50Cr-50Ti alloy pack was in all cases thinner than coatings formed from a 60Cr-40Ti alloy pack, process parameters being equal. In fact, the heaviest overlay formed from a 50Cr-50Ti pack was thinner than the thinnest overlay formed from a 60Cr-40Ti alloy pack. The opposite trend was observed in the thickness of the titanium enriched diffusion zone. Obviously, this change in the morphology of the Cr-Ti alloy coatings is directly associated with the relative amounts of the two pack constituents in the vapor phase surrounding the columbium alloy coupons. Increasing the titanium content of the pack constituents increases the vapor phase titanium content. This effect is no doubt

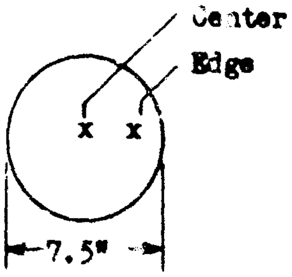
TABLE 8

Metallographic Data for Cr-Ti Alloy Coatings Formed on D-14 and D-43 Alloys in the Pilot Scale Furnace

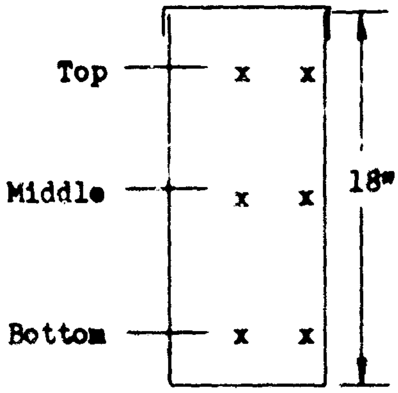
Processing Conditions(1)				Cr-Ti Alloy Coating Measurements for Various Pack Locations(2)			
				Pack Center		Pack Edge	
Pressure mm	w/o KF	Alloy	Vertical Position	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils
10^{-2}	0.30	D-14	Top	0.1-0.3	1.0-1.2	0.1-0.3	1.5-1.7
"	"	"	Middle	0.2-0.4	1.0-1.3	0.2-0.4	1.6-2.2
"	"	"	Bottom	0.2-0.4	1.5-1.7	0.2-0.4	2.0-2.5
10^{-2}	0.30	D-43	Top	0.15	0.3-0.5	0.1-0.2	0.1-0.3
"	"	"	Middle	0.4	1.0	0.4	1.5-1.8
"	"	"	Bottom	0.4-0.6	1.1-1.3	0.4-0.6	1.7-2.0
1.5	0.30	D-14	Top	0.1-0.[illegible]	1.3-1.5	0-0.1	1.8-2.2
"	"	"	Middle	0.2-0.3	1.4-1.6	0.1-0.3	1.8-2.0
"	"	"	Bottom	0-0.2	1.6-2.0	0-0.2	2.4-2.7
1.5	0.30	D-43	Top	0.15	0.3-0.5	0.1-0.2	0.1-0.3
"	"	"	Middle	0.4	1.0	0.4	1.5-1.8
"	"	"	Bottom	0.4-0.6	1.1-1.3	0.4-0.6	1.7-2.0
1.5	0.15	D-14	Top	0.1-0.2	1.3-1.5	0-0.1	1.8-2.2
"	"	"	Middle	0.2-0.3	1.4-1.6	0.1-0.3	1.8-2.0
"	"	"	Bottom	0-0.2	1.6-2.0	0-0.2	2.4-2.7
1.5	0.15	D-43	Top	0.1-0.2	0.5-0.6	0.2-0.4	1.0-1.2
"	"	"	Middle	0.3-0.5	0.8-1.0	0.4-0.6	1.0-1.2
"	"	"	Bottom	0.4-0.5	1.0-1.2	0.4-0.5	1.5-2.0

(1) All coatings applied using 50Cr-50Ti pack at 2300°F for 8 hours

(2) Specimen location in pack:



Top View of Retort



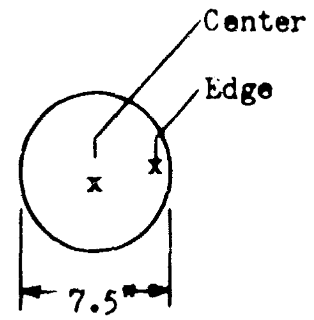
Side View of Retort

TABLE 9

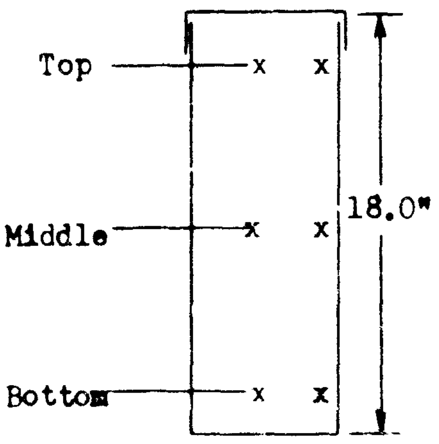
Metallographic Data from Cr-Ti Alloy Coatings Formed on D-14 and D-43 Alloys in the Pilot Scale Furnace

Processing Conditions(1)		Alloy	Cr-Ti-Alloy Coating Measurements for Various Pack Locations(2)				
				Pack Center		Pack Edge	
Pressure mm	w/o KF		Vertical Position	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils
10^{-2}	0.30	D-14	Top	0.2-0.3	0.6	0.2-0.4	0.8
"	"	"	Middle	0.4-0.5	0.6-0.8	0.3-0.5	1.0-1.2
"	"	"	Bottom	0.5-0.7	1.0-1.2	0.4-0.7	1.0-1.4
10^{-2}	0.30	D-43	Top	0.1-0.3	0.3	0.3-0.4	0.5
"	"	"	Middle	0.5-0.6	0.5	0.5-0.7	0.8-1.0
"	"	"	Bottom	0.7-0.8	0.8	0.7-0.9	1.0-1.2
1.5	0.30	D-14	Top	0.1-0.3	0.8-1.0	0.1-0.3	0.8-1.0
"	"	"	Middle	0.4-0.6	0.8-1.2	0.4-0.7	1.2-1.5
"	"	"	Bottom	0.4-0.7	1.0-1.4	0.4-0.7	1.6-1.8
1.5	0.30	D-43	Top	0.2-0.3	0.4-0.5	0.2-0.4	0.5-0.6
"	"	"	Middle	0.7-0.8	0.6-0.8	0.7-0.8	0.8-1.0
"	"	"	Bottom	0.9-1.0	0.8-1.0	0.8-1.0	1.0-1.1
1.5	0.15	D-14	Top	0.1-0.3	0.8-1.0	0.1-0.4	0.8-1.0
"	"	"	Middle	0.4-0.6	1.0-1.2	0.4-0.7	1.2-1.4
"	"	"	Bottom	0.5-0.8	1.0-1.3	0.4-0.9	1.8-2.0
1.5	0.15	D-43	Top	0.3-0.4	0.3-0.4	0.2-0.4	0.5-0.6
"	"	"	Middle	0.5-0.8	0.5-0.6	0.6-0.8	0.8-1.2
"	"	"	Bottom	0.9-1.0	0.8-1.0	0.9-1.0	1.0-1.2

(1) All Coatings applied using 60Cr-40Ti pack at 2300°F for 8 hours
(2) Specimen location in pack:



Top View of Retort



Side View of Retort

TABLE 10

Average Metallographic and Cyclic Oxidation Results from Cr-Ti Alloy Coating Optimization Study in Pilot Scale Furnace

Cr-Ti Coating Cycle Parameters(1)			Cr-Ti Coating				Cr-Ti-Si Coating(2)				Cyclic Oxidation Protective Life Hours					
Pack Comp.	Pressure mm	w/o KF	Overlay Mils		Diffusion Zone-Mils		Overlay Mils		Diffusion Zone-Mils		1800°F(3)		2500°F(4)		2700°F(4)	
			D-14	D-43	D-14	D-43	D-14	D-43	D-14	D-43	D-14	D-43	D-14	D-43	D-14	D-43
50Cr-50Ti	1.5	0.30	0.14	0.37	1.80	1.10	1.90	1.75	1.25	0.90	200* (4)	200* (0)	96	96	3	7
50Cr-50Ti	1.5	0.15	0.20	0.31	1.80	1.10	1.80	1.77	1.40	0.75	200* (3)	200* (0)	108	97	4	10
50Cr-50Ti	10-2	0.30	0.27	0.35	1.60	1.05	1.92	1.75	1.12	0.62	200* (1)	200* (0)	103	114	6	6
60Cr-40Ti	1.5	0.30	0.43	0.66	1.20	0.80	1.75	1.80	1.05	0.75	200* (1)	200* (0)	74	78	5	10
60Cr-40Ti	1.5	0.15	0.47	0.67	1.20	0.75	2.00	1.85	0.70	0.39	200* (0)	200* (0)	90	88	5	9
60Cr-40Ti	10-2	0.30	0.43	0.54	0.90	0.67	1.85	1.97	0.50	0.35	200* (0)	200* (0)	82	79	3	4

(1) All specimens coated in 8 hours at 2300°F
(2) All specimens silicon coated in 4 hours at 2050°F, 0.30 w/o KF, 10-2 mm pressure
* Denotes tests discontinued - no visible coating failure
(3) Number in parenthesis denotes number of specimens which failed in less than 200 hours. (A total of twelve (12) specimens are represented by each value)
(4) Average values represent the results of twelve (12) specimens

magnified, in relation to the change in pack composition, due to the higher vapor pressure of the titanium halides as compared to the chromium halides. This same result is also achieved by an increase in the system pressure. Vaporization of the more volatile titanium compounds suppresses vaporization of the chromium compounds. This, combined with the increased residence time of the vapor phase constituents which results from use of a higher pressure, produces an increase in the depth of titanium and chromium diffusion and a corresponding reduction in the Cr-Ti overlay thickness. This effect has been thoroughly investigated in previous development efforts. Observed changes in Cr-Ti coating morphology resulting from pack composition variation in the pilot scale furnace are comparable to changes observed in the laboratory scale furnace.

The decreased depth of titanium diffusion obtained with the D-43 alloy substrate is undoubtedly associated with the higher melting point of D-43 alloy. As the titanium content of columbium alloys is increased, both the rate of diffusion and solid solubility of chromium is increased. The rate of diffusion of titanium into D-14 alloy is greater than that into the higher melting D-43 alloy. Thus, a good deal of chromium is taken into solution during Cr-Ti coating D-14 alloy and a thin overlay layer results. The D-43 alloy, being titanium poor in comparison with D-14, builds up a heavier chromium rich overlay layer.

The coatings formed from a 50Cr-50Ti alloy pack exhibited an extremely non-uniform overlay layer thickness as compared to coatings deposited from a 60Cr-40Ti alloy pack. This probably results from localized differences in diffusion rates caused by compositional variations within the diffusion zone.

Cyclic oxidation tests at 1800, 2500 and 2700° F were used to comparatively evaluate the Cr-Ti coatings formed in the pilot scale furnace. All specimens were siliconized in 4 hours at 2050° F using 0.30 w/o KF activation and a system pressure of 10^{-2} mm. In order to avoid the additional variable of location of the coupons in the silicon pack, all specimens were placed near the center of the retort during the silicon cycle.

The oxidation protective life data obtained at these test temperatures is presented in Table 11. These data are also summarized and presented as average values in Table 10 for comparison with the metallographic data.

The most significant result of the cyclic oxidation tests at 1800° F was the occurrence of several premature failures associated with coatings produced from a 50Cr-50Ti alloy pack. All failures which occurred in less than 200 hours at 1800° F involved D-14 alloy. Of nine such failures, out of 144 specimens tested, all but one were associated with the 50Cr-50Ti pack composition. Failures of this type are felt to be associated with regions of high titanium concentration (produced by particle sticking) in which no chromium rich overlay layer was produced in the Cr-Ti cycle due to high localized chromium diffusion inward.

TABLE 11

Cyclic Oxidation Test Results for Cr-Ti Alloy Coating Optimization Study in Pilot Scale Furnace

Coating Conditions(1)				Cr-Ti-Si Cyclic Oxidation Protective Properties - Hours(3)					
				D-14 Alloy			D-43 Alloy		
Pack Comp.	Pressure mm	w/o KF	Pack(2) Position	1800°F(4)	2500°F	2700°F	1800°F(4)	2500°F	2700°F
60Cr-40Ti	10^{-2}	0.30	TC	200*,200*	31,48	1,1	200*,200*	48,54	1,2
			MC	200*,200*	72,72	2,3	200*,200*	31,48	4,4
			BC	200*,200*	94,94	4,4	200*,200*	118,150	1,7
			TE	200*,200*	54,72	2,3	200*,200*	48,72	3,6
			ME	200*,200*	72,102	2,4	200*,200*	72,72	4,7
			BE	200*,200*	126,147	2,4	200*,200*	72,166	5,8
60Cr-40Ti	1.5	0.30	TC	200*,200*	48,55	6,6	200*,200*	32,48	2,5
			MC	200*,200*	72,72	4,4	200*,200*	72,120	7,13
			BC	200*,200*	72,104	4,6	200*,200*	72,96	11,27
			TE	30,200*	55,72	2,3	200*,200*	48,55	5,6
			ME	200*,200*	72,96	6,16	200*,200*	80,96	5,14
			BE	200*.200*	72,96	3,5	200*,200*	96,120	9,15
60Cr-40Ti	1.5	0.15	TC	200*,200*	48,72	2,9	200*,200*	31,48	3,3
			MC	200*,200*	104,128	8,8	200*,200*	104,120	3,18
			BC	200*,200*	103,103	2,3	200*,200*	72,96	5,18
			TE	200*,200*	48,48	2,2	200*,200*	48,48	4,6
			ME	200*,200*	72,127	5,12	200*,200*	72,96	4,16
			BE	200*,200*	104,120	2,3	200*,200*	120,195	8,16

(1) All coatings applied in 8 hours at 2300°F
(2) First letter designates vertical position - T-top, M-middle, B-bottom
Second letter designates horizontal position - C-center, E-edge
(3) All specimens Si coated in 4 hours at 2050°F using 0.30 w/o KF and 10^{-2} mm pressure
(4) * Denotes test discontinued - no visible coating failure

TABLE 11 (Continued)

Cyclic Oxidation Test Results for Cr-Ti Alloy Coating
Optimization Study in Pilot Scale Furnace

Coating Conditions(1)				Cr-Ti-Si Cyclic Oxidation Protective Properties - Hours(3)					
				D-14 Alloy			D-43 Alloy		
Pack Comp.	Pressure mm	w/o KF	Pack(2) Position	1800°F(4)	2500°F	2700°F	1800°F(4)	2500°F	2700°F
50Cr-50Ti	10^{-2}	0.30	TC	200*,200*	48,72	5,27	200*,200*	30,48	3,8
			MC	200*,200*	76,96	7,8	200*,200*	72,72	4,21
			BC	200*,200*	120,144	1,2	200*,200*	144,144	1,8
			TE	200*,200*	76,96	2,2	200*,200*	72,120	5,6
			ME	6,200*	120,127	3,3	200*,200*	150,168	3,6
			BE	200*,200*	120,144	4,5	200*,200*	120,222	2,9
50Cr-50Ti	1.5	0.30	TC	200*,200*	72,88	3,3	200*,200*	56,56	8,10
			MC	200*,200*	76,96	2,3	200*,200*	96,104	9,21
			BC	200*,200*	72,120	2,2	200*,200*	72,104	3,14
			TE	4,200*	72,96	5,5	200*,200*	48,72	3,4
			ME	6,200*	144,150	4,4	200*,200*	144,152	4,6
			BE	6,6	56,73	2,2	200*,200*	96,150	3,3
50Cr-50Ti	1.5	0.15	TC	200*,200*	96,120	2,6	200*,200*	72,72	6,19
			MC	200*,200*	72,96	2,2	200*,200*	72,120	9,9
			BC	200*,200*	72,120	4,6	200*,200*	96,120	11,23
			TE	6,200*	72,144	2,6	200*,200*	72,72	6,8
			ME	6,144	144,144	4,7	200*,200*	72,144	5,9
			BE	200*,200*	96,120	4,5	200*,200*	127,144	3,4

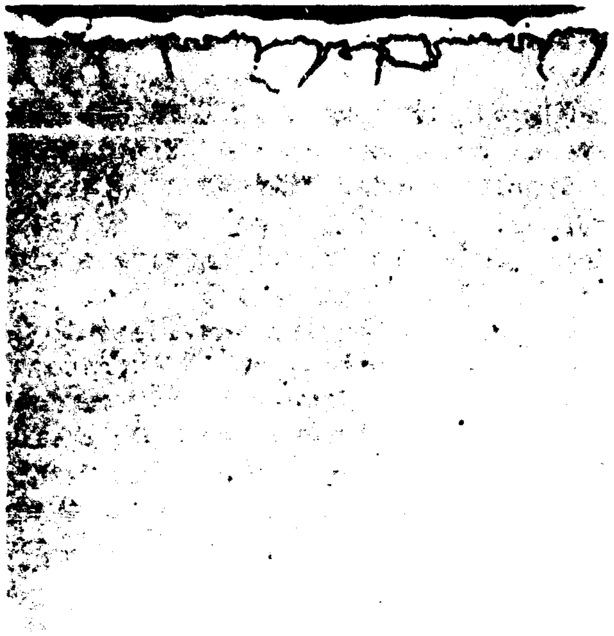
(1) All coatings applied in 8 hours at 2300°F
(2) First letter designates vertical position - T-top, M-middle, B-bottom
Second letter designates horizontal position - C-center, E-edge
(3) All specimens Si coated in 4 hours at 2050°F using 0.30 w/o KF and 10^{-2} mm pressure
(4) * Denotes test discontinued - no visible coating failure

Cyclic oxidation protective life at 2500°F for Cr-Ti coatings produced by a given set of parameters appeared to be directly associated with the thickness of the chromium rich overlay layer formed during the Cr-Ti coating cycle. Greater life was obtained from specimens Cr-Ti coated in the lower regions of the retort. At a given retort level, the coupons placed near the retort wall evidenced greater protective life (increasing coating overlay thickness followed the same pattern). The variation in the 2500°F oxidation protective life associated with the different sets of processing parameters also appears to be related to the thickness of the coatings produced. However, in this instance, it is the thickness ratio or the actual thickness of both the retained titanium enriched diffusion zone and the Cr-Ti-Si alloy overlay (after siliconizing) which controls the life at higher temperatures. Obviously, the thickness of the diffusion zone and the chromium rich overlay produced during the Cr-Ti coating cycle influence the morphology and composition of the Cr-Ti-Si coating. Thus, it appears that the observed requirements for the Cr-Ti coating to provide both low and high temperature protection, discussed for the laboratory scale furnace also apply to the pilot scale furnace. In this furnace, however, these requirements are best achieved utilizing a 60Cr-40Ti pack, coating for 8 hours at 2300°F under a system pressure of 10^{-2} mm (continuous mechanical pump evacuation) with 0.30 w/o KF activation. The Cr-Ti coating formed under these process conditions is shown in Figure 16 for comparison with the Cr-Ti coatings formed in the smaller furnace.

Protective life at 2700°F appears to be associated with both the thickness of the chromium rich overlay layer and the titanium rich diffusion zone formed in the Cr-Ti coating cycle. Both an adequate chromium rich overlay layer and a reasonably thick diffusion zone are required for adequate life at 2700°F. However, the mechanism of failure at 270C°F suggests that the melting point of the various layers of the Cr-Ti-Si coating may control the protective life at this temperature. Figure 17 shows the structure of a coated specimen after 6 hours exposure at 2700°F. The presence of the eutectic phase between the Cr-Ti-Si overlay and the titanium enriched diffusion zone supplies proof that a liquid phase developed with time during exposure at 2700°F. It is felt that vaporization of chromium during exposure at 2700°F produced a decrease in the melting point of the chromium depleted region and was responsible for the formation of the molten phase. A low melting eutectic of titanium and silicon (melting point approximately 2450°F) occurs at a composition containing 8.5 w/o silicon. Apparently, this composition was reached at some point in the exposure cycle and ultimately caused failure. Thus, the protective life at this temperature is as much a result of coating composition as it is a result of coating thickness. Adjustments in the composition of the Cr-Ti-Si coating, aimed at higher chromium contents, may effect greater life at temperatures on the order of 2700°F with some sacrifice of low temperature protective capability.

5.2.2 Silicon Coating Cycle

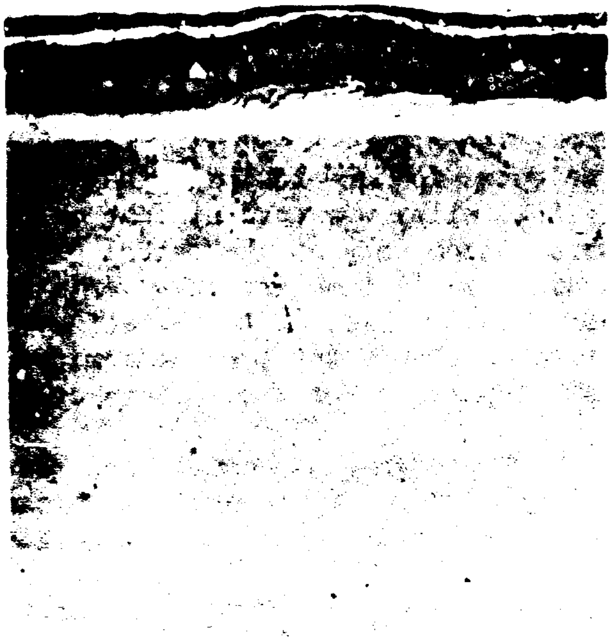
The silicon coating cycle was investigated in the pilot scale furnace in much the same manner as in the case of the laboratory scale furnace. Prior coating experience with this size furnace tentatively established acceptable



Cr-Ti Coated D-14 Alloy

Figure 16 Cr-Ti Alloy Coating Formed in Pilot Scale Furnace - 60Cr-40Ti Alloy Pack - 8 Hours at 2300°F - 10^{-2} mm 250X

Specimen Edge



Specimen Surface

Figure 17 Cr-Ti-Si Coated D-14 Alloy Exposed at 2700°F (One Atmosphere) Showing Eutectic Formation 100X silicon coating parameters as 4 hours at 2050°F with 0.30 w/o KF activation and a pressure of 10^{-2} mm. Based on these parameters and the results of studies conducted in the 3 inch diameter retort, the following silicon coating variables were investigated:

a) temperature - 1900-2150°F

b) heat-up rate - (use of intermediate hold at low temperature)

c) time - 4 and 8 hours

d) furnace pressure - 10^{-2} and 1.5 mm

e) quantity and type of activator (0.30 to 0.60 w/o using both KF and NaF)

As in the optimization study for the Cr-Ti coating cycle in the 7-1/2 inch retort, six pack positions were investigated. Three Cr-Ti coated columbium alloy substrate materials were evaluated: B-66, D-43 and D-14. All specimens in the initial phase of this study were Cr-Ti coated in a single coating run using a 50Cr-50Ti alloy pack, 8 hours coating time at 2300°F under 10^{-2} mm pressure. A comparison was then conducted as to the effect of an adjustment in Cr-Ti coating parameters utilizing a 60Cr-40Ti alloy pack. Evaluation of the Cr-Ti-Si coatings produced in this study involved both metallographic examination and cyclic oxidation tests at 1800, 2500 and 2700°F. Table 12 lists the metallographic results regarding coating thickness, Table 13 is a tabulation of the oxidation test results; and Table 14 is a summary of the average values of these test results.

The three alloys selected for use in this study were not distributed equally throughout the retort. D-14 alloy was used at four of the six pack positions, but D-43 and B-66 alloys were placed only at the retort "middle-center" position. It was felt that the D-14 alloy would then indicate variations within the pack and that a direct comparison could be made as to the effect of substrate composition. Total variation in coating thickness had been determined for the Cr-Ti cycle and thus provided a basis of comparison for the silicon cycle.

The variations in the processing parameters for the silicon coating cycle did not produce a sufficient spread in the coating thickness to effectively ascertain the effect of thickness on oxidation protective life.

A general trend in the coating thickness variation within the retort was observed to coincide with the variation found in the Cr-Ti coating cycle: the bottom retort position produced heavier coatings than the top and the edge position produced heavier coatings than the retort center.

An attempt to produce a heavier build up of the Cr-Ti-Si outer layer without causing a greater inward diffusion of silicon was unsuccessful, resulting in the subsequent loss of the titanium enriched diffusion zone and associated intermetallic compound. This was attempted by holding the retort at various intermediate tempera-

TABLE 12

Cr-Ti-Si Thickness Measurements for Silicon Cycle Optimization Study in Pilot Scale Furnace

Cr-Ti(1) Pack Comp.	Silicon Coating Conditions	Pack(2) Location	Cr-Ti-Si Coating Measurements					
			D-14 Alloy		B-66 Alloy		D-43 Alloy	
			Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils
50Cr-50Ti	4 Hrs.	TC	1.9-2.0	1.8-2.0	-	-	0.4-0.6	1.8-2.0
	2050°F	MC	0.6-0.8	1.9-2.0	-	-	0.4-0.6	1.8-2.0
	0.30 w/o KF	BC	1.1-1.3	2.0-2.1	-	-	0.8-1.0	1.8-2.0
	10^{-2} mm	TE	0.7-1.0	2.3-2.5	-	-	0.5-0.8	2.0-2.3
		ME	1.0-1.2	2.0-2.3	-	-	0.8-1.2	1.7-1.8
		BE	1.0-1.4	2.1-2.3	-	-	0.8-1.0	2.0-2.3
50Cr-50Ti	4 Hrs.	TC	0.6-0.8	1.5-2.0	-	-	-	-
	2150°F	MC	0.8-1.0	1.5-2.0	0.6-0.8	1.5-2.0	0.5-0.8	1.6-2.0
	0.30 w/o KF	BC	1.0-1.2	1.8-2.0	-	-	-	-
	10^{-2} mm	ME	0.5-0.8	2.3-2.5	-	-	-	-
50Cr-50Ti	8 Hrs.	TC	1.0-1.2	1.7-2.0	-	-	-	-
	2050°F	MC	0.8-1.0	1.9-2.1	0.4-0.7	1.8-2.0	0.5-0.7	1.9-2.0
	0.30 w/o KF	BC	0.7-1.0	2.0-2.1	-	-	-	-
	10^{-2} mm	ME	0.5-0.7	2.4-2.6	-	-	-	-
50Cr-50Ti	4 Hrs.	TC	0.9-1.1	1.5-1.7	-	-	-	-
	2050°F	MC	1.0-1.1	1.5-1.8	0.7-1.0	1.5-1.7	0.6-0.8	1.6-1.8
	0.60 w/o KF	BC	0.6-1.0	1.8-2.0	-	-	-	-
	10^{-2} mm	ME	0.5-1.0	2.3-2.5	-	-	-	-
50Cr-50Ti	1 Hr. 1600+	TC	0.5-0.8	2.1-2.3	-	-	-	-
	4 Hrs. 2150°F	MC	0.7-1.0	2.2-2.5	0.5-0.7	2.2-2.5	0.4-0.6	2.3-2.5
	0.42 w/o NaF	BC	0.5-0.8	2.4-2.7	-	-	-	-
	+ 0.12 w/o KF 10^{-2} mm	ME	0.5-0.7	2.9-3.4	-	-	-	-

(1) All Cr-Ti coatings applied in 8 hours at 2300°F

(2) First letter denotes vertical pack position - T-top, M-middle, B-botton
Second letter denotes horizontal pack position - C-center, E-edge

TABLE 12 (Continued)

Cr-Ti-Si Thickness Measurements for Silicon Cycle Optimization Study in Pilot Scale Furnace

			Cr-Ti-Si Coating Measurements					
			D-14 Alloy		B-66 Alloy		D-43 Alloy	
Cr-Ti(1) Pack Comp.	Silicon Coating Conditions	Pack(2) Location	Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils	Diffusion Zone Depth Mils	Overlay Thickness Mils
50Cr-50Ti	4 Hrs. 2050°F 0.30 w/o KF 1.5 mm	TC	0.6-1.0	1.9-2.0	-	-	-	-
		MC	0.6-0.8	1.8-2.0	0.9-1.1	1.9-2.1	0.5-0.7	1.8-2.0
		BC	0.5-0.8	2.4-2.7	-	-	-	-
		ME	0.4-0.8	2.5-2.8	-	-	-	-
50Cr-50Ti	2 Hrs. 1900+ 2 Hrs. 2150°F 0.30 w/o NaF+ 0.15 w/o KF 10^{-2} mm	TC	0.8-1.0	1.9-2.1	-	-	-	-
		MC	0.9-1.1	2.0-2.2	0.9-1.1	1.9-2.2	0.6-1.0	1.9-2.1
		BC	0.7-1.0	2.3-2.5	-	-	-	-
		ME	0.2-0.5	2.9-3.2	-	-	-	-
60Cr-40Ti	2 Hrs. 1900+ 2 Hrs. 2150°F 0.30 w/o NaF+ 0.15 w/o KF 10^{-2} mm	TC	0.2-0.5	2.0-2.2	0-0.1	2.0-2.2	0.2	1.8-2.0
		MC	0-0.1	2.5-3.0	0-0.1	2.8-3.0	0-0.3	2.8-3.0
		ME	0.2-0.4	1.8-2.2	0-0.2	2.3-2.5	0.2-0.4	2.2-2.5
60Cr-40Ti	4 Hrs. 2050°F 0.30 w/o KF 10^{-2} mm	TC	0.1	1.9-2.1	-	-	0.1	1.7-2.0
		ME	0.9-1.0	1.5-1.9	-	-	0.4-1.0	1.9-2.1

(1) All Cr-Ti coatings applied in 8 hours at 2300°F

(2) First letter denotes vertical pack position - T-top, M-middle, B-bottom
Second letter denotes horizontal pack position - C-center, E-edge

TABLE 13

Cyclic Oxidation Protective Life for Silicon Cycle Optimization
Study in Pilot Scale Furnace

Cr-Ti(1) Pack Comp.	Silicon Coating Conditions	Pack(2) Location	Cyclic Oxidation Protective Life - Hours(3)								
			D-14 Alloy			B-66 Alloy			D-43 Alloy		
			1800°F	2500°F	2700°F	1800°F	2500°F	2700°F	1800°F	2500°F	2700°F
50Cr-50Ti	4 Hrs.	TC	200,200	102					200,200	72	
	2050°F	MC	200,200	94					200,200	119	
	0.30 v/o KF	BC	200,200	78					200,200	118	
	10-2 mm	TE	200,200	118					200,200	78	
		ME	200,200	102					200,200	48	
		BE	200,200	7					200,200	78	
50Cr-50Ti	4 Hrs.	TC	200,200,200	48,56,56	6,7,7	200,200,200	24,72,96	3,4,6	200,200,200	31,72,72	5,6,6
	2150°F	MC	200,200,200	56,56,72	3,3,4						
	0.30 v/o KF	BC	24,48,200	56,56,56	2,2,4						
	10-2 mm	ME	200,200,200	48,72,80	7,7,7						
50Cr-50Ti	8 Hrs.	TC	29,29,200	72,72,80	4,5,5	200,200,200	48,48,144	2,3,3	200,200,200	48,48,48	4,13,14
	2050°F	MC	8,8,24	72,72,80	4,4,4						
	0.30 v/o KF	BC	6,6,24	96,96,96	2,2,2						
	10-2 mm	ME	200,200,200	72,72,80	2,2,2						
50Cr-50Ti	4 Hrs.	TC	6,200,200	31,48,56	1,2,2	200,200,200	29,29,31	2,3,7	200,200,200	31,31,48	6,11,11
	2050°F	MC	24,200,200	48,72,72	2,2,3						
	0.60 v/o KF	BC	200,200,200	48,48,56	2,3						
	10-2 mm	ME	200,200,200	48,56,72	20,24,34						
50Cr-50Ti	1 Hr. 1600 +	TC	80,200,200	31,31,48	3,7,8	200,200,200	96,104,104	4,7,10	200,200,200	48,55,55	8,10,11
	4 Hrs. 2150°F	MC	200,200,200	30,48,48	6,7,14						
	0.42 v/o NaF +	BC	6,200,200	72,80,96	5,7,15						
	0.12 v/o KF	ME	72,200,200	72,72,72	2,4,23						
	10-2 mm										

(1) All Cr-Ti coatings applied in 8 hours at 2300°F
(2) First letter denotes vertical pack position - T-top, M-middle, B-bottom, second letter denotes horizontal position, C-center, E-edge
(3) All test results designated as 200 were discontinued at 200 hours - no visible coating failure

TABLE 13 (Continued)

Cyclic Oxidation Protective Life for Silicon Cycle Optimization Study in Pilot Scale Furnace

Cr-Ti(1) Pack Comp.	Silicon Coating Conditions	Pack(2) Location	Cyclic Oxidation Protective Life - Hours(3)								
			D-14 Alloy			B-66 Alloy			D-43 Alloy		
			1800°F	2500°F	2700°F	1800°F	2500°F	2700°F	1800°F	2500°F	2700°F
50Cr-50Ti	4 Hrs 2050°F 0.30 v/o KF 1.5 mm	TC	200,200,200	22,56,80	3,4,5	200,200,200	32,56,80	8,11,11	200,200,200	56,72,96	8,9,21
		MC	8,8,24	56,56,56	2,5						
		BC	200,200,200	56,72,72	8,11,17						
		ME	168,200,200	72,72,96	3,6,21						
50Cr-50Ti	2 Hrs. 1900+ 2 Hrs, 2150°F 0.30 v/o NaF + 0.15 v/o KF 10^{-2} mm	TC	24,200,200	56,104,168	2,2,4	200,200,200	72,80,96	3,4,9	200,200,200	56,72,192	9,13,14
		MC	200,200,200	56,72,72	2,3,7						
		BC	6,200,200	56,56,72	2,2,3						
		ME	200,300,200	80,96,96	3,6,12						
60Cr-40Ti	2 Hrs. 1900 + 2 Hrs. 2150°F 0.30 v/o NaF + 0.15 v/o KF 10^{-2} mm	TC	26,45,200	69,75,75	4,10,20	200,200,200	29,45,50	8,10	200,200,200	69,69,77	3,10,10
		MC	45,50,52	73,93,93	8,13	200,200	50,50,69	6	200,200,200	117,117,117	8,10
		ME	24,24,24	93,93,117	8,9,14	200,200,200	69,69,93	9,14	200,200,200	77,118,141	10,19,19
60Cr-40Ti	4 Hrs. 2050°F 0.30 v/o KF 10^{-2} mm	TC	200,200	31,48	1,1				200,200	48,54	1,2
		MC	200,200	72,72	2,3				200,200	31,48	4,4
		BC	200,200	94,94	4,4				200,200	118,150	1,7
		TE	200,200	52,72	2,3				200,200	48,72	3,6
		ME	200,200	72,102	2,4				200,200	72,72	4,7
		BE	200,200	126,147	2,4				200,200	72,166	5,8

(1) All Cr-Ti coatings applied in 8 hours at 2300°F
(2) First letter denotes vertical pack position - T-top, M-middle, B-bottom, second letter denotes horizontal position, C-center, E-edge
(3) All test results designated as 200 were discontinued at 200 hours - no visible coating failure

TABLE 14

Summary of Average Metallographic and Cyclic Oxidation Test Results for Silicon Cycle Optimization Study in Pilot Scale Furnace

Cr-Ti(1) Pack Comp.	Silicon Coating Conditions				Cr-Ti-Si Coating Thickness-Avg.(D-14)		Average Cyclic Oxidation Protective Life Hours(2)								
	Time Hours	Temp. °F	Pres. mm	w/o Activator	Overlay Thickness Mils	Diffusion Zone Depth Mils	1800°F(3) D-14	1800°F(3) B-66	1800°F(3) D-43	2500°F D-14	2500°F B-66	2500°F D-43	2700°F D-14	2700°F B-66	2700°F D-43
50Cr-50Ti	4	2050	10^{-2}	0.60 KF	1.90	0.90	200* (3)	200*	200*	55	30	37	9	4	9
50Cr-50Ti	4	2150	10^{-2}	0.30 KF	1.95	0.84	200* (2)	200*	200*	59	64	58	5	4	6
50Cr-50Ti	8	2050	10^{-2}	0.30 KF	2.10	0.86	200* (8)	200*	200*	80	80	48	3	3	10
50Cr-50Ti	4	2050	1.5	0.30 KF	2.30	0.69	200* (4)	200*	200*	64	56	75	9	10	13
50Cr-50Ti	1 4	1600 2150	10^{-2}	(0.42 NaF 0.12 KF)	2.60	0.70	200* (3)	200*	200*	58	101	53	8	7	10
50Cr-50Ti	4	2050	10^{-2}	0.30 KF	2.10	1.20	200* (0)	-	200*	84	-	86	-	-	-
50Cr-50Ti	2 2	1900 2150	10^{-2}	(0.30 NaF 0.15 KF)	2.40	0.80	200* (2)	200*	200*	82	83	106	4	5	12
60Cr-40Ti	2 2	1900 2150	10^{-2}	(0.30 NaF 0.15 KF)	2.30	0.30	200* (8)	200*	200*	87	112	57	11	9	11
60Cr-40Ti	4	2050	10^{-2}	0.30 KF	1.90	0.40	200* (0)		200*	82	-	79	-	-	-

(1) All Cr-Ti coatings applied in 8 hours at 2300°F
(2) Averages represent 12 values for D-14 alloy and 3 each for B-66 and D-43 alloy
(3) Number in parenthesis denotes number of tests which failed in less than 200 hours
* Denotes tests discontinued - no visible coating failure

tures (1600 and 1900°F) for 1-2 hours and then raising the temperature to the prescribed coating temperature. Variations in activator type and quantity were also included in this investigation.

The minor variation in Cr-Ti-Si coating thickness which resulted from the use of various process conditions correlated with time and temperature parameters. In general, increased coating time or temperature effected some increase in coating thickness. However, the magnitude of the thickness variation was less than observed in the smaller furnace for comparable ranges of time and temperature.

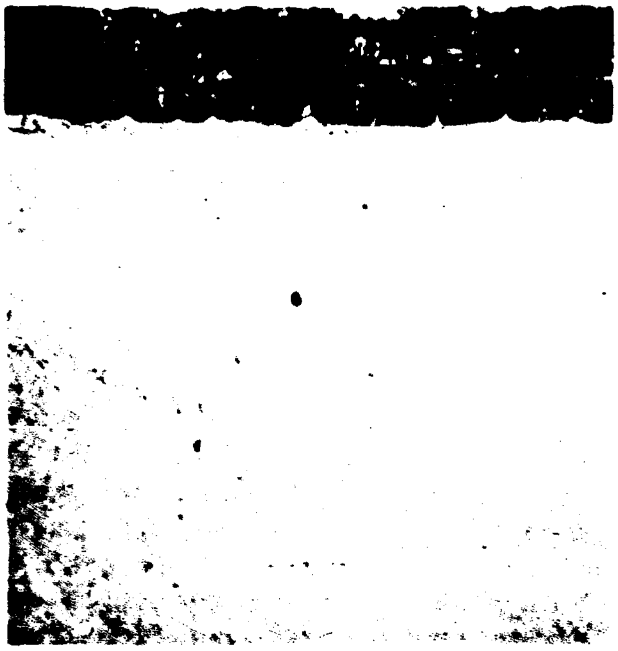
The majority of the coatings produced in this study afforded greater than 200 hours protection at 1800°F. However, a number of premature failures (less than 200 hours protection) were encountered at 1800°F with D-14 alloy. These are believed to be associated with regions in which little or no Cr-Ti alloy overlay layer was formed during the Cr-Ti deposition cycle. As discussed in Section 5.2.1, Cr-Ti coatings formed in a 50Cr-50Ti alloy pack contain small areas in which the overlay is very thin or non-existant. All premature failures occurred on Cr-Ti-Si coated specimens which had been Cr-Ti coated in a 50Cr-50Ti alloy pack. Those coatings formed on specimens Cr-Ti coated in a 60Cr-40Ti alloy pack (continuous Cr-Ti alloy overlay layer) were in all cases protective for in excess of 200 hours. Figure 18 depicts the Cr-Ti-Si coating formed on specimens Cr-Ti coated in a 60Cr-40Ti alloy pack.

At 2500°F the oxidation protective life was, in general, increased with increasing coating thickness, corresponding to results obtained in the laboratory scale furnace. Protective life did not vary widely with substrate alloy composition.

Both 1800 and 2500°F protective life follow the same trend with respect to thickness as previously determined for the studies conducted in the laboratory scale furnace.

No concise explanation of the relation of the 2700°F life to coating thickness can be given in view of the rather small differences in coating thickness. However, the mechanism of failure in this case was the same as observed during the Cr-Ti coating investigation and the apparent correlation with melting point of the various coating layers would still apply.

Based on these studies, acceptable coatings can be applied under a rather wide range of process parameters. For an acceptable Cr-Ti coating an excellent balance between low and high temperature Cr-Ti coating life can be achieved using a silicon deposition cycle of 4 hours at 2050°F, 0.30 v/o KF and a system pressure of 10^{-2} mm. However, where variations in the thickness of the Cr-Ti-Si coatings are required, or where protective life at a particular temperature is to be emphasized, adjustments in either time or temperature should be made to adjust thickness and coating composition. Adjustments in the Cr-Ti alloy pack composition may also be necessary to achieve optimum life at a particular temperature.



Cr-Ti-Si Coated D-14 Alloy

Figure 18 Cr-Ti-Si Alloy Coating Formed in Pilot Scale Furnace - Silicon Cycle - 4 Hours at 2050°F - 10^{-2} mm 250X

5.3 Coating Studies in the Resistance Heated Bell Furnace

The objective of this portion of the program was to pinpoint the problem areas associated with the application of the Cr-Ti-Si coating to columbium alloys in a relatively large furnace.

Figure 19 depicts the large resistance heated bell furnace with the water cooled shell in place. The electrodes consist of water cooled copper pipe fed by a 75 KW D.C. power supply. Molybdenum hairpins are used as heating elements and are pinned to the alumina brick insulation along each of the long walls. The free space within the furnace is approximately 25" long, 13" wide, and 36" high. The columbium retort currently used in this furnace is 24" long, 8" wide, and 24" high.

D-14 (Cb-5Zr) coupons (1/2" x 1/2" x 0.040") served as the test samples for this study. The principal aim of the initial work was to determine the effect of sample location within the retort on coating buildup. Past experience had shown that irregular Cr-Ti coatings were produced on the substrate surface adjacent to and facing the retort wall. It was found that this condition could be improved by the insertion of a shield between the work and the wall. Therefore, this practice was employed for this series of Cr-Ti coating runs resulting in the utilization of a total of eighteen key positions within the retort. Figure 20 is a schematic showing the key to sample location. Five coupons were placed at each of the eighteen positions. Those containing the letter "S" in their identification were adjacent to the retort wall which had a columbium sheet interposed between the coupons and the wall. The letter "E" identifies those samples adjacent to the unshielded retort wall, "C" refers to centrally located samples, "T" refers to top layer specimens, "M" refers to middle layer coupons, and "B" refers to those samples located near the bottom of the retort. In all cases the 1/2" x 1/2" sample dimension was placed parallel to the 24" x 24" dimension of the retort.

Since both sodium and potassium vapor, formed as a result of reaction of the activator with the pack material, have a corrosive effect on the brick insulation, it is desirable to determine the minimum amount of activator necessary to produce a satisfactory coating. Therefore, one of the variables chosen for study was the amount of halide activator. The location of activator within the pack also varied.

Six initial coating runs were made, four using a -8+30 mesh, 60Cr-40Ti alloy pack and two using a -8+30 mesh, silicon pack. The rate of heating in each case was adjusted to approximately 10°F per minute. An equilibrium temperature of 2350°F measured at the midpoint of the retort surface was chosen for the Cr-Ti runs and 2100°F for the silicon runs. The time at temperature for each Cr-Ti run was 9 hours and for each silicon run it was 4 hours.

The following are a tabulation of the runs performed:

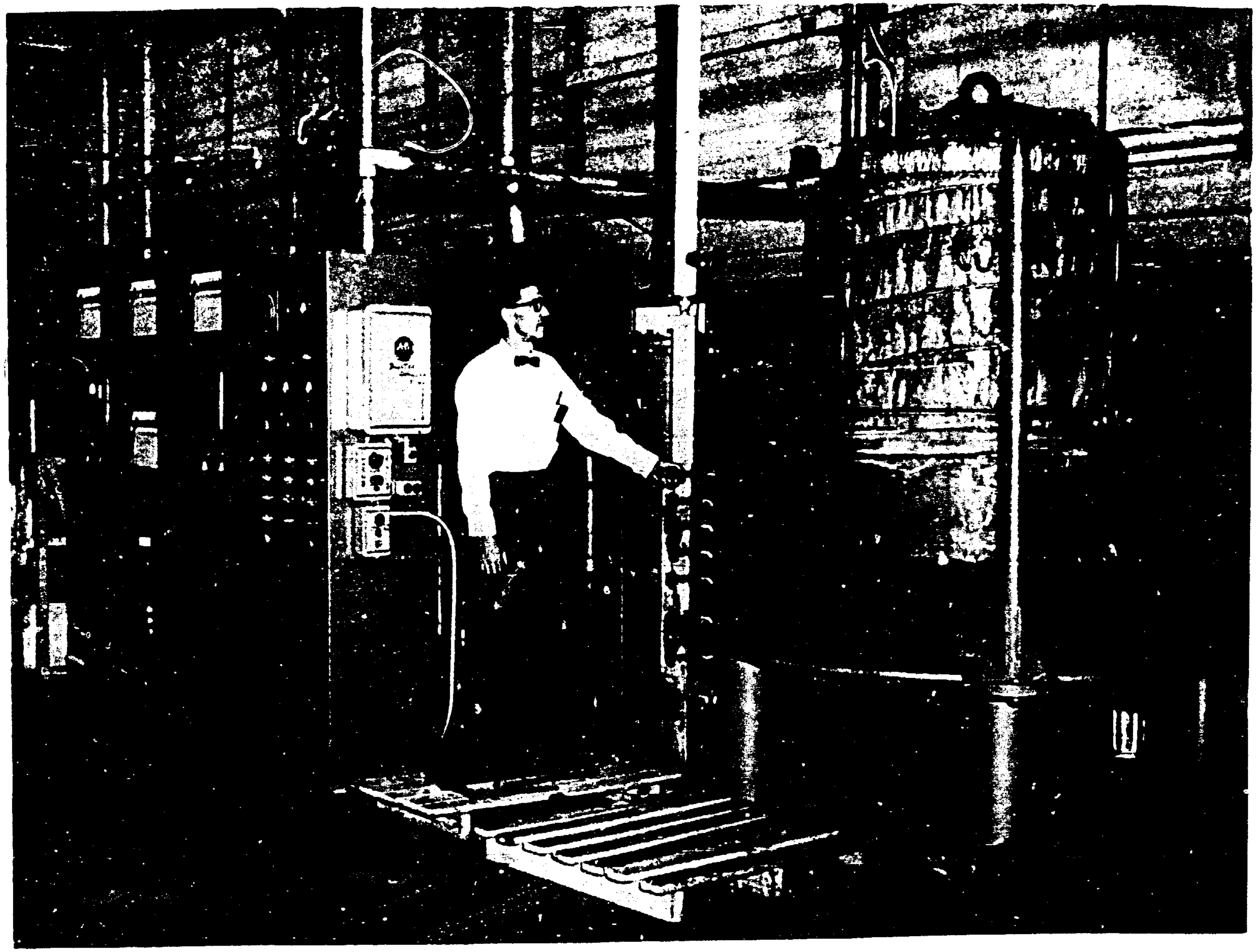


Figure 19 Resistance Element Heated Bell Furnace and Pack Retort

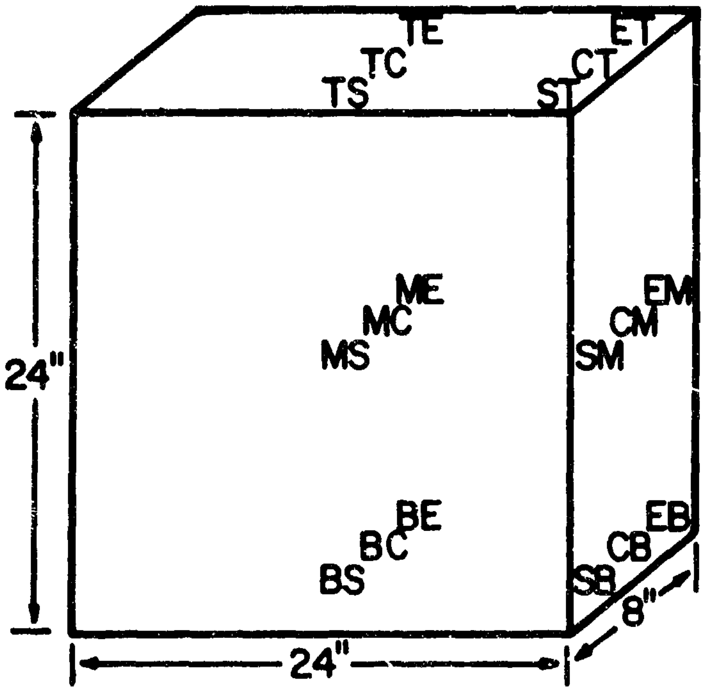


Figure 20 Key to Sample Identification in Retort

Run No. 1 - A Cr-Ti pack was employed with 300 grams (0.16 w/o pack) of NaF activator mixed throughout

Run No. 2 - A Cr-Ti pack was employed with 200 grams (0.11 w/o pack) of NaF mixed throughout

Run No. 3 - A Cr-Ti pack was employed with 100 grams (0.05 w/o pack) of NaF mixed throughout

Run No. 4 - A Cr-Ti pack again was used with 100 grams NaF placed in the bottom center of the pack and 100 grams of NaF placed in the top center of the pack

Run No. 5 - A silicon pack was used with 200 grams (0.4 w/o pack) of KF placed in the top center of the pack

Run No. 6 - A silicon pack was used with 200 grams of NaF placed in the top center of the pack

Table 15 lists the results obtained from the first four (Cr-Ti) runs. Tabulated are the average overlay thicknesses, average diffusion zone thicknesses, and the ratio of outside to inside face overlay thickness for samples at each of the key positions. The diffusion zone thicknesses were relatively uniform from side to side and were not tabulated. The heaviest average overlay thickness was obtained for Run No. 4 in which the 200 grams of NaF were equally divided between the top center and bottom center portions of the pack. This, however, resulted in the thinnest average diffusion zone thickness. The thinnest average overlay thickness was derived from Run No. 3 in which only 100 grams of NaF was employed. There was considerable scatter from run to run with regard to the ratio of side to side overlay thickness. In all cases the heaviest overlay was obtained on the sample surface which faced the nearest retort wall. As was expected, those samples located in the vertical center of the pack showed the least variation in side to side overlay thickness.

Table 16 shows the average overlay and diffusion zone thicknesses for selected groups of samples for Runs 1-4. Each group of six samples lie in a common plane. For instance, the first six samples listed all have a "T" in their identification guide and were all located at the top of the pack. The next group of six samples all contain the letter "M" and were located in the horizontal middle of of the pack, etc. An orderly comparison of the first three groups of samples shows, in all cases, an increase in overlay thickness from the top to the bottom of the pack. This relationship was also true for the average diffusion zone thickness, with the exception of Run No. 4 which showed a minimum thickness for the group of samples located in the middle of the pack. It should be noted at this point that no activator was located in the middle of the pack for Run No. 4.

The next three groups of samples (Table 16) represent specimen locations on vertical sections through the retort, all parallel to the 24" x 24" retort dimension. The average overlay thickness for the centrally located samples in all runs was far

TABLE 15

Cr-Ti Coating Thickness Observed on Samples from Runs 1-4

	Average Overlay Thickness (Mils)				Average Diffusion Zone Thickness (Mils)				Ratio of Side to Side Overlay Thickness			
Position	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
BE	0.45	0.50	0.37	0.52	0.70	0.70	0.60	0.75	1.0	1.5	2.0	3.2
BC	0.17	0.25	0.12	0.25	0.80	0.55	0.77	0.57	2.5	1.1	1.0	1.0
BS	0.50	0.45	0.40	0.50	0.62	0.70	0.57	0.67	1.0	1.2	1.7	2.3
TE	0.38	0.22	0.32	0.45	0.45	0.52	0.45	0.67	2.0	1.0	1.6	3.5
TC	0.06	0.07	0.04	0.11	0.25	0.25	0.25	0.25	1.0	1.0	1.0	1.2
TS	0.30	0.32	0.17	0.24	0.40	0.40	0.40	0.45	1.0	1.6	2.5	3.0
ME	0.67	0.37	0.37	0.37	0.62	0.72	0.57	0.50	3.5	2.0	2.0	2.0
MC	0.07	0.12	0.05	0.12	0.35	0.33	0.25	0.25	1.1	1.0	1.0	1.0
MS	0.25	0.50	0.25	0.42	0.77	0.65	0.50	0.37	1.0	3.0	1.7	2.4
EB	0.30	0.40	0.32	0.65	1.10	0.62	0.75	0.60	2.0	1.7	2.1	1.4
CB	0.19	0.27	0.19	0.20	0.95	0.80	0.82	0.75	2.0	1.2	2.0	1.0
SB	0.30	0.37	0.38	0.50	0.65	0.97	0.70	0.67	1.0	2.0	1.0	1.0
ET	0.25	0.28	0.25	0.44	0.70	0.40	0.60	0.45	1.0	1.2	1.0	1.3
CT	0.06	0.06	0.06	0.06	0.45	0.50	0.60	0.50	1.0	1.6	1.0	1.1
ST	0.22	0.25	0.32	0.30	0.32	0.30	0.35	0.30	2.2	1.0	2.2	1.4
EM	0.45	0.39	0.28	0.54	0.50	0.60	0.50	0.55	2.0	1.0	1.2	1.9
CM	0.10	0.12	0.08	0.20	0.60	0.65	0.75	0.35	1.0	1.0	1.7	1.0
SM	0.17	0.37	0.37	0.45	0.95	0.67	0.60	0.47	3.0	2.0	2.0	2.0
Ave.	0.28	0.30	0.24	0.35	0.61	0.58	0.58	0.51				

TABLE 16

Average Cr-Ti Coating Thicknesses of Selected Groups of Samples

Sample Group	Average Overlay Thickness (Mils)				Average Diffusion Zone Thickness (Mils)			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
TE, ET, TC CT, TS, ST	0.21	0.20	0.19	0.27	0.42	0.40	0.44	0.44
ME, EM, MC CM, MS, SM	0.28	0.31	0.23	0.35	0.63	0.60	0.53	0.42
BE, EB, BC CB, BS, SB	0.32	0.38	0.30	0.44	0.88	0.72	0.70	0.67
TS, ST, MS SM, BS, SB	0.29	0.38	0.32	0.40	0.62	0.62	0.52	0.49
TC, CT, MC CM, BC, CB	0.11	0.15	0.07	0.16	0.58	0.51	0.57	0.45
TE, ET, ME EM, BE, EB	0.42	0.36	0.32	0.50	0.67	0.59	0.59	0.59

less than that obtained for samples located near the retort walls. In general, those samples which had the columbium sheet interposed between them and the retort wall had both a thinner overlay and diffusion zone than those samples located at the opposite unshielded wall. The only exception was Run No. 2 in which essentially similar results were obtained for both the "S" and "E" samples.

Table 17 shows the Cr-Ti-Si coating thicknesses obtained for silicon coating Runs No. 5 and 6. The samples had been previously Cr-Ti coated in Runs 1-4. Since no columbium barrier sheet was utilized in these runs only twelve key positions were evaluated. As noted previously, KF activation was utilized in Run No. 5 and NaF in Run No. 6. In general, the results were essentially the same for the two runs although very little of the NaF activator sublimed in Run No. 6.

Table 18 shows the average Cr-Ti-Si coating thicknesses obtained in Runs No. 5 and 6 for selected sample groups. In comparing the first three groups listed, or proceeding from the top to bottom of the pack, it can be seen that the least amount of coating was obtained on those samples at the pack bottom. The activator in both of these runs was placed only at the top of the pack. Those samples located adjacent to the retort wall had the heaviest coating build up and those in the vertical center of the pack had the least thickness of coating.

It is known that there is approximately a 100°F temperature increase from top to bottom of the pack, as indicated by thermocouples located externally to the pack. The fact that the Cr-Ti overlay thicknesses increased in the same direction indicates the influence of temperature on overlay thickness. The fact that centrally located ("C") samples for both the Cr-Ti and silicon coating cycles had far thinner coatings than samples located nearer the walls of the retort indicates that there was a severe temperature lag within the pack. The effects of time at temperature and activator concentration on the Cr-Ti coating formation is evident from Runs No. 5 and 6. The top center samples in the coolest region, but nearest the activator, received a nearly normal coating. Samples in the bottom center of the pack at a slightly higher temperature received little coating whereas, samples located in the pack bottom near the retort wall, approximately the same distance from the initial activator position as the bottom center samples but approximately 50°F higher in temperature, received a heavier than normal coating.

In an attempt to minimize the difference in coating thickness obtained between a sample near the retort wall and one at the center, a Cr-Ti run was made in which the heat up cycle included a hold period at 1900°F for 3 hours. This should have lessened the difference between edge and center temperatures before any coating deposition occurred. This hold step was then followed by the full coating treatment at 2350°F for 8 hours. The average overlay thicknesses and diffusion zones obtained for selected groups of samples are shown in Table 19. Of chief significance is the fact that in the four initial Cr-Ti runs the sample group TC, CT, MC, CM, BC and CB had average overlay thicknesses which varied from 0.07 to 0.16 mils whereas this run had an average of 0.38 mils. For the other goups there was about a fifty percent increase in coating thickness over and above the previous runs without the hold treatment. There were increases in average diffusion zone thicknesses in all cases except for the top layer of

TABLE 17

Cr-Ti-Si Coating Thicknesses Observed on Samples from Runs 5 and 6

Position	Average Coating Thickness (Mils)	
	Run 5	Run 6
BE	1.3	1.0
BC	0.0	0.0
TE	1.0	1.3
TC	0.0	0.7
ME	1.3	0.6
MC	0.3	1.3
EB	0.7	1.3
CB	0.0	0.0
ET	1.0	1.0
CT	0.5	0.4
EM	1.1	1.3
CM	0.0	0.2
Ave.	0.60	0.76

TABLE 18

Average Cr-Ti-Si Coating Thicknesses of Selected Groups of Samples

Sample Group	Average Coating Thickness (Mils)	
	Run 5	Run 6
TE, ET, TC, CT	0.6	0.8
ME, EM, MC, CM	0.7	0.8
BE, EB, BC, CB	0.5	0.6
BC, TC, MC, CB, CT, CM	0.1	0.4
BE, TE, ME, EB, ET, EM	1.1	1.1

TABLE 19

Average Cr-Ti Coating Thicknesses of Selected Groups of Samples

Sample Group	Average Overlay Thickness (Mils)	Average Diffusion Zone Thickness (Mils)
TE, ET, TC CT, TS, ST	0.43	0.[illegible]
ME, EM, MC CM, MS, SM	0.55	0.76
BE, EB, BC CB, BS, SB	0.66	0.92
TS, ST, MS SM, BS, SB	0.57	0.80
TC, CT, MC CM, BC, CB	0.38	0.53
TE, ET, ME EM, BE, EB	0.69	0.69

of samples which actually showed a twenty percent decrease. Figures 21 and 22 show the microstructure of centrally located samples of the hold run and an identical run which did not include the hold treatment.

In the nine subsequent coating runs in which columbium alloy honeycomb panels were coated the following process parameters were used:

Cr-Ti Cycle

1. 100 grams NaF top of pack
   100 grams NaF bottom of pack

2. Hold at 2000°F for 2 hours

3. Coat at 2350°F for 9 hours

Silicon Cycle

1. 75 grams KF top of pack
   75 grams KF bottom of pack

2. Hold at 1500°F for 2 hours

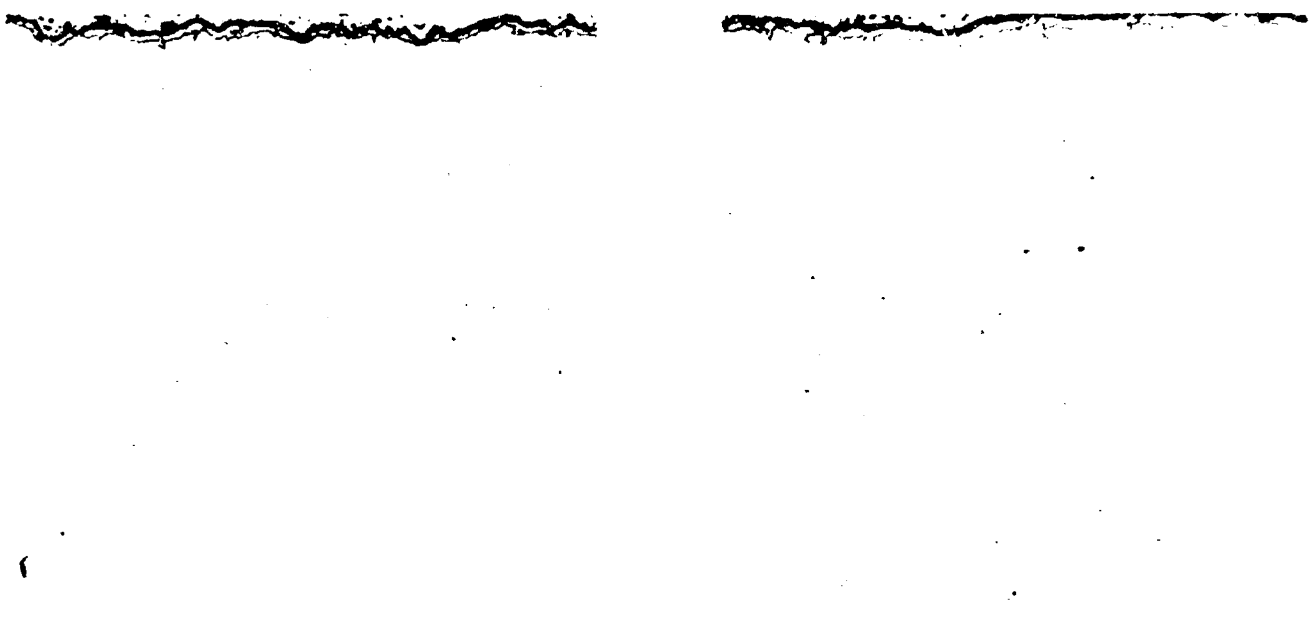
3. Coat at 2100°F for 5 hours

In all runs control specimens were coated with the panels. The average cyclic oxidation lives obtained at 2500°F with these specimens are presented below:

2500°F Cyclic Oxidation Test Results on D-14 Alloy Control Specimens Coated in the Bell Furnace

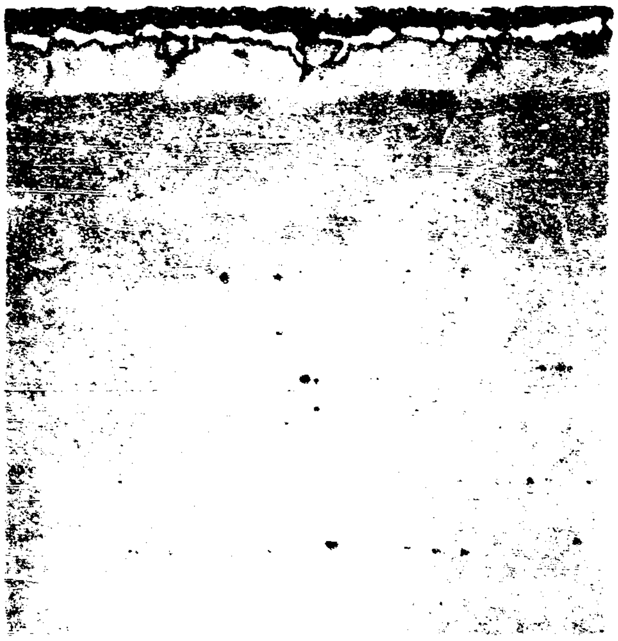
Sample Location	Average Life (Hours)
CT	Not Available
ET	Not Available
TE	25
TC	27
MC	64
CM	35
ME	70
EM	43
BC	72
CB	Not Available
BE	Not Available
EB	Not Available

The average lives shown above are based on results of up to eight specimens at each sample location. The minimum life obtained for all specimens was 20 hours (on



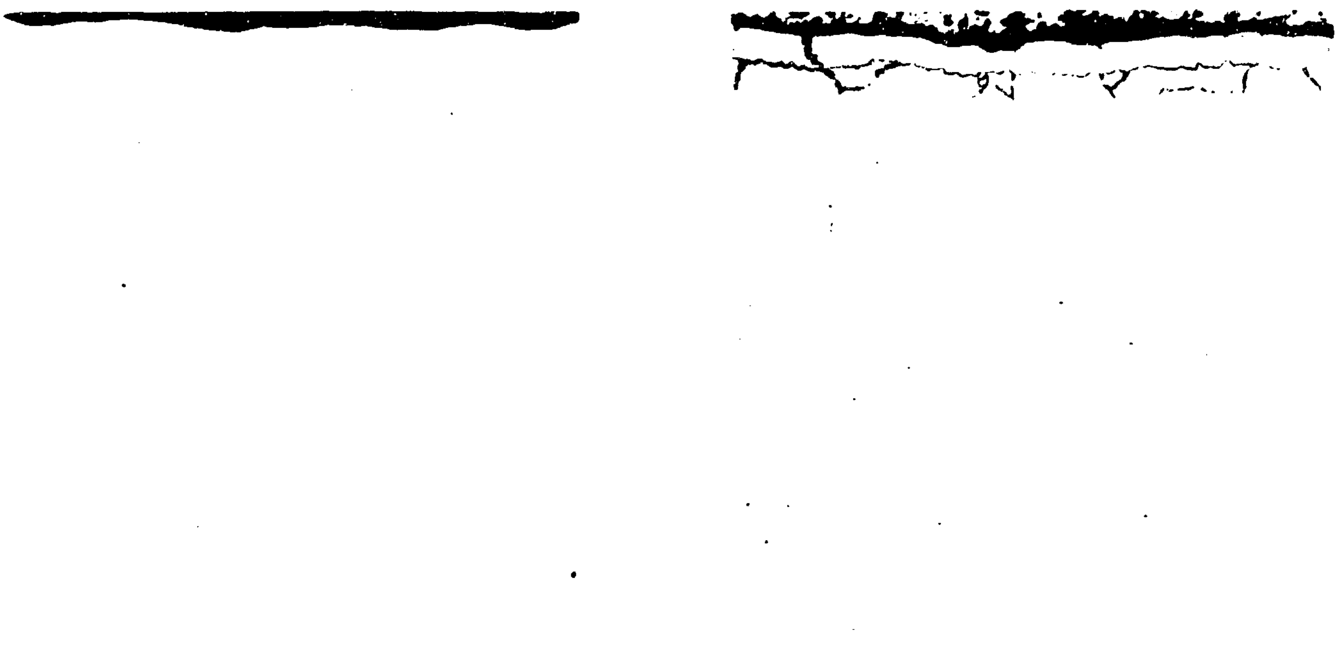
Top Center
Retort Position

Middle Center
Retort Position



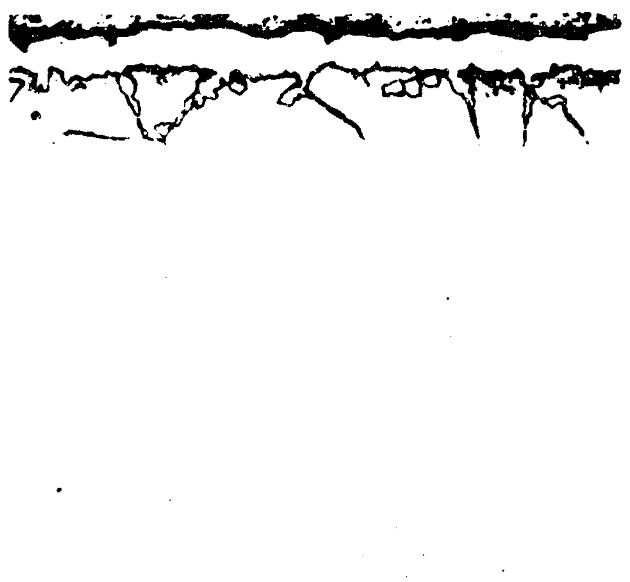
Bottom Center
Retort Position

Figure 21 Cr-Ti Alloy Coatings Formed in Resistance Element Heated Bell Furnace - 60Cr-40Ti Alloy Pack - Heated Directly to 2350°F and Held for 9 Hours 250X



Top Center
Retort Position

Middle Center
Retort Position



Bottom Center
Retort Position

Figure 22 Cr-Ti Alloy Coating Formed in Resistance Element Heated Bell Furnace - 60Cr-40Ti Alloy Pack - Heated to 1900° F, Held 3 Hours, Then Heated to 2350° F and Held 9 Hours specimen at the top of the pack). The maximum protective lives obtained at 2500°F were 124 hours. The data indicates that life expectancy increases from pack top to bottom.

6. GAS FLOW PROCESS STUDY

The formation of the Cr-Ti alloy coating layer by a gas flow technique was investigated as part of the previous program. Deposition of silicon by a completely vapor phase process, wherein intimate contact between pack particles and the material to be coated is not required, was investigated on a limited basis. Two approaches were investigated utilizing a single piece of equipment: (a) a continuous gas flow process not involving a vacuum and (b) a closed retort technique utilizing a continuously evacuated system with a constant input of chlorine gas. The intent of this investigation was to demonstrate the feasibility of the process since it has possible merits as an alternate to forming the Cr-Ti-Si coating by the vacuum pack process.

During the previous coating development program a laboratory scale apparatus was constructed to investigate formation of the Cr-Ti-Si coating by a gas flow technique not requiring the use of a vacuum. The furnace consisted of a vertical alumina tube with two adjacent and independently globar heated hot zones. An argon-chlorine gas mixture was passed through an alumina diluted Cr-Ti alloy coating pack which was heated in the lower hot zone. The reacted gas subsequently passed over columbium specimens placed both in the pack and also freely suspended above the pack in the free vapor space. A sketch of this furnace was shown in a previous final report (1). It was demonstrated by a limited effort in this apparatus that Cr-Ti coatings could be formed by this technique. Upon subsequent alloying with silicon by the vacuum process, reasonably protective Cr-Ti-Si coatings were produced.

Several problems were encountered with this apparatus: (a) pack sintering, (b) contamination of the columbium substrate, (c) channeling of the gases through the pack and (d) extremely low coating deposition rates in the reaction zone. Modifications were made in this equipment to reduce the level of contaminating gases entering into the system, and to reduce the channeling effect of gases passing through the pack. A schematic of the modified apparatus is shown in Figure 23. Major changes involved: (a) the use of wax vacuum seals between the alumina tube and the water cooled copper tube fittings, (b) insertion of a plenum to reduce gas channeling and (c) the use of O ring seals between copper tube fittings. A bellow was also used to allow tube expansion without the introduction of stresses on the tube.

The limited effort conducted during this program involved demonstration of the feasibility of alloying silicon with Cr-Ti coatings formed by the vacuum pack process. The Cr-Ti alloy coating layer was deposited on D-43 substrate material using a 60Cr-40Ti alloy pack run for 8 hours at 2300°F at 1.5 mm in the 3" diameter x 8" high retort.

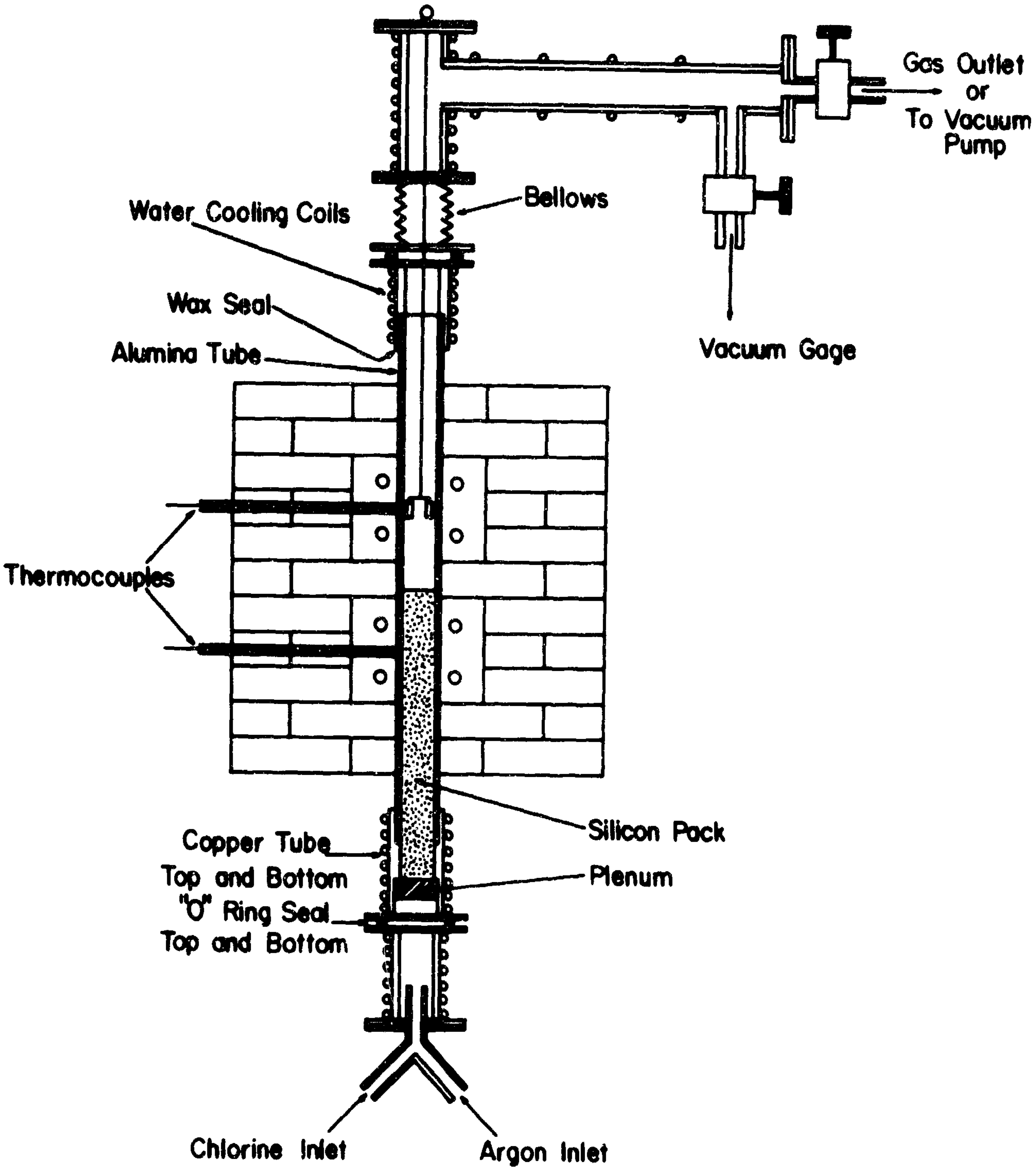


Figure 23 Schematic Drawing of the Gas Flow Coating Apparatus

Six 4 hour silicon coating runs were performed in the gas flow apparatus and the process parameters employed are summarized in Table 20. Four runs were made in which the system was essentially under a positive gas pressure (chlorine plus argon input) and two runs were made during which the system was evacuated to 10^{-1} mm and subsequently operated with a chlorine gas input of 50 cc/min. The system pressure was then maintained at a nominal pressure of 1 mm by controlling the vacuum pumping rate. Specimens were placed in the pack, on the pack and in the free vapor space above the pack. Coating thickness measurements and specimen weight changes recorded for the silicon coating cycle are included in Table 20.

The first two runs were made using a total flow rate of 450 cc/min. (50 cc/min. Cl_2 and 400 cc/min. argon). In the first run both the pack and the reaction zone were maintained at 1900°F and in the second run the pack and reaction zone temperature was raised to 2100°F. Coatings formed both in and on the pack in these two runs were metallographically very similar to coatings applied by the vacuum pack process. However, coatings formed in the reaction zone contained several voids and were extremely non-uniform in thickness. (Photomicrographs of specimens coated in the second run are shown in Figure 24). The coatings formed in the reaction zone were much thinner than those formed either in or on the pack. The coatings deposited at 2100°F in and on the pack were considerably thicker than those formed at 1900°F. However, coatings formed in the reaction zone at 2100°F were thinner than those formed at the lower temperature. In fact, at the higher temperature weight losses were recorded for specimens suspended in the reaction zone.

The third and fourth runs were made also utilizing pack and reaction zone temperatures of 1900 and 2100°F (both zones maintained at the same temperature), respectively. The total flow rate (Cl_2 + argon) was kept constant at 450 cc/min. as in the first two runs. However, the Cl_2 flow rate was decreased by 50% to 25 cc/min. The thickness of the Cr-Ti-Si coatings formed in and on the pack was not altered greatly in comparison with those formed at the higher Cl_2 flow rates. Coatings formed in the free vapor space above the pack were less subject to void formation, but were still non-uniform in thickness. Figures 25 and 26 show representative coatings formed in these two runs. As in the case of coatings formed at the higher Cl_2 flow rates, a weight loss was recorded for specimens placed in the reaction zone at the 2100°F process temperature.

The last two runs were made utilizing an evacuated system rather than by the use of a positive pressure system. The technique of using a free vapor space was maintained, however. The system was evacuated to approximately 10^{-1} mm after which Cl_2 was introduced. The Cl_2 flow rate was approximately 50 cc/min.

The system pressure was maintained at a nominal pressure of 1 mm and continuously evacuated. Again, one run was made at a pack and reaction zone temperature of 1900°F and one run at 2100°F. Coatings formed in and on the pack were much thinner than those formed utilizing a positive pressure system (Figure 27) and showed correspondingly less weight gain. Those specimens suspended in the reaction zone showed much greater weight changes (positive) than those suspended in

Table 20

Coating Thickness Measurements for D-43 Alloy Silicon Coated by the Gas Flow Technique

Run No.	Temperature - °F		Cl_2 Flow cc/min.	Argon Flow cc/min.	Cr-Ti-Si Coating Thickness - Mils(2) and Weight Change-mg(3)		
	Pack(1)	Reaction Zone			In Pack(4)	On Pack(4)	In Reaction Zone(4)
1	1900	1900	50	400	3.3-4.0 (+76.1)	2.5-3.5 (+56.1)	0.6-2.0 (+1.9)
2	2100	2100	50	400	5.5-6.5 (+105.8	3.8-4.5 +86.2	0.2-0.9 (-22.3)
3	1900	1900	25	425	3.5-4.0 (+78.6)	2.5-3.0 +66.4)	0.6-1.6 (+3.8)
4	2100	2100	25	425	3.5-5.0 (+96.9)	3.0-3.5 (+75.1)	0.6-1.0 (-1.8)
(5) 5	1900	1900	50	0	0.6-1.5 (+12.2)	1.0-1.4 (+10.6)	0.8-1.3 (+9.8)
(5) 6	2100	2100	50	0	0.6-1.6 (+7.3)	0.3-2.0 (+0.5)	0.9-1.4 (+11.3)

(1) Pure silicon pack used for all runs

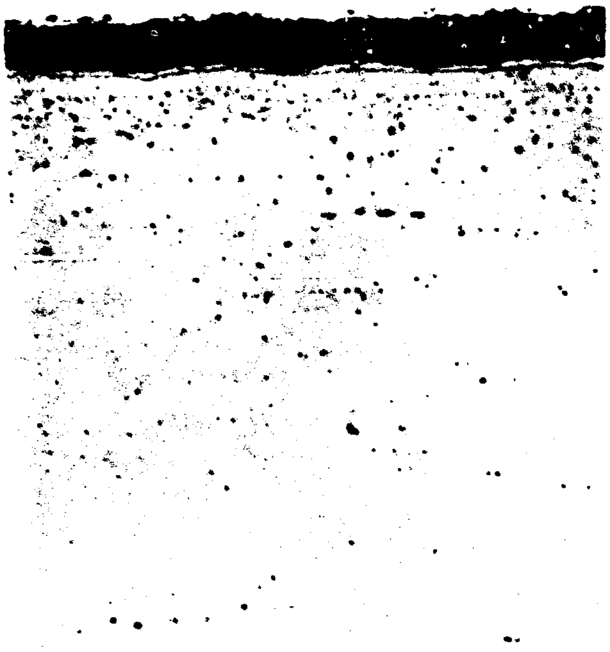
(2) Cr-Ti coating (applied by vacuum pack process) thickness 0.7-0.9 mils

(3) Figures shown in brackets beneath thickness measurements are weight changes recorded for silicon coating cycle

(4) Specimen location in the gas flow coating apparatus and for silicon coating cycle was in the pack, on the pack and suspended 5 inches above the pack in an independently controlled reaction zone

(5) System evacuated to nominal 1 mm pressure during entire run

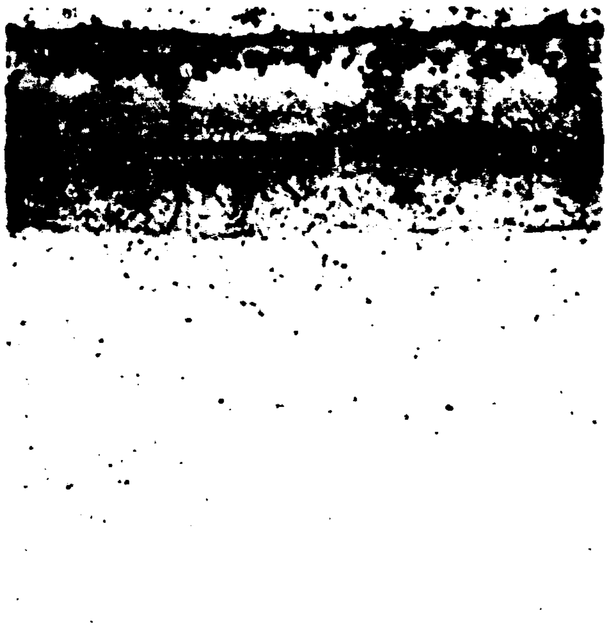
Specimen Located in the Pack



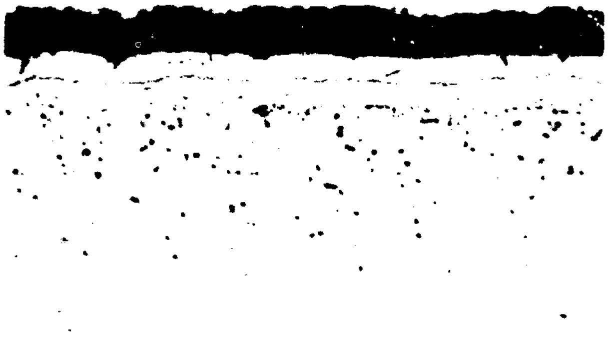
Specimen Located in the Reaction Zone

Silicon Coating Process Parameters:
Pack and Reaction Zone Temperature - 2100°F
Cl_2 Flow Rate - 50 cc/min.
Argon Flow Rate - 400 cc/min.

Figure 24 Cr-Ti-Si Coated D-43 Alloy - Silicon Coating Applied by the Gas Flow Technique 250X



Specimen Located in the Pack

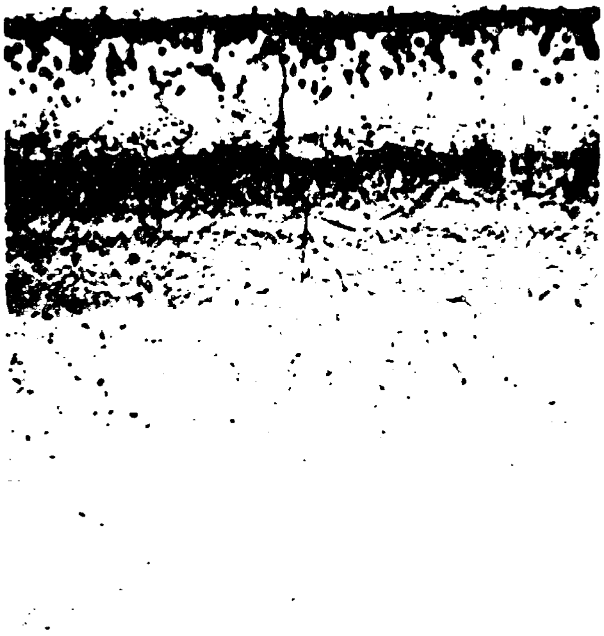


Specimen Located in the Reaction Zone

Silicon Coating Process Parameters:

Pack and Reaction Zone Temperature - 1900°F
Cl_2 Flow Rate - 25 cc/min.
Argon Flow Rate - 475 cc/min.

Figure 25 Cr-Ti-Si Coated D-43 Alloy - Silicon Coating Applied by the Gas Flow Technique 250X



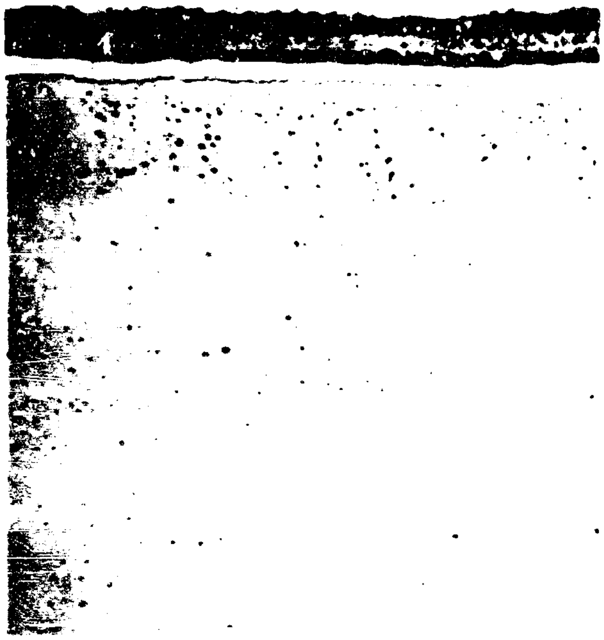
Specimen Located in the Pack

Specimen Located in the Reaction Zone

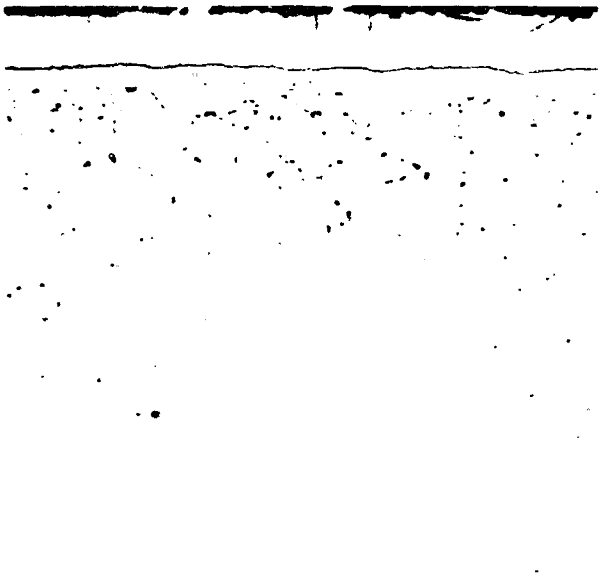
Silicon Coating Process Parameters:

Pack and Reaction Zone Temperature - 2100° F
Cl_2 Flow Rate - 25 cc/min.
Argon Flow Rate - 425 cc/min.

Figure 26 Cr-Ti-Si Coated D-43 Alloy - Silicon Coating Applied by the Gas Flow Technique 250X



Specimen Located in the Pack



Specimen Located in the Reaction Zone

Silicon Coating Process Parameters:

Pack and Reaction Zone Temperature - 2100°F
Cl_2 Flow Rate - 50 cc/min.
System Continuously Evacuated to Nominal 1 mm Pressure

Figure 27 Cr-Ti-Si Coated D-43 Alloy - Silicon Coating Applied by the Gas Flow Technique 250X

a non-evacuated system. The coatings formed in this zone contained only a few small voids and were reasonably uniform in thickness.

It should be noted that in no case was pack sintering a problem. All specimens did show some slight contamination in the substrate. Apparently some contaminating gases entered the system during operation, however, this problem can no doubt be eliminated.

It is felt that this coating process can be described by the following equations:

$$Si + Cl_2 \longrightarrow SiCl_2 \quad (1)$$

$$2SiCl_2 \longrightarrow Si + SiCl_4 \quad (2)$$

$$Si + Cl_2 \longrightarrow SiCl_2 \xrightarrow{\text{excess } Cl_2} SiCl_4 \quad (3)$$

The first two equations would describe the desired situation, wherein the $SiCl_2$ vapor phase reacts at the specimen surface to form silicon and stable $SiCl_4$. The third equation would apply to a situation involving an excess of chlorine. Here the stable $SiCl_4$ phase is formed immediately outside the pack and does not react to deposit silicon on the specimen surface in the free vapor space.

As seen in the results of the first 4 runs, less silicon was deposited on the specimens suspended above the pack at the higher chlorine flow rate (and associated higher chlorine concentration). Increased temperature for a given chlorine concentration caused a decrease in silicon deposition. This apparently resulted from an increase in the reaction rate to form stable $SiCl_4$. The application of an evacuated system to this process increased the silicon deposition rate in the reaction zone as compared to the positive pressure system for equivalent chlorine concentrations. This would appear to be associated with the residence of the gaseous species and the reaction rate to form stable $SiCl_4$. Thus for a given chlorine concentration less stable $SiCl_4$ would be formed as residence time (a function of pumping rate) was decreased. In order to compare the protective capability of coatings formed by the gas flow process with coatings formed by the vacuum pack process, the various specimens coated in this study were cyclic oxidation tested at 1800 and 2500°F. The results of these tests are listed in Table 21. Reasonably good protective properties were afforded by coatings formed either in or on the pack using the positive pressure technique. Specimens similarly located in the evacuated system exhibited much lower protective life, no doubt primarily a result of the thinner coatings formed in the more dynamic system. Coatings formed in the reaction zone above the pack were more protective when formed in the evacuated system. The coatings formed in the positive pressure system were more protective when formed at the lower chlorine flow rates. This was found for both oxidation test temperatures. The results of the oxidation tests are in good agreement with the results of metallographic examination.

Although limited, these coating runs have shown that the silicon coating (siliconizing Cr-Ti alloy coatings) can be accomplished by a gas flow technique involving coating in the free vapor space over a silicon pack. This is evidenced

TABLE 21

Cyclic Oxidation Protective Life at 1800 and 2500°F of Cr-Ti-Si Coatings on D-43 Alloy Silicon Coating Applied by the Gas Flow Technique(1)

	Cr-Ti-Si Coating Protective Life - Hours at 1800 and 2500°F					
	In Si Pack(2)		On Si Pack(2)		In Reaction Zone(2)	
Run No.	1800°F	2500°F	1800°F	2500°F	1800°F	2500°F
1	27	77	24	74	4	1,1
2	99	150*	28	102	5	3,7
3	29	72	53	72	24	3,3
4	28	77	28	96	5	3,24
5	4	3	26	3	24	24,24
6	4	3	4	1	150*	6

(1) Cr-Ti coating applied by the vacuum pack process

(2) Specimen location in the gas flow coating apparatus used for silicon coating cycle was in the pack, on the pack, and suspended 5 inches above the silicon pack in an independently controlled reaction zone

* Denotes test discontinued - no visible coating failure

by the 24 hour - 2500°F protective life obtained from specimens in Run No. 5. Considerable development work will be necessary to thoroughly, evaluate the merits of the process and to determine its limitations. The feasibility of forming the Cr-Ti alloy layer by this technique was shown in the previous program. Obviously, the variables involved in a process of this type need to be investigated on a comprehensive basis which might result in modifications to the existing process.

7. REPRODUCIBILITY AND RELIABILITY STUDY

The objective of Phase II of this program was to conduct a statistically meaningful analysis of the reproducibility and protective reliability of the Cr-Ti-Si coating on two columbium base sheet alloys, B-66 and D-43. Many thousands of coated columbium alloy coupons have been evaluated by cyclic oxidation testing at one atmosphere during previous coating development programs. Although a certain degree of process reproducibility has been established in these evaluation studies, no statistical evaluation study has been conducted to accurately assess the protective reliability of the Cr-Ti-Si coating.

7.1 Reproducibility Analysis

The optimized Cr-Ti-Si coating parameters established in Phase I of this program were employed in coating the sheet coupons for this study. The following variables were evaluated.

1. columbium base alloys - B-66 and D-43
2. coating furnace sizes - two induction heated furnaces utilizing 3" diameter x 8" high and 7-1/2" diameter x 18" high retorts
3. coating thicknesses - nominally 1.5, 2.0 and 2.5 mils (2.5 mils coating in 7-1/2" retort only)
4. number of similarly prepared batches - six
5. specimen locations in the retort - top, middle and bottom at both retort center and edge
6. coupon sizes 1/2" x 1/2" and 2" x 2" x 0.030"

Two methods were utilized to evaluate these specimens: (1) metallographic examination of specimens representing each process variable to determine coating thickness, depth of coating element diffusion, variations in coating morphology and coating uniformity throughout the retort and (2) cyclic oxidation in air at one atmosphere at 2000, 2500 and 2700°F.

The desired coating thicknesses were achieved through control of both the Cr-Ti and the siliconizing cycles. The initial Cr-Ti coating layer was formed utilizing the same processing parameters for both nominal 1.5 and 2.0 mils Cr-Ti-Si coatings.

The process parameters were, however, somewhat different for the two furnace sizes. The Cr-Ti coating employed for the nominal 2.5 mil coating, applied only in the 7-1/2 inch retort, was varied in order to maintain consistent composition with the thicker coating. The various processing parameters selected were discussed in the previous section and are summarized in Table 22. Of importance is the fact that the process parameters were selected to provide relatively good protective life over the entire test temperature range. Some improvement in protective life could be achieved for a high temperature range (2400-2700°F) or a low temperature range (1800-2400°F) if the process parameters were adjusted to give a coating tailored to operate in that particular temperature range. Therefore, the coatings investigated for the reliability study would not necessarily provide maximum protective characteristics at any one test temperature.

For this study an equal number of B-66 and D-43 alloy 1/2" x 1/2" coupons (1440 each) were utilized. Only 60 2" x 2" coupons were fabricated from D-43 alloy. The actual distribution of these specimens is shown in Figure 28. This figure shows the distribution of one set of specimens for one combination of variables, all other sets are duplicates of this. In addition, the specimen distribution for the evaluation tests is indicated.

The effects of alloy, retort size, silicon and Cr-Ti cycle process parameters and specimen location within the retort as related to coating thickness were analysed utilizing a random balance analysis technique. Repetition of each silicon cycle process parameter - retort size - substrate alloy composition provided statistically meaningful data on process reproducibility.

The results of the metallographic examination (coating thickness) of representative specimens from each coating run are tabulated in Tables 23 through 27. Also included are the results of the oxidation tests at 2000, 2500 and 2700°F.

All thickness measurements were determined metallographically. A range in thickness (minimum to maximum) was determined for each specimen examined. These measurements coincide with the schematic drawing of the Cr-Ti-Si coating shown in Tables 8 and 9 for both the Cr-Ti alloy layer and the Cr-Ti-Si coating overlay and diffusion zone thickness. It should be noted that the reported variation in diffusion zone thickness occurs over very short distances relative to the variation in coating overlay thickness with distance as shown in the following sketch.

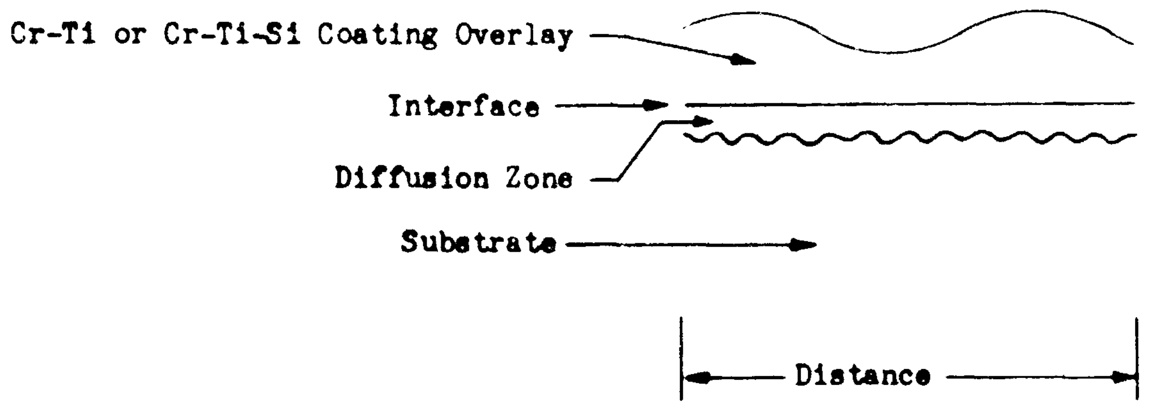


TABLE 22

Coating Process Parameters for Reliability Study

3" Diameter x 8" High Retort

	Cr-Ti Coating Cycle	Silicon Coating Cycle (1.5 mils thick)	Silicon Coating Cycle (2.0 mils thick)
Pack Composition	60Cr-40Ti	Si	Si
Coating Time	8 Hours	4 Hours	6 Hours
Retort Temperature	2300°F	2000°F	2100°F
System Pressure	1.5 mm.	10^{-2} mm.	10^{-2} mm.
Activator	0.5 w/o KF	1.0 w/o KF	1.0 w/o KF

7-1/2" Diameter x 18" High Retort

	Cr-Ti Coating Cycle		Silicon Coating Cycle	
	(1.5 and 2.0 mils thick)	(2.5 mils thick)	(1.5 mils thick)	(2.0 and 2.5 mils thick)
Pack Composition	60Cr-40Ti	60Cr-40Ti	Si	Si
Coating Time	8 Hours	10 Hours	4 Hours	6 Hours
Retort Temperature	2300°F	2350°F	2000°F	2100°F
System Pressure	10^{-2} mm.	10^{-2} mm.	10^{-2} mm.	10^{-2} mm.
Activator	0.3 w/o KF	0.3 w/o KF	0.3 w/o KF	0.3 w/o KF

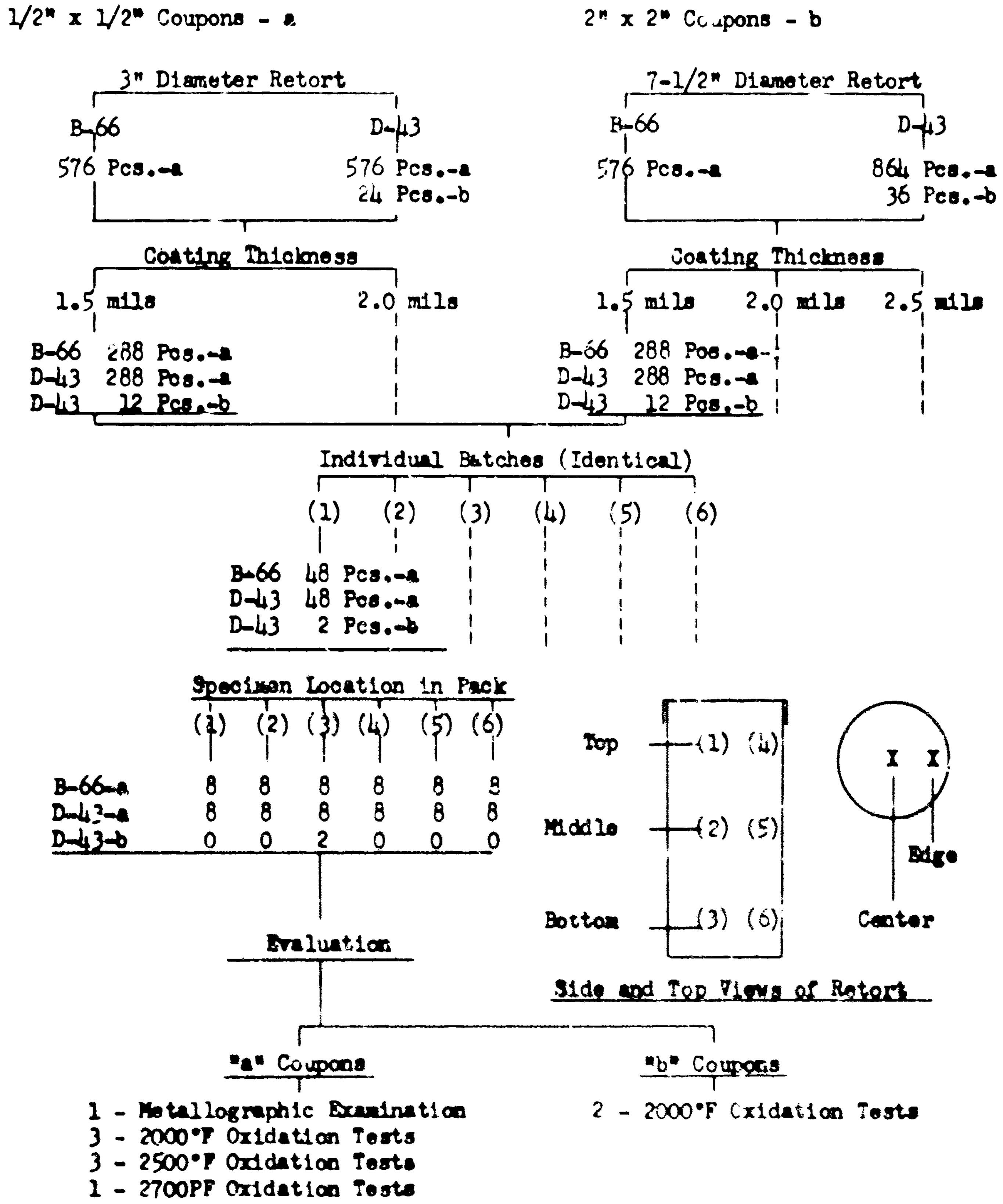


Figure 28

Specimen Distribution for Reliability Study

TABLE 23

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens Cr-Ti Coated in 3 Hours at 2300°F and Silicon Coated in 4 Hours at 2000°F in the 3" Diameter x 8" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
1	TC	0.2-0.9	0.8-1.0	0.4-0.8	0.2-0.7	1.4-1.8	1.1-1.6	0.5-0.9	0.2-0.8	147,150,150	150,150,150	24,48,72	48	2	1
	MC	0.6-1.4	1.0-1.2	0.5-0.7	0.4-0.7	1.5-2.0	1.7-2.1	0.7-1.2	0.3-0.9	150,150,150	150,150,150	-	72,72,96	2	2
	BC	0.9-1.2	1.0-1.4	0.5-1.0	0.4-0.9	1.9-2.1	1.9-2.1	0.8-1.2	0.4-0.9	150,150,150	150,150,150	48,72	48,53	2	2
	TE	0.2-0.9	0.7-1.0	0.5-0.9	0.3-0.7	1.6-1.9	1.3-1.6	0.5-1.0	0.3-0.8	150,150,150	150,150,150	26,48,48	48,48,50	2	2
	ME	0.4-1.2	1.0-1.3	0.6-1.1	0.4-0.8	1.3-2.0	1.8-2.0	0.8-1.2	0.3-0.8	150,150,150	150,150,150	96,96,150	50,72,104	2	5
	BE	0.7-1.1	0.7-1.3	0.6-1.0	0.4-0.9	1.6-2.0	1.5-2.1	0.6-0.9	0.4-0.9	150,150,150	150,150,150	48,56,72	48,72	2	3
	*MC	-	-	-	-	-	-	-	-	-	150, 150	-	-	-	-
2	TC	0.3-0.8	0.6-0.8	0.3-0.5	0.2-0.8	1.2-1.4	1.3-1.5	0.2-0.5	0.2-0.5	150,150,150	150,150,150	29,48,48	55,72,72	2	5
	MC	0.6-1.0	0.2-1.0	0.7-0.9	0.3-0.8	1.3-1.7	1.8-2.0	0.4-0.8	0.3-0.8	150,150,150	150,150,150	72,77,77	72,78,96	5	7
	BC	0.9-1.2	0.6-1.1	0.6-1.0	0.5-1.0	1.5-1.9	1.5-2.0	0.4-0.8	0.4-0.7	150,150,150	150,150,150	72,74,96	48,125,144	5	5
	TE	0.3-0.8	0.2-0.8	0.4-0.8	0.2-0.7	1.3-1.6	1.5-1.7	0.4-1.0	0.3-0.6	150,150,150	150,150,150	32,48,48	48,72,96	2	6
	ME	0.9-1.0	0.6-1.0	0.8-1.0	0.4-1.0	1.6-1.8	0.8-1.0	0.6-1.0	0.5-1.0	150,150,150	150,150,150	74,96,96	54,54,96	5	6
	BE	0.8-1.0	0.9-1.2	0.7-1.0	0.5-0.8	1.5-1.9	1.5-2.2	0.6-1.0	0.6-1.0	150,150,150	150,150,150	126,144,144	72,96,127	5	7
	*MC	-	-	-	-	-	-	-	-	-	150, 150	-	-	-	-
3	TC	0.8-1.2	0.5-1.0	0.4-0.7	0.4-0.8	1.4-1.8	1.4-1.7	0.5-1.0	0.5-0.8	150,150,150	150,150,150	48,53,55	24,24,24	3	9
	MC	0.6-1.2	0.7-1.2	0.5-0.9	0.4-0.5	1.5-1.9	1.7-1.8	0.5-1.0	0.8-1.1	150,150,150	150,150,150	53,54,72	32,48,55	7	6
	BC	1.1-1.4	0.6-1.4	0.8-1.1	0.7-1.0	1.3-1.9	1.5-2.0	0.8-1.2	0.8-1.2	150,150,150	150,150,150	48	48,72,96	9	9
	TE	0.6-1.0	0.6-1.1	0.5-0.8	0.4-0.8	1.4-1.8	1.5-1.7	0.5-1.1	0.5-1.0	150,150,150	150,150,150	53,55,72	24,48,50	5	7
	ME	0.7-1.1	0.7-1.2	0.6-1.0	0.5-0.9	1.8-2.0	1.8-2.0	0.6-1.0	0.7-1.0	150,150,150	150,150,150	48,53,72	55,72,79	5	5
	BE	0.9-1.3	0.5-1.3	0.6-1.0	0.7-1.1	1.3-1.8	1.8-2.0	0.6-1.0	0.5-0.8	150,150,150	150,150,150	78,101	79,96,96	9	5
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
4	TC	0.3-1.0	0.2-0.9	0.4-0.8	0.4-0.8	1.3-1.6	1.5-1.8	0.5-1.0	0.3-0.8	150,150,150	150,150,150	24,24,24	26,27	3	7
	MC	0.2-1.0	0.7-1.3	0.4-1.0	0.4-0.8	1.8-2.0	1.8-2.0	0.5-1.2	0.3-0.8	150,150,150	150,150,150	24,53,78	8,48	6	7
	BC	0.6-1.2	0.6-1.2	0.8-1.2	0.4-0.9	1.6-2.0	1.9-2.1	0.8-1.2	0.5-0.8	150,150,150	150,150,150	48,74,77	120	7	7
	TE	0.3-0.8	0.6-0.8	0.5-1.0	0.4-0.8	1.4-1.6	1.5-1.6	0.8-1.2	0.3-0.7	150,150,150	150,150,150	24,24,24	26	2	13
	ME	0.5-1.1	0.2-1.0	0.7-1.2	0.4-0.9	1.7-2.0	1.8-2.0	0.8-1.2	0.5-1.0	150,150,150	150,150,150	24,32,96	31,48	6	13
	BE	0.9-1.4	0.9-1.2	0.8-1.2	0.6-0.9	1.6-2.0	1.8-1.9	0.8-1.2	0.5-1.0	150,150,150	150,150,150	48,72,72	8,48,96	8	13
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

TABLE 23 (CONTINUED)

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens Cr-Ti Coated in 8 Hours at 2300°F and Silicon Coated in 4 Hours at 2000°F in the 3" Diameter x 8" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2100°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
5	TC	0.2-0.9	0.8-1.0	0.4-0.8	0.2-0.7	1.2-1.6	1.2-1.8	0.3-0.6	0.2-0.5	150,150,150	150,150,150	28,48,74	48,48,72	5	8
	MC	0.6-1.4	1.0-1.2	0.5-0.7	0.4-0.7	1.2-2.1	1.6-1.8	0.3-0.7	0.4-0.7	150,150,150	150,150,150	55,72,72	72,72,96	10	9
	BC	0.9-1.2	1.0-1.4	0.5-1.0	0.4-0.9	1.7-2.0	1.9-2.1	0.5-0.9	0.4-0.7	150,150,150	150,150,150	96,150,150	53,120,126	10	11
	TE	0.2-0.9	0.7-1.0	0.5-0.9	0.3-0.7	1.3-1.8	1.2-1.8	0.4-1.0	0.3-0.6	150,150,150	150,150,150	55,72,101	48,72,96	5	8
	ME	0.4-1.2	1.0-1.3	0.6-1.1	0.4-0.8	1.2-1.9	1.4-2.2	0.6-0.9	0.3-0.7	150,150,150	150,150,150	55,120,120	96,104,104	7	12
	BE	0.7-1.1	0.7-1.3	0.6-1.0	0.4-0.9	1.4-2.0	1.7-2.0	0.6-0.9	0.5-0.8	150,150,150	150,150,150	24,150,150	55,96,98	11	13
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
6	TC	0.6-0.8	0.5-0.8	0.1-0.4	0.1-0.5	1.3-1.5	1.2-1.4	0.1-0.4	0.1-0.4	150,150,150	150,150,150	51,56,79	48,50,96	3	3
	MC	0.5-1.1	0.8-1.0	0.2-0.5	0.2-0.5	1.5-1.8	1.4-1.7	0.2-0.6	0.3-0.6	150,150,150	150,150,150	31,52,74	31,78,96	4	7
	BC	0.6-1.2	0.9-1.2	0.2-0.5	0.4-0.8	1.6-1.9	1.6-2.3	0.3-0.8	0.2-0.6	150,150,150	150,150,150	96,96,96	78,96,96	6	7
	TE	0.1-0.9	0.6-0.8	0.1-0.4	0.2-0.5	1.4-1.6	1.4-1.7	0.1-0.4	0.1-0.4	150,150,150	150,150,150	30,77,77	30,72,72	5	2
	ME	0.9-1.2	0.6-1.0	0.1-0.5	0.3-0.5	1.3-2.0	1.6-2.0	0.2-0.5	0.2-0.5	150,150,150	150,150,150	48,72,96	72,72,96	4	8
	BE	0.9-1.2	0.9-1.1	0.2-0.5	0.3-0.6	1.6-1.8	1.5-2.1	0.3-0.8	0.3-0.8	150,150,150	150,150,150	72,98,149	72,96,96	5	10
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

(1) Pack position code - T-top, M-middle, B-bottom, C-center and E-edge
(2) All tests listed as 150 hours were discontinued - no visible coating failure
* Indicates data for 2" x 2" coupons - all other values for 1/2" x 1/2" coupons

TABLE 24

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 8 Hours at 2300°F and Silicon Coated in 6 Hours at 2100°F in the
3" Diameter x 8" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
1	TC	0.4-08	0.4-1.0	0.2-0.6	0.2-0.4	1.7-1.9	1.8-2.0	0.2-0.5	0.3-0.6	122,150,150	150,150,150	24,24,26	48,48,72	2	2
	MC	0.6-1.2	0.2-1.2	0.4-0.6	0.3-0.6	1.6-2.2	1.9-2.1	0.5-0.8	0.4-0.7	150,150,150	150,150,150	27,48,72	48,72,96	2	2
	BC	1.1-1.2	0.8-1.4	0.4-0.8	0.4-0.8	2.0-2.8	2.1-2.4	0.7-0.9	0.4-0.9	150,150,150	150,150,150	75,78	72	2	2
	TE	0.4-1.1	0.6-1.2	0.2-0.6	0.2-0.6	1.5-1.9	1.8-2.5	0.3-0.6	0.2-0.6	150,150,150	150,150,150	26,79,96	96,96	2	2
	ME	0.6-1.2	1.0-1.2	0.4-0.8	0.5-0.8	2.0-2.9	2.0-3.0	0.7-0.9	0.3-0.8	150,150,150	150,150,150	24,48,150	55,72	2	3
	BE	0.8-1.4	0.4-1.2	0.5-1.0	0.4-0.8	2.0-2.2	2.4-3.0	0.7-1.0	0.4-0.9	150,150,150	121,150,150	120	72,72,72	2	4
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
2	TC	0.2-0.7	0.5-0.8	0.2-0.5	0.2-0.5	1.6-1.8	1.8-2.0	0.3-0.6	0.2-0.5	150,150,150	150,150,150	104,104,108	56,62,80	2	5
	MC	0.4-1.0	0.9-1.1	0.5-0.7	0.3-0.6	1.5-1.7	1.8-2.0	0.5-0.8	0.2-0.7	150,150,150	150,150,150	111,128,150	34,37,56	4	7
	BC	0.5-1.0	0.6-1.0	0.5-0.8	0.3-0.6	1.8-2.3	1.8-2.1	0.4-0.6	0.2-0.7	150,150,150	150,150,150	128,133,150	39,56,56	5	5
	TE	0.3-0.7	0.8-1.0	0.5-0.8	0.3-0.6	1.5-1.7	2.0-2.5	0.3-0.6	0.2-0.5	150,150,150	150,150,150	85,88,135	34,39,56	2	5
	ME	0.2-0.8	0.8-1.0	0.5-0.7	0.4-0.6	1.7-1.9	1.9-2.0	0.5-0.8	0.2-0.7	150,150,150	150,150,150	128,150,150	34,37,38	3	6
	BE	0.4-0.9	0.9-1.2	0.5-1.0	0.2-0.5	1.9-2.2	2.1-2.4	0.5-0.8	0.2-0.7	150,150,150	150,150,150	104,150,150	39,39,40	5	4
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
3	TC	0.1-0.8	0.2-1.0	0.4-0.7	0.2-0.5	1.5-2.0	1.6-1.8	0.3-0.6	0.2-0.5	150,150,150	150,150,150	72,96,96	48,72	5	2
	MC	0.2-1.1	0.6-1.2	0.9-1.1	0.4-0.6	1.6-1.9	1.9-2.1	0.6-1.0	0.4-0.9	150,150,150	150,150,150	79,99,120	78,128	5	7
	BC	0.4-1.2	0.6-1.1	0.7-1.0	0.4-0.8	1.8-2.0	2.0-2.2	0.5-1.0	0.5-0.8	150,150,150	150,150,150	120,127,127	51,51	2	6
	TE	0.6-0.8	0.6-0.8	0.6-0.8	0.4-0.6	1.6-1.8	1.8-2.0	0.6-1.0	0.3-0.7	150,150,150	150,150,150	72,96,120	32	6	5
	ME	0.8-1.3	0.4-1.0	0.7-1.1	0.4-0.6	2.0-2.5	2.0-2.5	0.8-1.2	0.2-0.6	150,150,150	150,150,150	150,150,150	55	6	9
	BE	0.3-1.0	0.4-1.2	0.6-0.9	0.4-0.6	1.9-2.5	1.9-2.0	0.5-1.0	0.5-1.0	150,150,150	150,150,150	72,80,128	72	3	5
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
4	TC	0.6-0.8	0.2-1.0	0.6-1.0	0.3-0.7	1.5-1.6	1.5-1.8	0.5-0.8	0.2-0.6	150,150,150	150,150,150	48,72,72	48,48,55	2	5
	MC	0.8-1.0	0.6-1.0	0.5-0.8	0.3-0.5	1.8-2.0	1.8-2.0	0.5-0.8	0.4-0.6	150,150,150	150,150,150	79,120,120	48,96,120	7	6
	BC	0.6-1.2	0.7-1.4	0.7-1.0	0.4-0.8	1.8-2.2	1.4-2.3	0.6-0.8	0.4-0.9	150,150,150	150,150,150	144,150,150	48,56,120	6	9
	TE	0.4-1.0	0.6-1.0	0.6-1.2	0.3-0.5	1.3-1.7	1.2-1.8	0.3-0.8	0.2-0.7	150,150,150	150,150,150	72,96,102	72,77,77	3	4
	ME	0.6-1.2	0.5-1.2	0.6-1.0	0.5-0.8	2.0-2.6	2.0-2.8	0.9-1.2	0.3-0.7	150,150,150	150,150,150	51,150,150	96,120,120	5	11
	BE	0.8-1.1	0.6-1.2	0.5-0.8	0.5-0.8	1.9-2.8	2.2-2.8	0.9-1.2	0.4-0.8	150,150,150	150,150,150	120,144,150	7,30,55	5	6
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

TABLE 24 (CONTINUED)

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 8 Hours at 2300° F and Silicon Coated in 6 Hours at 2100° F in the
3" Diameter x 8" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000° F		2500° F		2700° F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
5	TC	0.4-0.8	0.4-1.0	0.2-0.6	0.2-0.4	1.5-1.8	1.3-1.8	0.2-0.4	0.[illegible].7	150,150	150,150,150	26,28,30	27,72,72	5	10
	MC	0.6-1.2	0.2-1.2	0.4-0.6	0.3-0.6	1.8-2.5	1.8-2.2	0.5-0.8	0.[illegible].8	150,150,150	150,150,150	48,54	96,96,127	6	10
	BC	1.1-1.2	0.8-1.4	0.4-0.8	0.4-0.8	1.8-2.8	2.1-2.3	0.6-0.8	0.4-0.8	150,150,150	150,150,150	-	72,72,120	7	13
	TE	0.4-1.1	0.6-1.2	0.2-0.6	0.2-0.6	1.8-1.9	1.8-2.0	0.3-0.6	0.3-0.6	150,150,150	150,150,150	72,103,103	31,48,72	2	3
	ME	0.6-1.2	1.0-1.2	0.4-0.8	0.5-0.8	2.0-2.5	2.1-3.2	0.5-0.8	0.4-0.8	103,150,150	150,150,150	-	48,96,96	6	11
	BE	0.8-1.4	0.4-1.2	0.5-1.0	0.4-0.8	2.0-2.2	2.5-2.8	0.6-0.9	0.4-0.8	150,150	150,150,150	-	55,72,96	6	13
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
6	TC	0.4-1.1	0.3-0.9	0.1-0.3	0.1-0.3	1.5-1.8	1.7-1.9	0.2-0.5	0.2-0.4	150,150,150	150,150,150	48,48,48	48,55,75	4	7
	MC	0.6-1.1	0.4-1.2	0.1-0.3	0.2-0.4	1.8-2.2	1.9-2.2	0.2-0.6	0.2-0.5	150,150,150	150,150,150	24,96,96	72,72,96	4	10
	BC	0.8-1.2	0.6-1.2	0.1-0.3	0.2-0.6	1.8-2.1	1.8-2.3	0.3-0.7	0.1-0.5	150,150,150	150,150,150	48,72,79	48,55,72	3	11
	TE	0.6-0.9	0.4-1.0	0.1-0.3	0.1-0.4	1.5-1.8	1.8-2.2	0.2-0.5	0.2-0.4	150,150,150	150,150,150	24,48,77	53,77,77	4	8
	ME	0.8-1.3	0.3-1.1	0.1-0.3	0.2-0.5	1.9-2.1	1.9-2.2	0.3-0.8	0.2-0.5	150,150,150	150,150,150	48,55,120	29,55,55	4	10
	BE	0.6-1.2	0.4-1.2	0.1-0.3	0.2-0.6	2.0-2.7	1.6-2.3	0.2-0.7	0.2-0.6	150,150,150	150,150,150	24,96,96	48,48,51	3	11
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

(1) Pack position code - T-top, M-middle, B-bottom, C-center and E-edge
(2) All tests listed as 150 hours were discontinued - no visible coating failure
* Indicate data for 2" x 2" coupons - all other values for 1/2" x 1/2" coupons

TABLE 25

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens Cr-Ti Coated in 8 Hours at 2300°F and Silicon Coated in 4 Hours at 2000°F in the 7-1/2" Diameter x 18" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
1	TC	0.3-0.4	0.2-0.4	0-0.1	0-0.3	1.0-1.2	0.9-1.1	0-0.1	0.1-0.2	150,150,150	150,150,150	24,24,28	-	1	2
	MC	0.4-0.7	0.4-0.7	0.1-0.3	0.3-0.5	1.1-1.3	1.1-1.3	0-0.1	0.1-0.3	150,150,150	150,150,150	52,58,76	52,76,76	1	2
	BC	0.2-0.6	0.4-0.6	0.3-0.5	0-0.3	1.2-1.5	1.2-1.4	0.2-0.3	0.2-0.4	150,150,150	150,150,150	52,58,56	28,28,76	2	2
	TE	0.3-0.6	0.3-0.5	0-0.3	0.3-0.6	1.3-1.8	1.5-1.8	0.1-0.3	0.1-0.2	150,150,150	77,150,150	24,28,52	52,52,52	1	2
	ME	0.3-0.7	0.3-0.7	0.5-0.9	0.3-0.5	1.7-1.9	1.6-2.0	0.2-0.3	0.3-0.6	150,150,150	150,150,150	100,100,124	76,76,105	1	4
	BE	0.2-0.6	0.2-0.6	0.5-0.7	0.3-0.7	1.7-1.9	1.5-1.8	0.1-0.3	0.2-0.5	150,150,150	150,150,150	76,76,100	57,58,76	1	2
	*MC	-	-	-	-	-	-	-	-	-	104,150	-	-	-	-
2	TC	0.2-0.4	0.1-0.4	0.2-0.4	0.2-0.4	1.4-1.6	1.5-1.7	0.1-0.3	0.1	150,150,150	150,150,150	32,32,48	5,7,48	2	3
	MC	0.2-0.6	0.2-0.7	0.4-0.6	0.3-0.5	1.4-1.6	1.4-1.6	0.2-0.5	0.2-0.3	150,150,150	150,150,150	77,96,72	53,54,56	3	4
	BC	0.2-0.6	0.4-0.6	0.5-0.7	0.2-0.4	1.8-2.0	1.6-1.8	0.2-0.4	0.1-0.3	150,150,150	150,150,150	75,79,96	48,53,54	2	4
	TE	0.2-0.6	0.3-0.6	0.5-0.7	0.4-0.6	1.6-1.8	1.2-1.7	0.2-0.5	0.1-0.4	150,150,150	150,150,150	48,48,74	48,48,45	2	5
	ME	0.4-0.8	0.6-0.8	0.7-1.0	0.5-0.7	1.9-2.1	1.7-1.9	0.8-1.0	0.2-0.5	150,150,150	150,150,150	103,126,150	53,72,72	2	7
	BE	0.2-0.6	0.5-0.6	0.8-1.0	0.3-0.6	2.0-2.1	1.9-2.0	0.4-0.6	0.2-0.5	150,150,150	150,150,150	103,126,149	48,54,72	2	3
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
3	TC	0.2-0.4	0.2-0.4	0.2-0.4	0.1-0.3	1.3-1.5	1.4-1.6	0.1-0.4	0.1-0.3	150,150,150	150,150,150	27,48,72	48,50,50	2	3
	MC	0.1-0.6	0.5-0.6	0.3-0.5	0.2-0.6	1.2-1.6	1.3-1.5	0.1-0.4	0.2-0.6	150,150,150	150,150,150	48,74,96	48,51,72	3	5
	BC	0.3-0.5	0.2-0.6	0.2-0.5	0.2-0.6	1.6-1.8	1.7-1.9	0.1-0.5	0.1-0.4	150,150,150	150,150,150	72,72,75	24,48,51	2	3
	TE	0.1-0.4	0.3-0.6	0.3-0.5	0.2-0.4	1.8-2.0	1.7-1.9	0.1-0.4	0.1-0.4	150,150,150	150,150,150	48,53,96	48,55,56	1	3
	ME	0.3-0.6	0.4-0.8	0.5-0.7	0.5-1.0	1.4-1.9	1.7-1.9	0.5-1.0	0.4-0.7	150,150,150	150,150,150	52,96,120	48,72,72	4	7
	BE	0.3-0.5	0.4-0.6	0.5-0.8	0.3-0.8	1.9-2.1	1.9-2.1	0.2-0.6	0.1-0.4	150,150,150	150,150,150	48,96,150	51,55,72	2	5
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
4	TC	0.2-0.4	0.1-0.4	0.2-0.5	0.2-0.5	1.5-1.8	1.7-1.8	0-0.2	0.1-0.2	150,150,150	150,150,150	29,48,48	48,48,48	1	3
	MC	0.1-0.6	0.4-0.6	0.3-0.7	0.2-0.5	1.8-2.2	1.9-2.1	0.3-0.6	0.2-0.6	150,150,150	150,150,150	48,48,56	24,48,76	2	3
	BC	0.4-0.7	0.5-0.6	0.3-0.6	0.2-0.6	1.6-2.1	1.9-2.1	0.3-0.6	0.2-0.3	150,150,150	150,150,150	76,81,106	52,52,53	1	2
	TE	0.3-0.6	0.2-0.4	0.3-0.8	0.2-0.6	1.4-1.9	1.8-1.9	0.2-0.5	0.2-0.5	150,150,150	150,150,150	48,48,72	48,48,52	1	1
	ME	0.4-0.8	0.3-0.7	0.6-0.8	0.3-0.7	1.7-2.0	2.1-2.2	0.7-1.0	0.5-0.7	150,150,150	150,150,150	72,72,76	24,50,56	2	2
	BE	0.4-0.6	0.3-0.8	0.6-1.0	0.4-0.8	2.0-2.2	2.0-2.2	0.5-0.3	0.2-0.4	150,150,150	150,150,150	74,83,108	31,52,58	6	2
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

TABLE 25 (CONTINUED)

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 8 Hours at 2300°F and Silicon Coated in 4 Hours at 2000°F in the
7-1/2" Diameter x 18" High Retort

		Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
Batch No.	Pack(1) Position	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
5	TC	0.3-0.4	0.2-0.4	0.2-0.5	0.02	1.0-1.5	1.2-1.4	0.1-0.2	0.2-0.4	150,150,150	150,150,150	51,72,72	24,48,48	1	1
	MC	0.3-0.5	0.3-0.6	0.3-0.5	0.3-0.5	1.2-1.4	1.3-1.5	0.2-0.5	0.1-0.4	150,150,150	150,150,150	31,48,48	72,72,72	2	2
	BC	0.3-0.6	0.4-0.6	0.3-0.5	0.2-0.5	1.6-1.8	1.7-1.9	0.2-0.5	0.3-0.5	150,150,150	150,150,150	48,55,72	26,26,72	3	8
	TE	0.3-0.4	0.3-0.4	0.3-0.5	0.3-0.5	1.6-1.8	1.6-1.8	0.1-0.2	0.1-0.4	150,150,150	150,150,150	48,72,103	48,53,53	1	2
	ME	0.4-0.7	0.4-0.6	0.6-0.8	0.3-0.6	1.6-2.0	1.8-2.0	0.2-0.5	0.4-0.7	150,150,150	150,150,150	48,72,103	48,50,72	2	2
	BE	0.4-0.6	0.4-0.6	0.3-0.6	0.2-0.5	1.7-2.0	1.9-2.1	0.3-0.5	0.3-0.5	150,150,150	150,150,150	48,90,101	72,72,72	2	4
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
6	TC	0.2-0.4	0.3-0.5	0.1-0.3	0.1-0.4	1.1-1.3	1.2-1.5	0.1-0.2	0.2-0.4	150,150,150	150,150,150	48,72,72	48,48,48	3	2
	MC	0.3-0.5	0.4-0.6	0.3-0.7	0.2-0.6	1.3-1.5	1.4-1.6	0.3-0.5	0.2-0.5	150,150,150	150,150,150	48,96,102	48,48,48	2	2
	BC	0.3-0.5	-	0.2-0.5	-	1.0-1.5	1.5-1.7	0.2-0.4	0.2-0.4	150,150,150	150,150,150	96,96,120	32,48,48	2	3
	TE	0.3-0.5	0.4-0.6	0.5-0.7	0.2-0.4	1.5-1.8	1.2-1.6	0.1-0.2	0.2-0.4	150,150,150	150,150,150	72,48,48	48,52,56	3	2
	ME	0.3-0.5	0.3-0.7	0.4-0.6	0.3-0.5	1.7-2.0	1.5-2.0	0.3-0.5	0.2-0.4	150,150,150	150,150,150	96,102,120	48,50,52	2	4
	BE	0.3-0.6	0.4-0.6	0.3-0.5	0.4-0.6	1.7-2.0	1.5-1.7	0.2-0.5	0.1-0.4	150,150,150	150,150,150	48,26,72	48,51,54	3	5
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

(1) Pack position code - T-top, M-middle, B-bottom, C-center and E-edge
(2) All tests listed as 150 hours were discontinued - no visible coating failure
* Indicates data for 2" x 2" coupons - all other values for 1/2" x 1/2" coupons

TABLE 26

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 8 Hours at 2300°F and Silicon Coated in 6 Hours at 2100°F in the
7-1/2" Diameter x 18" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
1	TC	0.3-0.4	0.1-0.3	0.2-0.4	0.2-0.4	1.3-2.5	1.4-1.8	0.1	0.1-0.2	150,150,150	150,150,150	31,31,50	31,52,56	2	2
	MC	0.5-0.6	0.2-0.4	0.4-0.6	0.3-0.6	1.5-1.8	1.5-2.0	0.3-0.5	0.2-0.4	150,150,150	150,150,150	54,54,54	24,72,77	4	5
	BC	0.2-0.6	0.2-0.5	0.3-0.6	0.5-0.6	1.7-1.9	1.8-2.0	0.2-0.3	0.2-0.4	150,150,150	150,150,150	54,54,56	54,56,72	5	4
	TE	0.3-0.5	0.3-0.5	0.4-0.6	0.3-0.6	2.2-2.5	1.7-2.0	0.1-0.5	0.1-0.2	150,150,150	150,150,150	26,31,48	24,48,72	2	2
	ME	0.6-0.8	0.6-0.8	0.6-0.8	0.4-0.6	2.3-2.6	2.0-2.8	0.2-0.5	0.1-0.2	150,150,150	150,150,150	96,126,126	32,72,72	3	6
	BE	0.4-0.6	0.6-0.7	0.6-0.8	0.3-0.6	2.3-2.5	1.8-2.5	0.2-0.4	0.1-0.2	150,150,150	150,150,150	56,72,72	54,54,72	4	4
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
2	TC	0.2-0.4	0.1-0.4	0.2-0.4	0.2-0.4	1.0-1.7	1.5-1.7	0.2-0.4	0.1-0.2	150,150,150	150,150,150	48,48,48	24,48,48	2	2
	MC	0.2-0.6	0.2-0.7	0.4-0.6	0.3-0.5	1.6-1.9	1.7-2.0	0.2-0.6	0.4-0.6	150,150,150	150,150,150	54,54,54	24,48,72	3	8
	BC	0.2-0.6	0.4-0.6	0.5-0.7	0.2-0.4	1.3-1.7	1.8-2.0	0.3-0.7	0.1-0.4	150,150,150	150,150,150	72,72,72	32,48,72	5	6
	TE	0.2-0.6	0.3-0.6	0.5-0.7	0.4-0.6	2.0-2.4	1.0-2.2	0.1-0.3	0.1-0.2	150,150,150	150,150,150	48,48,48	48,48,51	6	6
	ME	0.4-0.8	0.6-0.8	0.7-1.0	0.5-0.7	2.4-2.8	2.5-3.0	0.4-0.6	0.4-0.7	150,150,150	150,150,150	80,96,96	53,72,72	6	6
	BE	0.2-0.6	0.5-0.6	0.8-1.0	0.3-0.6	2.0-2.4	2.2-2.6	0.2-0.5	0.1-0.4	150,150,150	150,150,150	56,96,101	52,72,72	6	7
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
3	TC	0.2-0.4	0.2-0.4	0.2-0.4	0.1-0.3	1.3-1.5	1.2-1.5	0.1-0.3	0.2-0.5	150,150,150	150,150,150	29,29,30	24,24,72	2	3
	MC	0.1-0.6	0.5-0.6	0.3-0.5	0.2-0.6	1.6-1.8	1.6-1.8	0.2-0.6	0.1-0.2	150,150,150	150,150,150	48,53,72	24,29,48	4	4
	BC	0.3-0.5	0.2-0.6	0.2-0.5	0.2-0.6	1.5-1.8	1.5-1.8	0.2-0.4	0.1-0.4	150,150,150	150,150,150	48,48,53	48,48,48	3	4
	TE	0.1-0.4	0.3-0.6	0.3-0.5	0.2-0.4	2.2-2.5	2.2.2.5	0-0.1	0.1-0.2	150,150,150	150,150,150	8,48,72	24,24,48	2	4
	ME	0.3-0.6	0.4-0.8	0.5-0.7	0.5-1.0	2.2-2.5	2.2-2.6	0.2-0.6	0.1-0.4	150,150,150	150,150,150	72,72,77	55,72,72	5	6
	BE	0.3-0.5	0.4-0.6	0.5-0.8	0.3-0.8	2.2-2.5	2.2-2.5	0.2-0.5	0.1-0.3	150,150,150	150,150,150	55,56,77	55,36,96	4	6
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
4	TC	0.2-0.4	0.1-0.4	0.2-0.5	0.2-0.5	1.6-1.8	1.7-1.9	0-0.1	0-0.1	150,150,150	150,150,150	29,29,29	24,24,27	3	3
	MC	0.1-0.6	0.4-0.6	0.3-0.7	0.2-0.5	1.1-1.7	2.4-2.8	0.1-0.3	0-0.2	150,150,150	150,150,150	48,48,53	48,51,72	3	5
	BC	0.4-0.7	0.5-0.6	0.3-0.6	0.2-0.6	1.6-2.0	2.0-2.6	0.1-0.4	0.1-0.4	150,150,150	150,150,150	48,72,72	48,72,124	3	3
	TE	0.3-0.6	0.2-0.4	0.3-0.8	0.2-0.6	2.1-2.5	2.0-2.4	0-0.2	0-0.1	150,150,150	150,150,150	31,48,48	27,48,50	3	4
	ME	0.4-0.8	0.5-0.7	0.6-0.8	0.3-0.7	1.6-2.2	2.4-2.8	0.1-0.4	0.1-0.4	150,150,150	150,150,150	75,101,120	50,51,72	3	5
	BE	0.4-0.6	0.3-0.8	0.6-1.0	0.4-0.8	2.0-2.4	2.3-2.5	0.1-0.4	0.1-0.4	150,150,150	150,150,150	48,100,107	54,72,80	3	6
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

TABLE 26 (Continued)

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 8 Hours at 2300° F and Silicon Coated in 6 Hours at 2100° F in the
7-1/2" Diameter x 18" High Retort

		Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000° F		2500° F		2700° F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
Batch No.	Pack(1) Position	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
5	TC	0.3-0.4	0.2-0.4	0.2-0.5	0-0.2	1.0-1.7	1.2-1.4	0-0.2	0-0.1	150,150,150	150,150,150	48,72,72	24,48,48	2	2
	MC	0.3-0.5	0.3-0.6	0.3-0.5	0.3-0.5	1.6-2.2	1.7-1.9	0.1-0.4	0.1-0.3	150,150,150	150,150,150	24,48,56	48,48,72	2	4
	BC	0.3-0.6	0.4-0.6	0.3-0.5	0.2-0.5	1.3-2.0	1.8-2.0	0.1-0.3	0.1-0.3	150,150,150	150,150,150	48,48,24	48,72,77	2	3
	TE	0.3-0.4	0.3-0.4	0.3-0.5	0.3-0.5	2.0-2.4	1.9-2.1	0-0.2	0-0.1	150,150,150	150,150,150	24,72,77	48,48,48	2	3
	ME	0.4-0.7	0.4-0.6	0.6-0.8	0.3-0.6	2.0-2.6	2.3-2.5	0.2-0.6	0.1-0.2	150,150,150	150,150,150	72,72,100	72,72,72	2	4
	BE	0.4-0.6	0.4-0.6	0.3-0.6	0.2-0.5	2.0-2.5	2.2-2.5	0.1-0.3	0.2-0.4	150,150,150	150,150,150	96,24,24	48,48,90	3	4
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
6	TC	0.2-0.4	0.3-0.5	0.1-0.3	0.1-0.4	1.6-1.8	1.6-1.8	0.1-0.3	0.2-0.4	150,150,150	150,150,150	53,72,72	48,48,51	2	3
	MC	0.3-0.5	0.4-0.6	0.3-0.7	0.2-0.6	1.6-2.0	1.6-1.8	0.1-0.3	0.1-0.3	150,150,150	150,150,150	24,48,80	48,48,53	3	5
	BC	0.3-0.5	-	0.2-0.5	-	1.5-2.0	1.7-2.0	0.1-0.3	0.1-0.3	150,150,150	150,150,150	48,48,72	48,48,48	3	4
	TE	0.3-0.5	0.4-0.6	0.5-0.7	0.2-0.4	2.2-2.5	2.0-2.2	0.1-0.2	0.1-0.3	150,150,150	150,150,150	56,72,96	48,48,48	2	3
	ME	0.3-0.5	0.3-0.7	0.4-0.6	0.3-0.5	2.0-2.4	2.1-2.3	0.2-0.5	0.1-0.3	150,150,150	150,150,150	55,96,127	53,53,79	3	3
	BE	0.3-0.6	0.4-0.6	0.3-0.5	0.4-0.6	2.0-2.4	2.2-2.4	0.1-0.3	0.1-0.2	150,150,150	150,150,150	77,96,96	48,48,75	3	5
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

(1) Pack position code - T-top, M-middle, B-bottom, C-center and E-edge
(2) All tests listed as 150 hours were discontinued - no visible coating failure
* Indicates data for 2" x 2" coupons - all other values for 1/2" x 1/2" coupons

TABLE 27

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 10 Hours at 2350°F and Silicon Coated in 6 Hours at 2100°F in the
7-1/2" Diameter x 18" High Retort

		Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
Batch No.	Pack(1) Position	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
1	TC	0.3-0.6	0.4-0.6	0.1-0.3	0.2-0.4	1.4-1.9	1.6-1.8	0.3-0.6	0.2-0.5	150,150,150	150,150,150	29,48,51	22,22,22	5	4
	MC	0.7-1.2	0.6-1.1	0.2-0.4	0.3-0.5	1.7-2.0	2.0-2.2	0.4-0.8	0.3-0.7	150,150,150	150,150,150	72,72,77	22,22,50	6	6
	BC	0.4-1.0	0.7-0.9	0.3-0.5	0.2-0.6	1.8-2.0	2.0-2.4	0.3-0.7	0.2-0.6	150,150,150	150,150,150	48,53,72	52,52,94	5	6
	TE	0.3-0.6	0.4-0.6	0.3-0.6	0.2-0.4	2.0-2.4	2.0-2.4	0.1-0.3	0.2-0.5	150,150,150	150,150,150	51,53,72	70,70,77	5	5
	ME	0.8-1.1	0.4-1.2	0.3-0.7	0.4-0.7	2.7-3.0	2.9-3.3	0.3-0.7	0.3-0.7	127,150,150	150,150,150	96,120,126	74,94,94	4	14
	BE	0.4-0.9	0.4-0.8	0.3-0.6	0.5-0.8	2.1-2.3	2.5-2.8	0.3-0.8	0.1-0.4	150,150,150	150,150,150	96,120,120	52,70,94	3	7
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
2	TC	0.3-0.6	0.4-0.6	0.1-0.3	0.2-0.4	1.6-2.0	1.3-1.8	0.1-0.3	0.1-0.2	95,150,150	150,150,150	48,48,48	55,72,72	3	6
	MC	0.7-1.2	0.6-1.1	0.2-0.4	0.3-0.5	1.8-2.2	1.8-2.0	0.5-0.8	0.2-0.6	150,150,150	150,150,150	72,96,120	48,72,72	5	10
	BC	0.4-1.0	0.7-0.9	0.3-0.5	0.2-0.6	1.8-2.5	2.2-2.4	0.3-0.6	0.2-0.4	150,150,150	150,150,150	48,72,96	48,48,72	5	4
	TE	0.3-0.6	0.4-0.6	0.3-0.6	0.2-0.4	1.8-2.5	2.3-2.8	0.1-0.3	0.1-0.2	150,150,150	150,150,150	48,72,96	72,72,96	4	5
	ME	0.8-1.1	0.4-1.2	0.3-0.7	0.4-0.7	2.3-3.0	2.2-2.8	0.5-0.8	0.4-0.8	122,150,150	150,150,150	120,144,149	72,96,96	4	11
	BE	0.4-0.9	0.4-0.8	0.3-0.6	0.5-0.8	2.3-3.0	2.8-3.0	0.4-0.8	0.4-0.6	150,150,150	150,150,150	96,120,144	56,72,72	3	7
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
3	TC	0.5-0.6	0.4-0.6	0.2-0.4	0.1-0.2	1.8-2.0	1.7-2.0	0.1-0.3	0.1-0.3	150,150,150	150,150,150	48,48,50	48,48,48	3	3
	MC	0.7-1.0	0.4-1.1	0.3-0.5	0.5-0.7	2.0-2.2	2.2-2.7	0.4-0.7	0.1-0.4	150,150,150	150,150,150	80,96,96	55,72,96	11	7
	BC	0.6-1.0	0.6-1.1	0.2-0.5	0.2-0.4	2.0-2.5	2.2-2.4	0.2-0.4	0.1-0.5	150,150,150	150,150,150	78,80,96	72,72,78	6	4
	TE	0.4-0.6	0.3-0.6	0.4-0.6	0.2-0.4	2.7-3.0	2.4-3.0	0.1-0.[illegible]	0.1-0.3	150,150,150	96,150,150	53,53,53	48,55,72	7	3
	ME	0.5-1.2	0.5-1.0	0.5-0.8	0.4-0.7	2.8-2.9	3.0-3.2	0.8-1.0	0.1-0.5	150,150,150	150,150,150	53,96,101	78,96,120	17	5
	BE	0.7-1.0	0.8-1.1	0.4-0.7	0.3-0.6	2.5-2.9	2.8-3.0	0.2-0.5	0.2-0.5	150,150,150	150,150,150	72,72,96	78,96,120	10	5
	*MC	-	-	-	-	-	-	-	-	-	72,150	-	-	-	-
4	TC	0.5-0.6	0.4-0.6	0.2-0.4	0.1-0.2	1.7-2.0	1.8-2.4	0.1-0.3	0.1-0.3	150,150,150	150,150,150	29,48,48	24,24,72	5	7
	MC	0.7-1.0	0.4-1.1	0.3-0.5	0.5-0.7	1.8-2.0	1.9-2.1	0.2-0.4	0.1-0.3	150,150,150	150,150,150	48,120,96	48,48,72	8	10
	BC	0.6-1.0	0.6-1.1	0.2-0.5	0.2-0.4	1.9-2.0	2.1-2.4	0.3-0.6	0.1-0.5	150,150,150	150,150,150	48,72,125	29,48,72	7	10
	TE	0.4-0.6	0.3-0.6	0.4-0.6	0.2-0.4	2.2-2.5	2.3-2.8	0.1-0.2	0.1-0.3	150,150,150	74,80,150	72,77,102	32,48,96	3	14
	ME	0.9-1.2	0.5-1.0	0.5-0.8	0.4-0.7	2.5-2.8	2.3-2.9	0.5-0.8	0.1-0.4	150,150,150	150,150,150	120,124,126	96,120,144	6	13
	BE	0.7-1.0	0.8-1.1	0.4-0.7	0.3-0.6	2.6-3.0	2.5-3.0	0.3-0.5	0.1-0.5	150,150,150	125,150,150	48,101,125	72,72,96	6	12
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

TABLE 27 (Continued)

Metallographic and Cyclic Oxidation Results for Reliability Study - B-66 and D-43 Alloy Specimens
Cr-Ti Coated in 10 Hours at 2350°F and Silicon Coated in 6 Hours at 2100°F in the
7-1/2" Diameter x 18" High Retort

Batch No.	Pack(1) Position	Coating Thickness Measurements - Mils								Cyclic Oxidation Protective Life - Hours(2)					
		Cr-Ti Coating				Cr-Ti-Si Coating				2000°F		2500°F		2700°F	
		Overlay		Diffusion Zone		Overlay		Diffusion Zone							
		B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43	B-66	D-43
5	TC	0.3-0.5	0.4-0.6	0.2-0.4	0.1-0.4	2.0-2.2	2.0-2.3	0.1-0.3	0-0.2	150,150,150	150,150,150	48,55,72	48,48,72	5	7
	MC	0.6-1.0	0.7-0.9	0.2-0.5	0.1-0.4	2.0-2.4	2.1-2.6	0.2-0.4	0.1-0.3	150,150,150	150,150,150	72,79,96	44,48,96	5	5
	BC	0.6-0.8	0.3-1.0	0.3-0.5	0.2-0.6	2.2-2.5	2.5-2.8	0.2-0.4	0.1-0.4	150,150,150	150,150,150	77,77,79	48,77,77	4	17
	TE	0.3-0.8	0.4-0.9	0.2-0.5	0.1-0.4	2.2-2.4	2.5-3.0	0.1-0.3	0-0.2	150,150,150	120,150,150	96,96,102	72,76,99	3	4
	ME	0.7-1.0	0.5-0.8	0.2-0.6	0.2-0.5	2.5-2.8	2.8-3.1	0.2-0.4	0.1-0.3	150,150,150	150,150,150	72,120,120	48,48,103	3	5
	BE	0.1-1.0	0.4-0.9	0.4-0.7	0.3-0.6	2.6-2.8	2.7-3.0	0.1-0.3	0.1-0.4	150,150,150	150,150,150	96,96,96	72,79,96	3	14
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-
6	TC	0.3-0.5	0.4-0.6	0.2-0.4	0.1-0.4	2.0-2.2	1.8-2.0	0-0.1	0-0.1	48,150,150	150,150,150	48,48,48	48,72,96	2	5
	MC	0.6-1.0	0.7-0.9	0.2-0.5	0.1-0.4	2.0-2.4	2.3-2.6	0.1-0.4	0.2-0.4	150,150,150	150,150,150	72,72,74	48,51,72	3	6
	BC	0.6-0.8	0.3-1.0	0.3-0.5	0.2-0.6	2.4-2.6	2.5-2.8	0.1-0.3	0-0.1	150,150,150	150,150,150	96,96,103	76,77,79	2	19
	TE	0.3-0.8	0.4-0.9	0.2-0.5	0.1-0.4	2.5-2.9	2.5-2.8	0-0.1	0-0.1	48,150,150	97,97,150	48,74,77	55,96,120	3	6
	ME	0.7-1.0	0.5-0.8	0.2-0.6	0.2-0.5	2.5-2.8	2.8-3.1	0.4-0.6	0-0.2	150,150,150	150,150,150	120,125,149	72,101,144	2	7
	BE	0.1-1.0	0.4-0.9	0.4-0.7	0.3-0.6	2.8-3.0	2.5-2.9	0.3-0.6	0.1-0.3	150,150,150	150,150,150	98,100,120	72,96,96	3	10
	*MC	-	-	-	-	-	-	-	-	-	150,150	-	-	-	-

(1) Pack position code - T-top, M-middle, B-bottom, C-center and E-edge
(2) All tests listed as 150 hours were discontinued - no visible coating failure
* Indicates data for 2" x 2" coupons - all other values for 1/2" x 1/2" coupons

In analysing the data obtained for coating thickness it was felt that an average thickness of the diffusion zone could be considered in view of the nature of the variation. In the case of the overlay thickness it was felt that the minimum thickness would be the determining factor with respect to coating protective life (extremely thick coating areas randomly distributed over the surface of the coated sheet would not increase protective capability of the coating). Therefore, the data analysis was made utilizing only minimum values for overlay thickness. When considering the total Cr-Ti-Si coating thickness the minimum overlay thickness was added to the average diffusion zone thickness to obtain a total thickness value.

The first consideration involved in analysing the coating thickness data was the determination of the relative effects of the various process parameters on resultant coating thickness. These variables included substrate alloy, specimen position in the retort, retort size and silicon cycle process parameters. The random balance analysis technique was selected to analyse the data. Figures 29 through 34 are scatter diagrams showing graphically the variation in (a) Cr-Ti-Si coating overlay thickness and (b) Cr-Ti-Si coating overlay plus diffusion zone thickness for the various process variables. Based on the median differentials which are noted on the diagrams, the Cr-Ti-Si coating overlay thickness was influenced by all process variables. For the 3" diameter x 8" high retort (Figure 29) the most significant variables were silicon coating parameters and vertical position within the retort. The influence of vertical retort position must be assumed to be temperature variation (and probably pressure variation) within the retort.

Note that horizontal position in the retort had little influence; apparently heat transfer from pack edge to center being sufficient to keep temperature gradients to a minimum. A temperature gradient within the retort would necessarily change the vapor phase composition to some extent thus causing differences in coating deposition rates (highest in hotter areas of retort). A pressure variation could possibly occur in the top of the retort due to volatile elements being pumped off. This could cause lower deposition rates in the top area of the retort.

In the 7-1/2" diameter retort (Figure 30) the effect of the silicon cycle parameters and the vertical position in the retort were much the same as for the smaller retort. In addition, an effect due to horizontal position (either center or edge) was observed, indicating that the center of the retort was at a slightly lower temperature for a longer time than the edge of the retort. Figure 31 is a combination of Figures 29 and 30 and shows the effect of retort size. This effect is seen to be small showing that the coating parameters selected produced nearly equivalent coating thicknesses in each furnace. Note that a slightly heavier coating build up was produced on D-43 alloy for the parameters selected.

The result of combining the diffusion zone thickness with the overlay thickness is demonstrated by Figures 32, 33 and 34. Essentially the same trends are observed as for the overlay thickness only. This points out that the diffusion zone thickness follows the same trend as the overlay thickness, otherwise a change in the relative

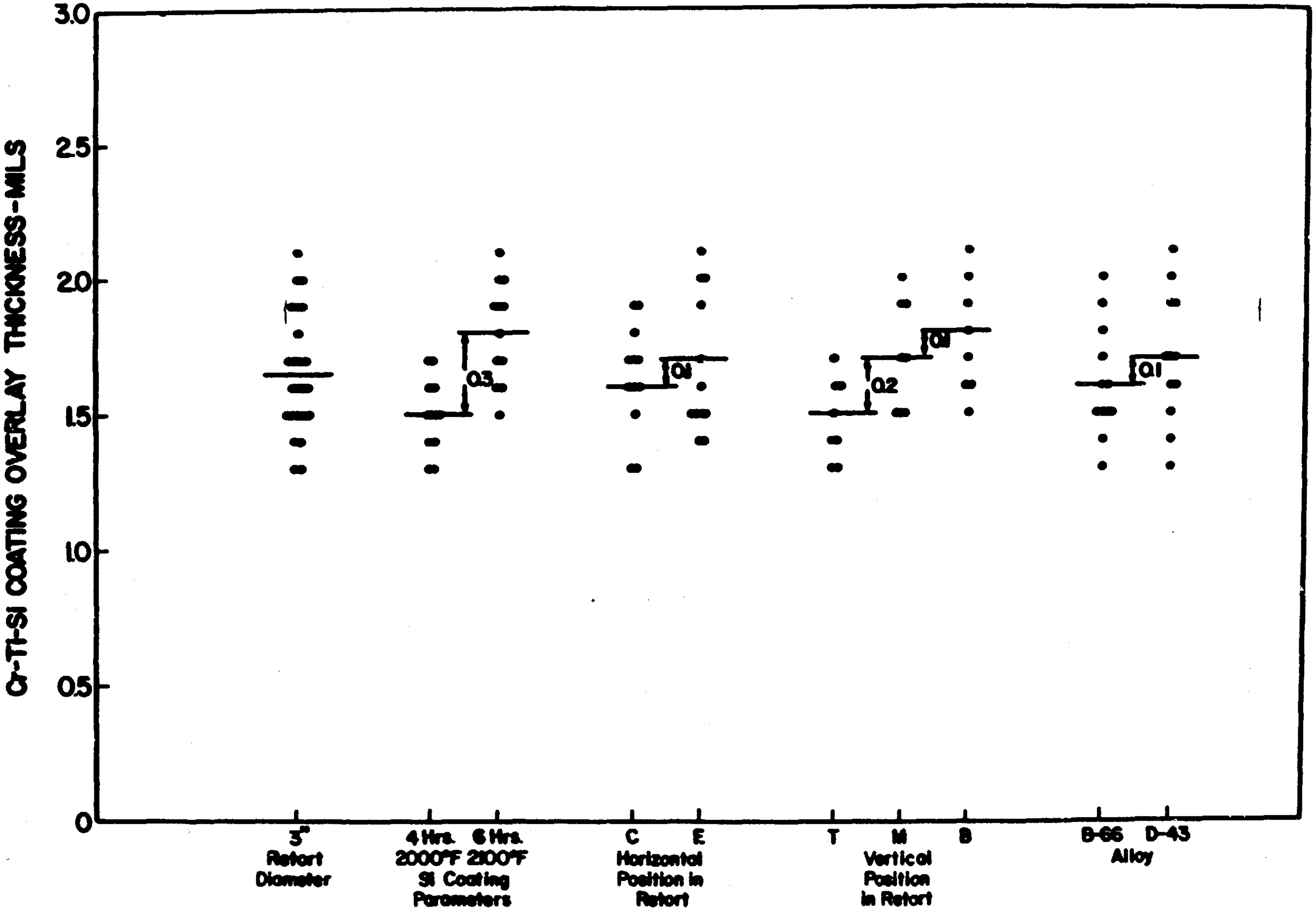


Figure 29 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Thickness for Various Process Variables in the 3" Diameter x 8" High Retort

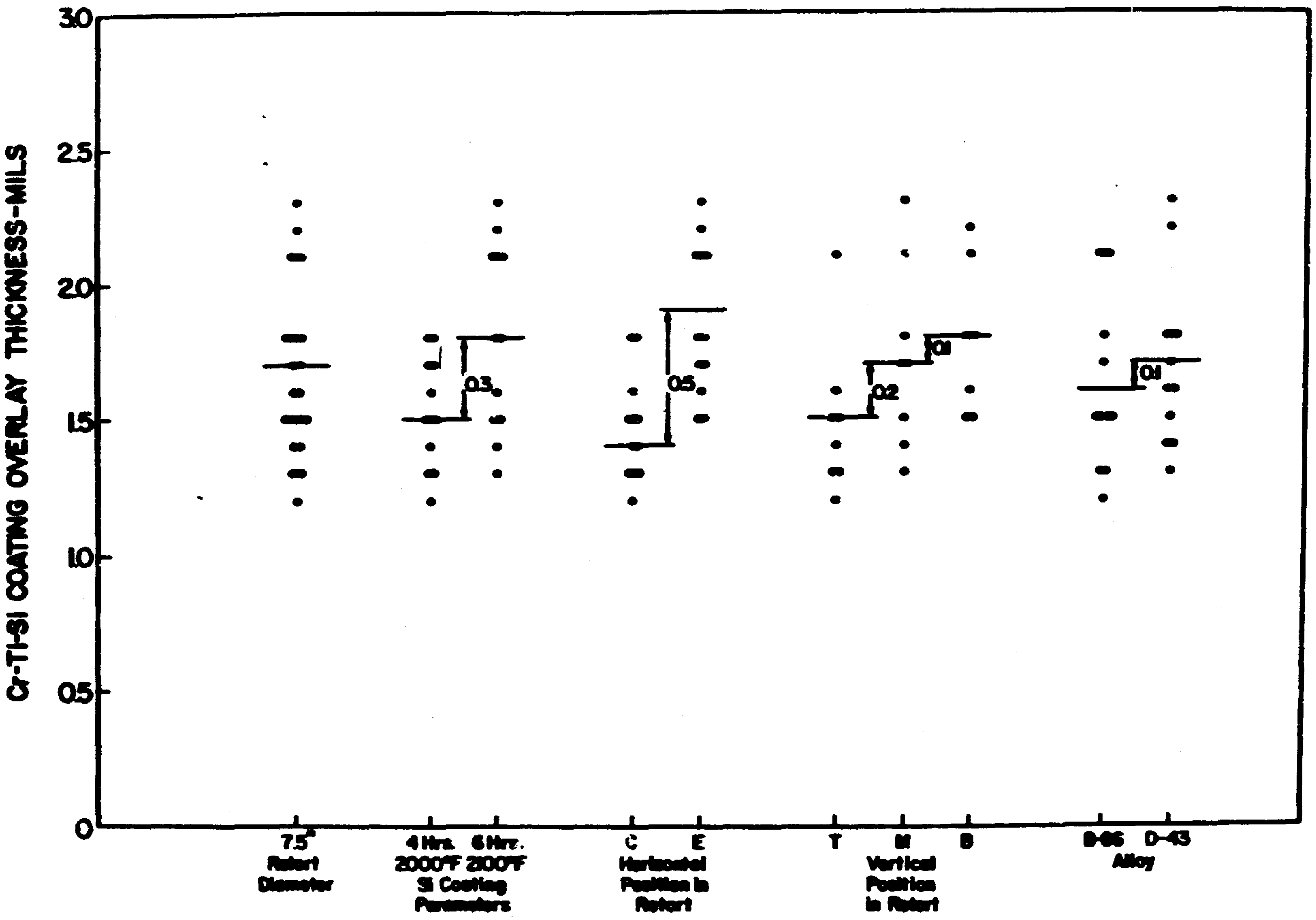


Figure 30 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Thickness for Various Process Variables in the 7-1/2" Diameter x 18" High Retort

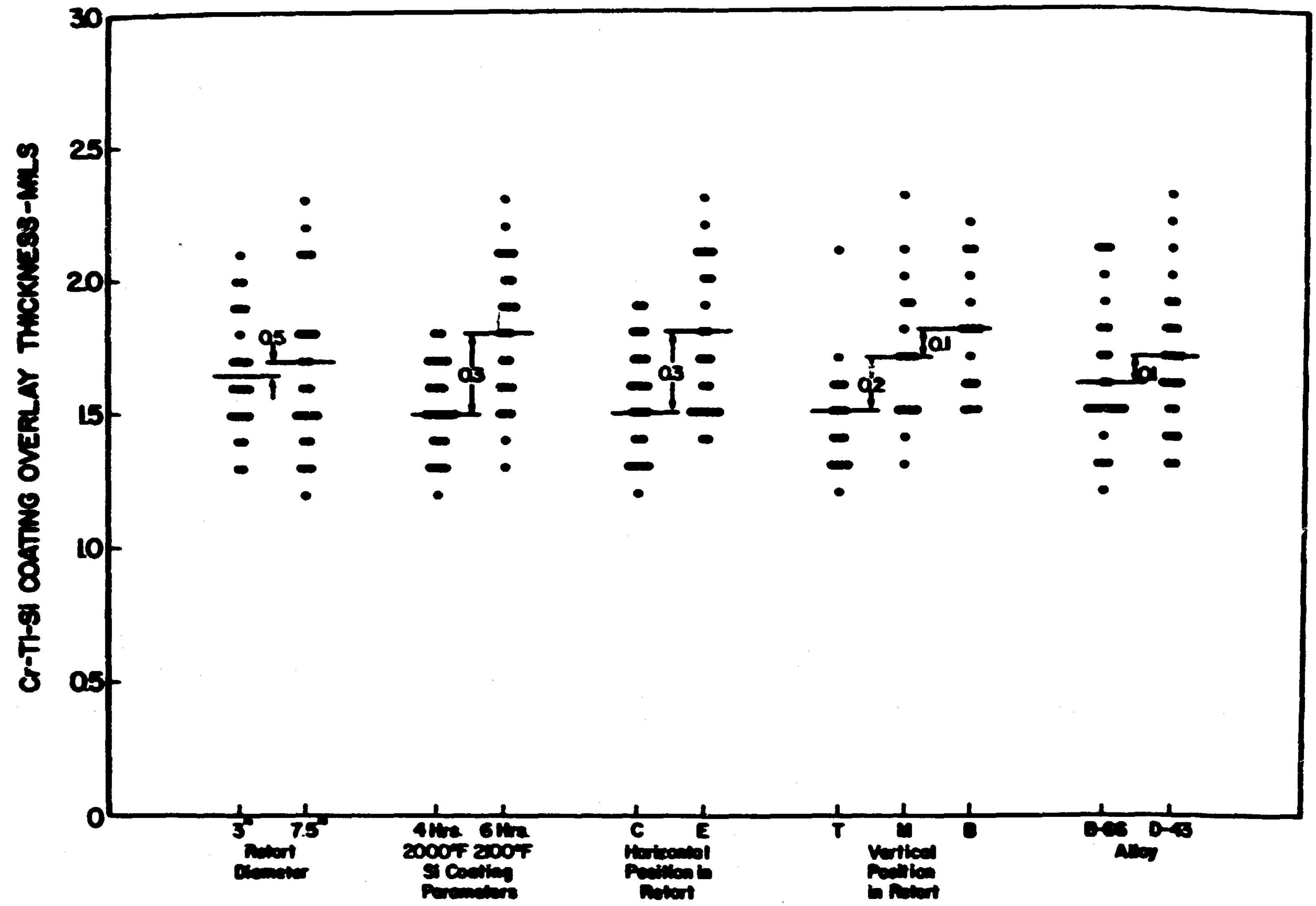


Figure 31 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Thickness for Various Process Variables and Two Retort Sizes

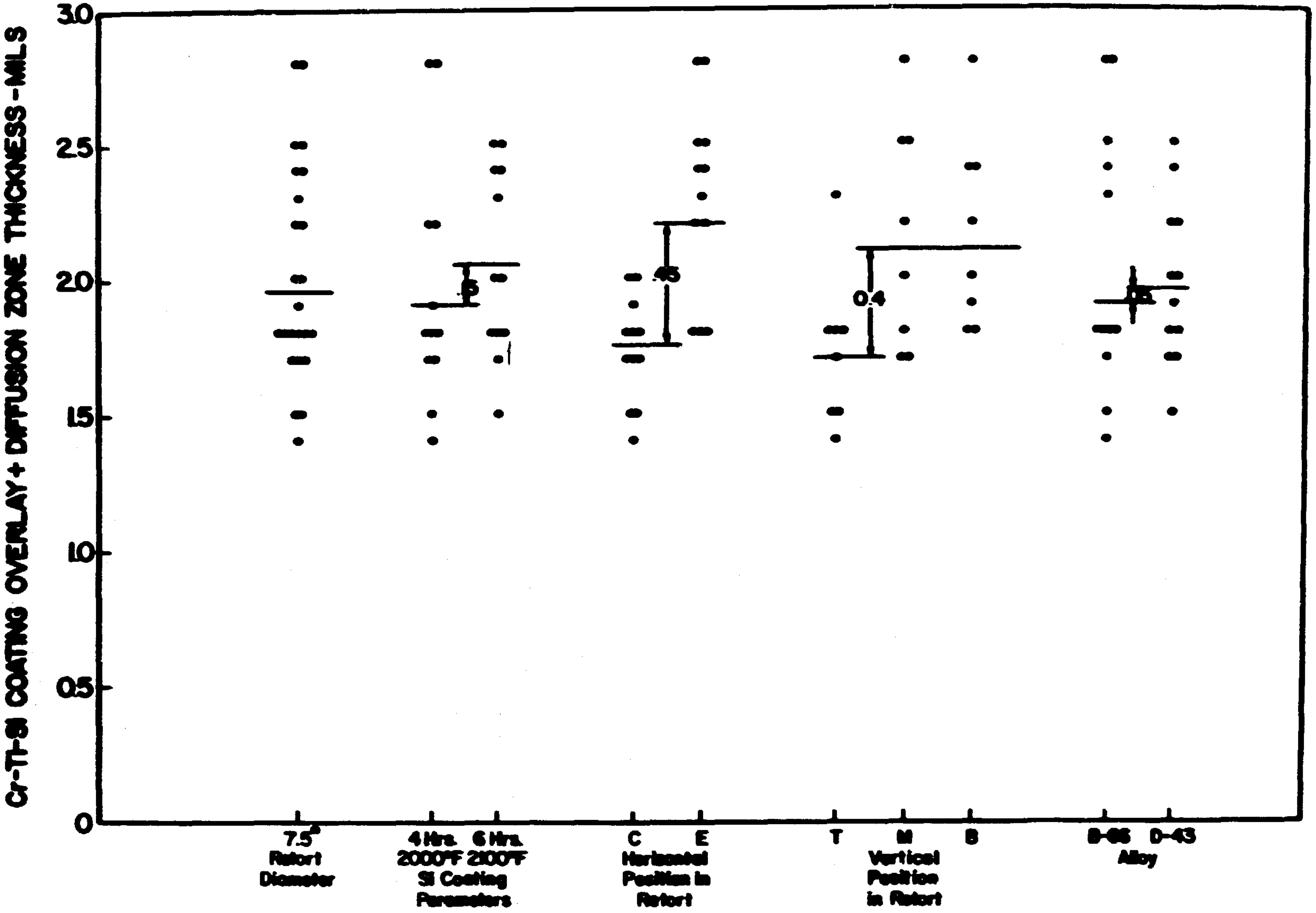


Figure 32 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Plus Diffusion Zone Thickness for Various Process Variables in the 7-1/2" Diameter x 18" High Retort

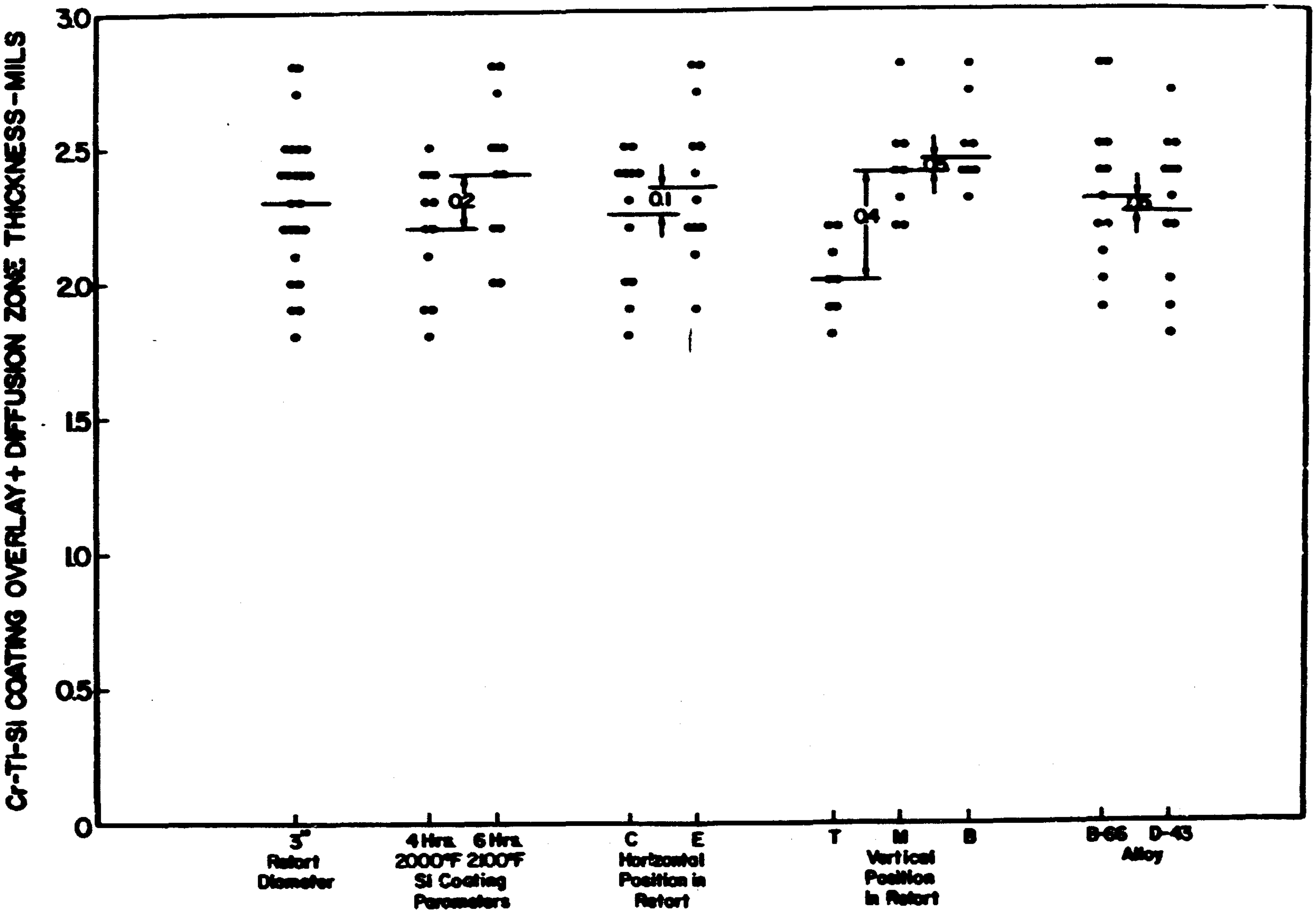


Figure 33 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Plus Diffusion Zone Thickness for Various Process Variables in the 3" Diameter x 8" High Retort

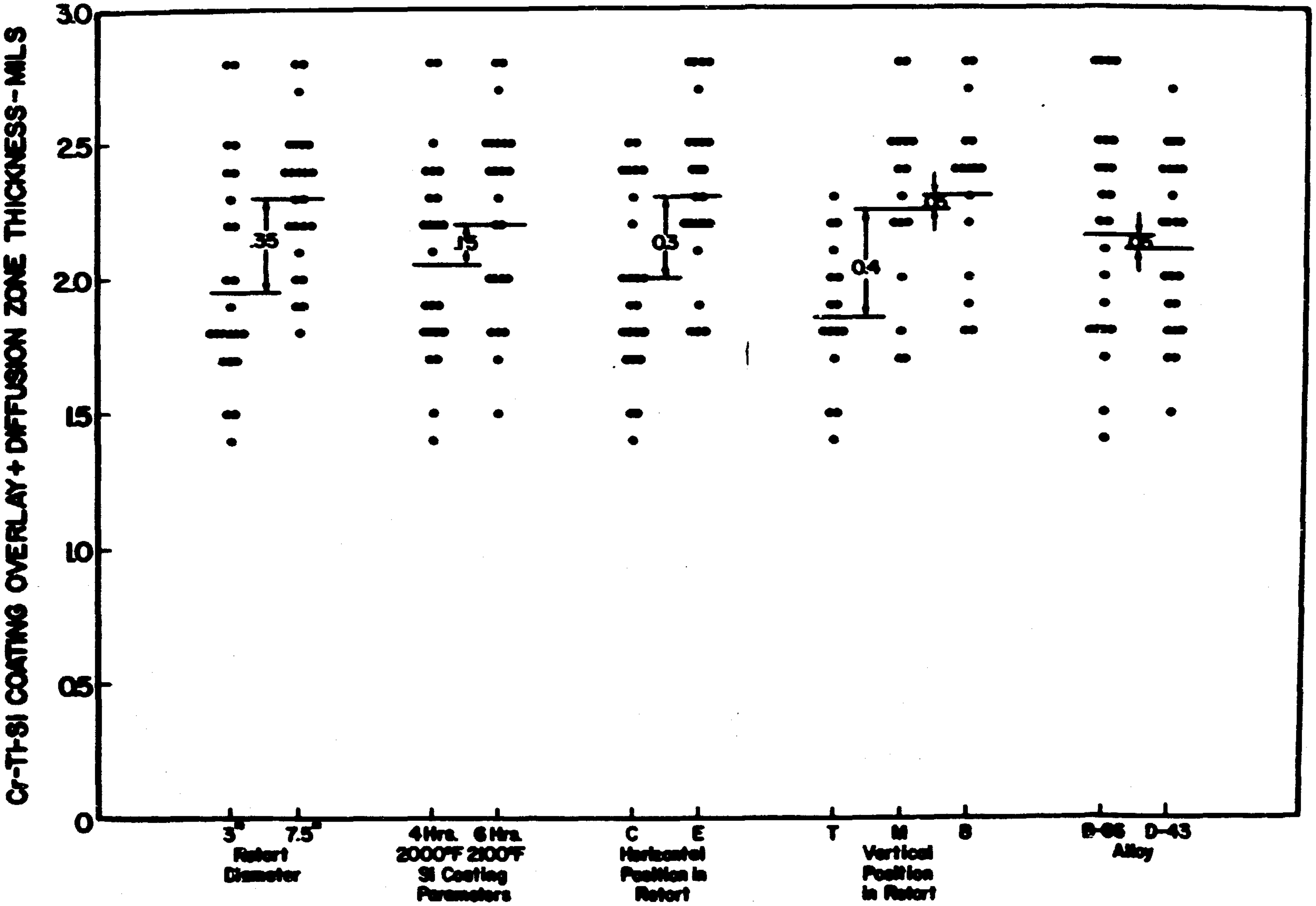


Figure 34 Scatter Diagrams Showing Variation in Cr-Ti-Si Coating Overlay Plus Diffusion Zone Thickness for Various Process Variables and Two Retort Sizes

effect of the process variables would be indicated. It should be noted that very little difference in coating thickness was observed for coatings applied in either the bottom or middle of the retort. Only in the top section was there a significant difference, showing little if any temperature variation between the middle and bottom positions. Taking all process variable combinations as a group, it can be seen that the position in the retort (top versus middle and bottom) had equal or greater influence than any other variable. This demonstrates that in order to maintain coating uniformity coatings should not be applied in the top 3 inch section of the retort.

Since the specimen position within the retort was found to exert a significant influence upon coating thickness a graphical analysis of this variable was made. An important point to be considered in analysing the data and its ramifications with respect to process scale up is that in the coating runs made for the reliability study no massive parts were contained in the retort. The addition of a large mass in the retort would measurably improve heat transfer, thus decreasing temperature gradients within the pack. Since only small coupons were used in this study it is considered that the heat transfer characteristics of the pack were at a minimum for this series of runs. Therefore, the recorded spread in coating thickness obtained from top to bottom of the retort is assumed to be a maximum and the corresponding protective capabilities of the coatings overall are assumed to be less than optimum.

Figures 35 through 38 show the effect of retort position on the Cr-Ti alloy overlay thickness, the Cr-Ti-Si coating overlay thickness and the Cr-Ti-Si coating overlay plus diffusion zone thickness. These figures were obtained using only the data generated for D-43 alloy, Cr-Ti coated using an 8 hour cycle at 2300°F and silicon coated using a 6 hour cycle at 2100°F. Data for each retort size is shown. The data presented in these figures includes all six batches processed utilizing the aforementioned process parameters. Thus the spread in fact represents batch-to-batch variation.

Figures 35 and 37 show the variation in Cr-Ti alloy overlay thickness with respect to retort position, Figure 35 for the 3" diameter retort and Figure 37 for the 7-1/2" diameter retort. The batch-to-batch variation in the small retort is seen to be nearly double that for the larger retort. Less scatter is noted for the center position of the 3" retort than for the edge, and the thicknesses obtained in the center fall within the range obtained at the edge position For the larger retort variation in the thicknesses noted at the bottom and middle vertical positions was essentially the same. However, the thicknesses of coatings formed at the edge of the retort were generally greater than for the center position.

For a given size retort, generally thinner coatings were formed in the top sections, corresponding to the effect noted in the scatter diagrams. This effect is again demonstrated for the total coating thickness (Cr-Ti-Si overlay plus diffusion zone), Figures 36 and 38. The range of values shown demonstrates batch-to-batch variation since each value applies to coatings applied in a particular batch. A rather wide range of Cr-Ti coating overlay thickness was found in the small retort. However, after silicon coating this range was considerably reduced. Thus it appears that the Cr-Ti coating cycle is slightly more sensitive to parameter variations within the retort than the silicon cycle.

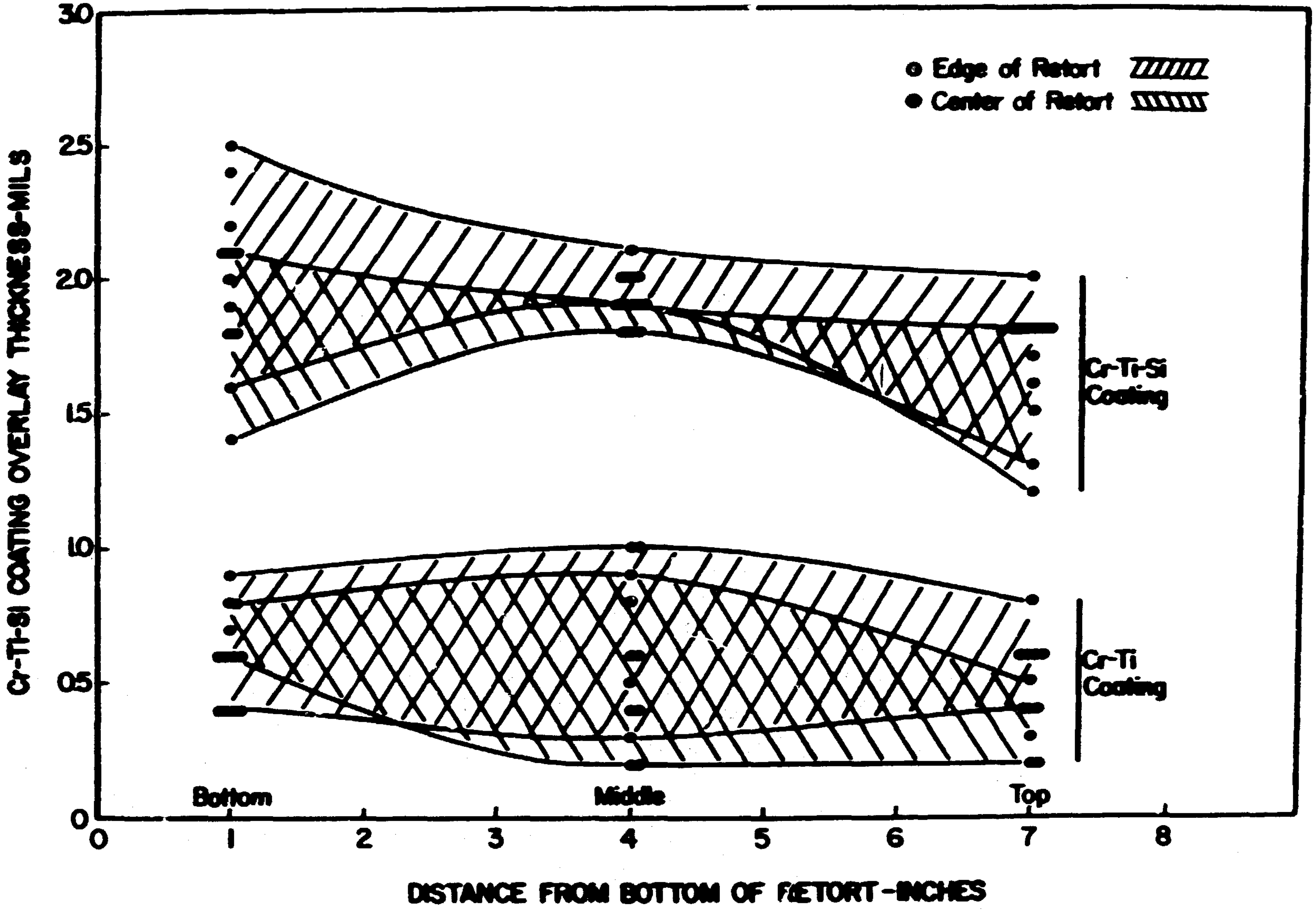


Figure 35 Relationship of Cr-Ti and Cr-Ti-Si Coating Overlay Thickness to Retort Position for D-43 Alloy Coating in the 3" Diameter x 8" High Retort

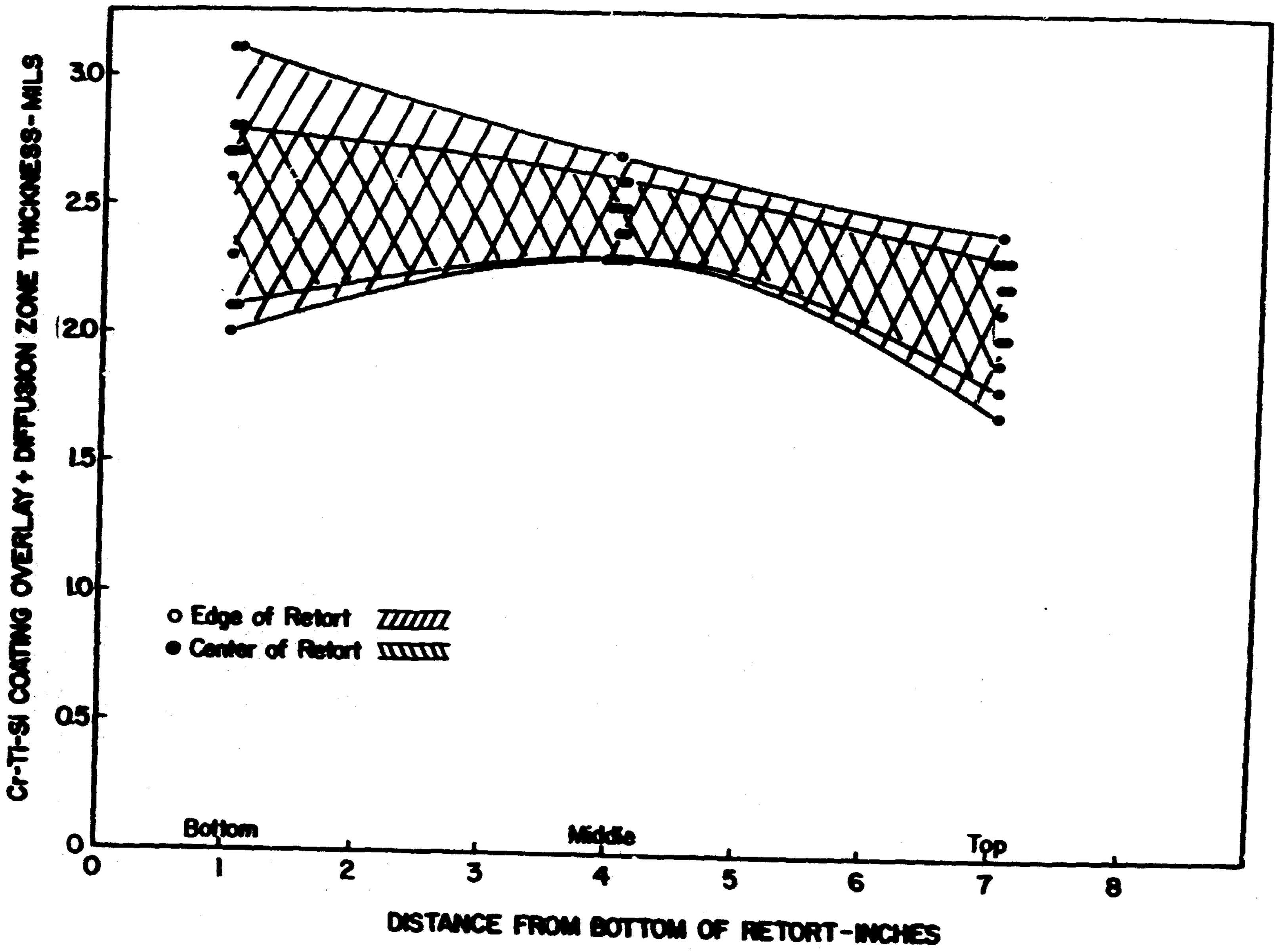


Figure 36 Relationship of Cr-Ti-Si Coating Overlay Plus Diffusion Zone Thickness to Retort Position for D-43 Alloy Coated in the 3" Diameter x 5" High Retort

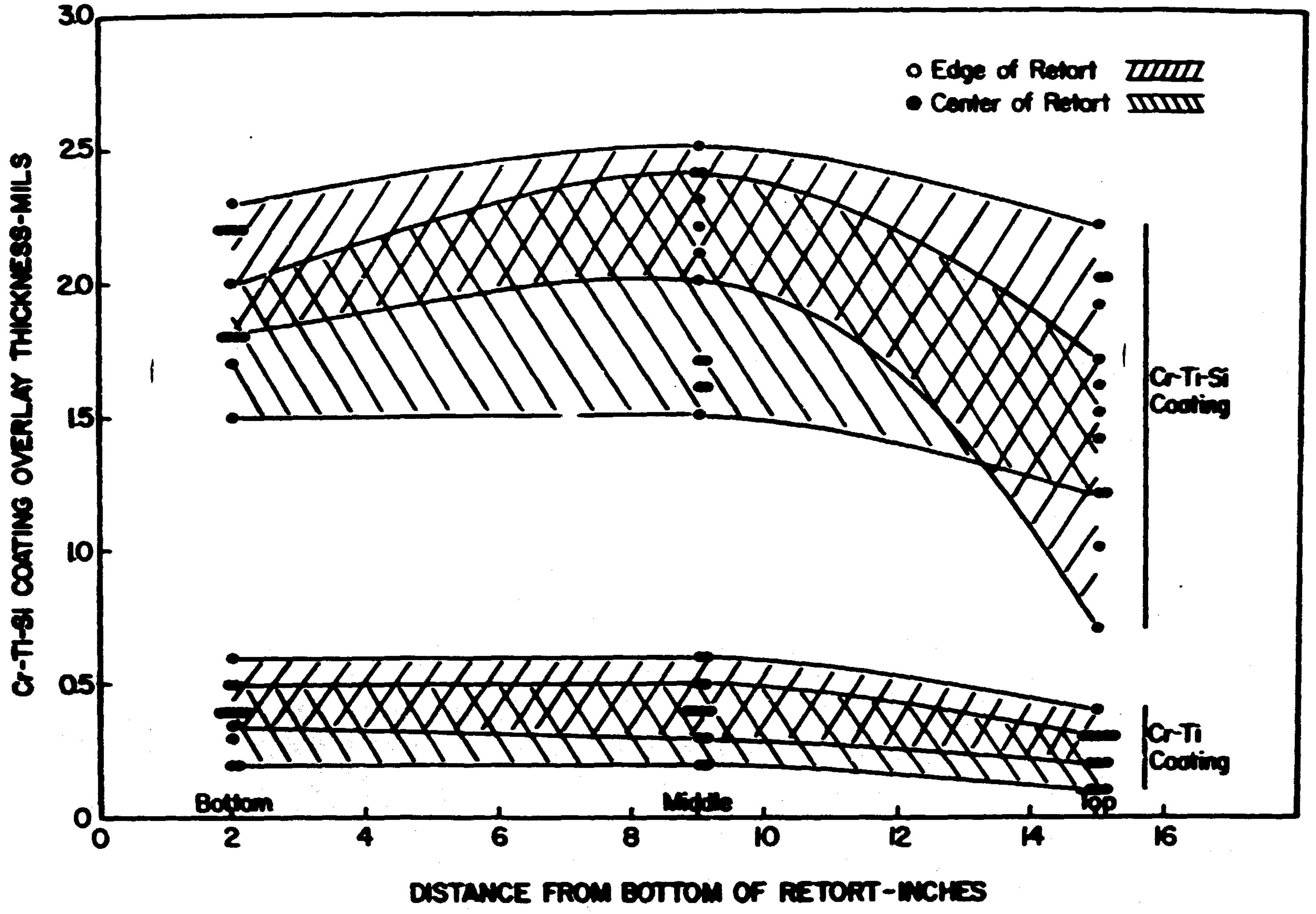


Figure 37 Relationship of Cr-Ti and Cr-Ti-Si Coating Overlay Thickness to Retort Position for D-43 Alloy Coated in the 7-1/2" Diameter x 18" High Retort

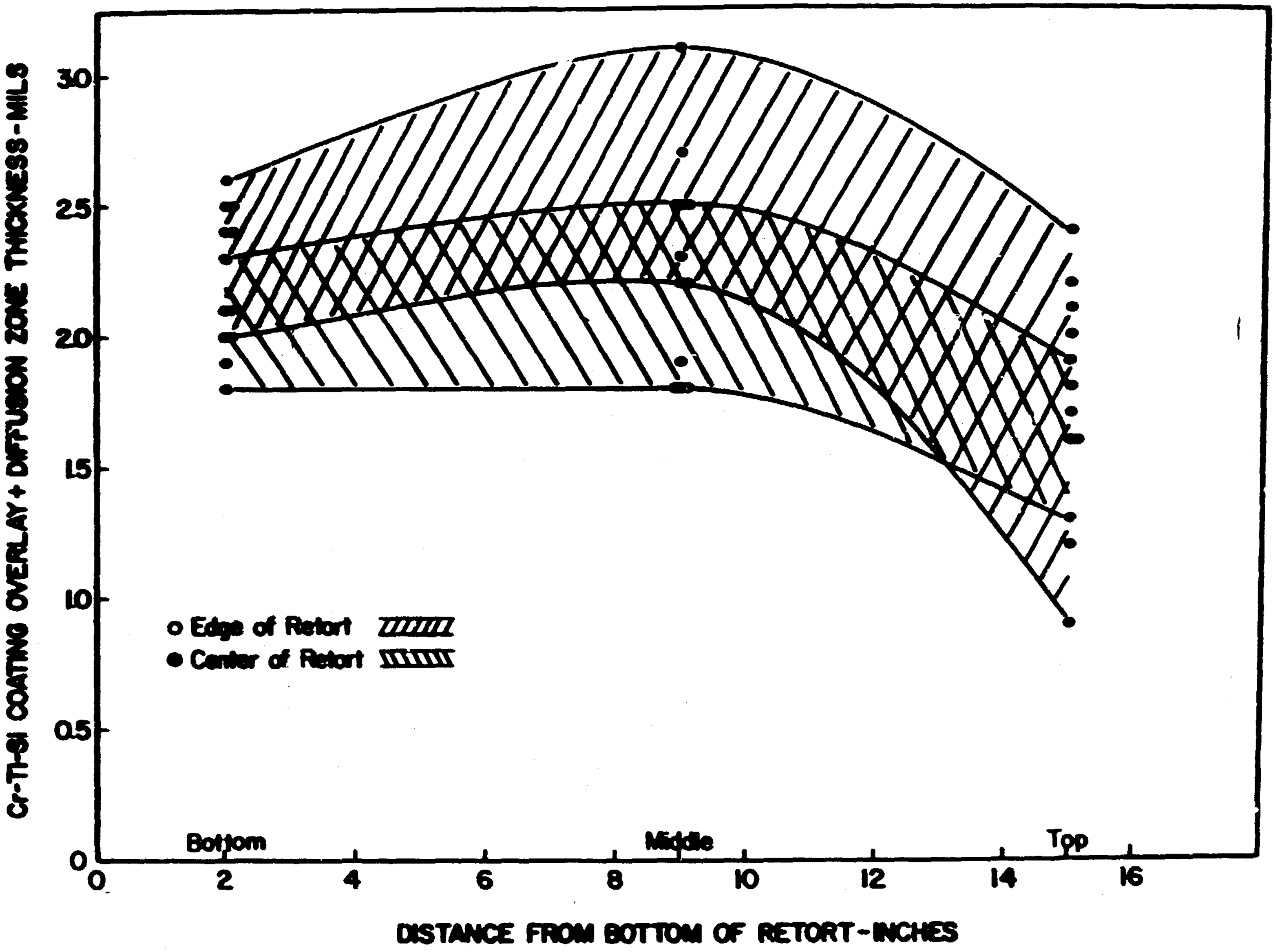


Figure 38 Relationship of Cr–Ti–Si Coating Overlay Plus Diffusion Zone Thickness to Retort Position for D-43 Alloy Coated in the 7-1/2" Diameter x 18" High Retort

Analysis of the data presented in Tables 23 through 27 shows that the thickness of the Cr-Ti alloy overlay coating does not necessarily determine resultant Cr-Ti-Si coating thickness. Therefore, some variation in coating composition can be expected for Cr-Ti-Si coatings of the same thickness. Obviously a thick Cr-Ti coating will result in a more chromium rich Cr-Ti-Si coating relative to a Cr-Ti-Si coating formed from a thinner Cr-Ti alloy layer. This being the case, it is postulated that the coatings formed in the top sections of the retort are somewhat different in composition than coatings formed in either the middle or bottom positions.

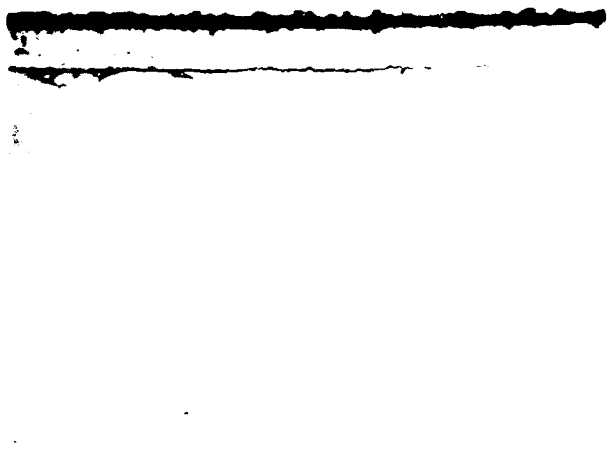
Figures 39 through 46 present photomicrographs of typical coatings produced under the various process parameters utilized in this investigation. These photomicrographs show the differences in coating thickness obtained in various positions in the retort and differences attributed to the various process parameter combinations. In all but Figure 45 only the extremes are shown, however, in Figure 45 all positions are shown to demonstrate thickness variation for all specimen locations.

After the effects of the various process parameters and process variables on coating thickness were determined, an analysis of the cyclic oxidation data was made. Tests were run at 2000, 2500 and 2700°F in air. The breakdown of the specimens for test from the various batches is shown in Figure 28. The protective life data is presented in Tables 23 through 27. The cyclic oxidation tests were run either to coating failure (defined as a visible growth of columbium oxide at the failure site) or to a limit of 150 hours. During the long testing period some difficulty with the oxidation test equipment was experienced. A few specimens in test at 2500°F were damaged or destroyed by a furnace temperature overshoot, thus no data was available in certain instances.

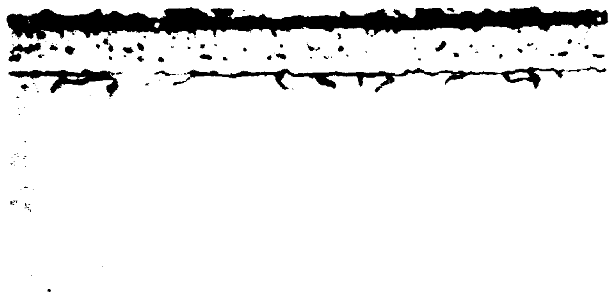
Past experience has shown low temperature life to be reduced as Cr-Ti-Si coating thickness exceeded approximately 3.0 mils. The accepted cause of this phenomenon relates to cracking after repeated cycling from the test temperature to room temperature due to the difference in thermal expansion characteristics of the coating and the substrate. At temperatures below approximately 2200°F the Cr-Ti-Si coating relies primarily upon Cr-Ti layer continuity and the $CbCr_2$ intermetallic phase at the coating-substrate interface for protective capability. Little selfhealing occurs at temperatures below 2200°F as opposed to higher temperatures. Thus, as coating thickness increases the susceptibility to low temperature failure increases since the thermal expansion mis-match increases with increasing thickness. This was substantiated by the fact that eleven of the sixteen failures in the 2000°F tests occurred on specimens (1/2" x 1/2") processed to achieve the thicker coatings. No correlation between coating thickness, specimen position in the pack, etc, can be made since the vast majority of the 2000°F tests were terminated at 150 hours prior to coating failure.

A much more comprehensive analysis of the protective characteristics of the Cr-Ti-Si coating at 2500°F was possible since the majority of the test coupons failed during the 150 hour test.

An initial determination of the relationship of the process variables to oxidation life at 2500°F was made using the random balance technique and resultant

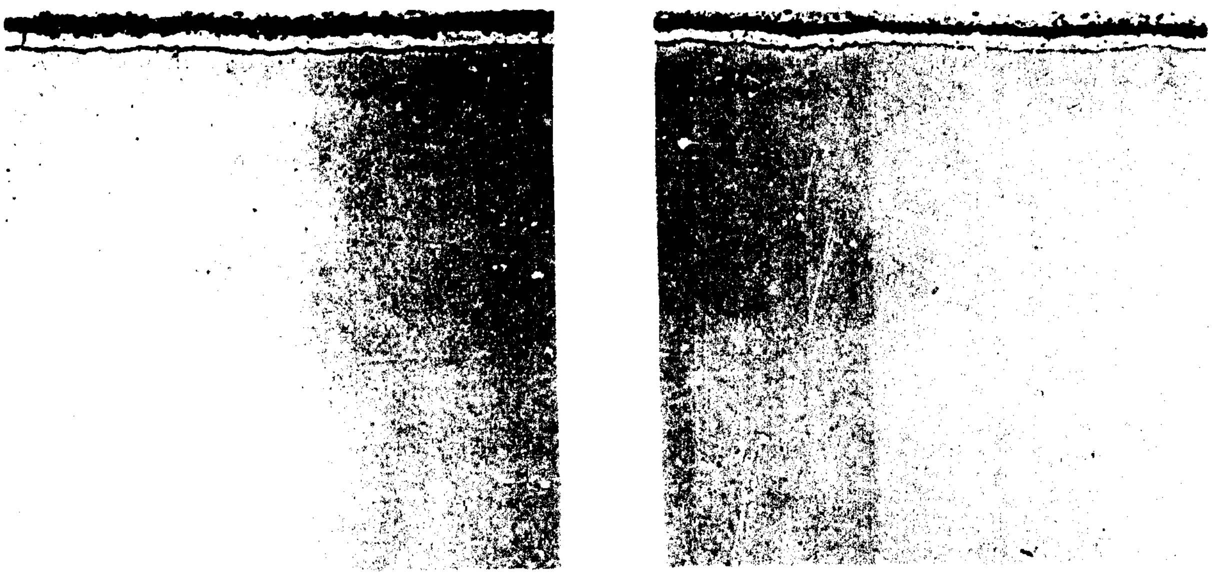


Top Center Retort Position



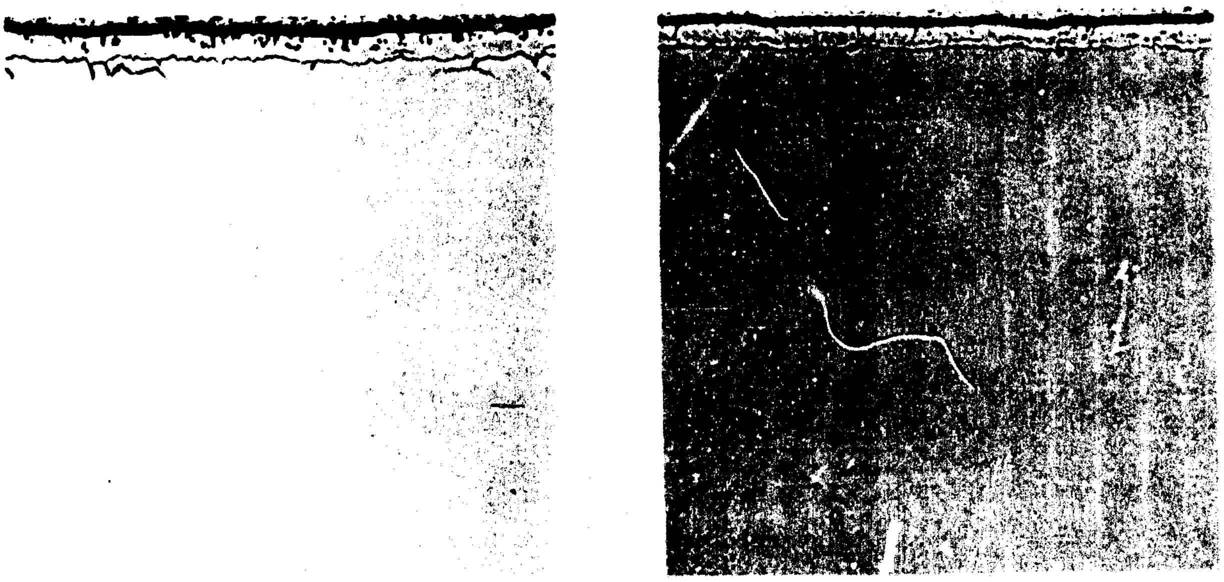
Middle Edge Retort Position

Figure 39 Typical Cr-Ti Alloy Coatings Formed on D-43 Alloy in 8 Hours at 2300° F Using a 60Cr-40Ti Alloy Pack - 3" Diameter x 8" High Retort 250X



B-66 Alloy D-43 Alloy

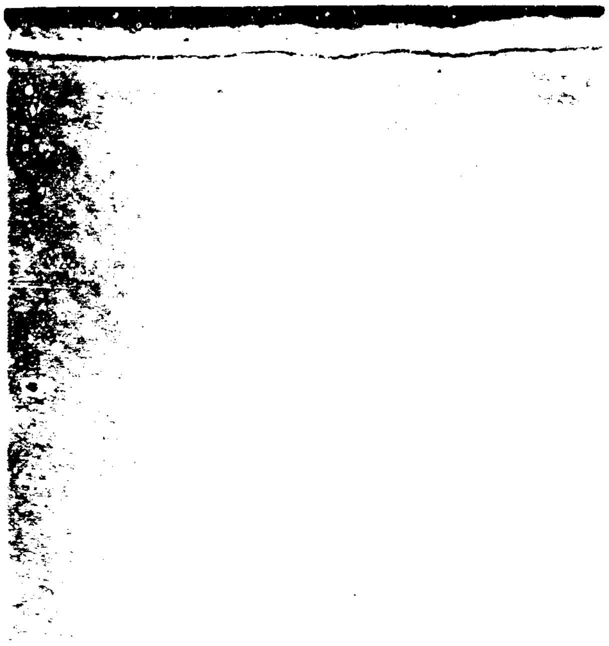
Top Center Retort Position



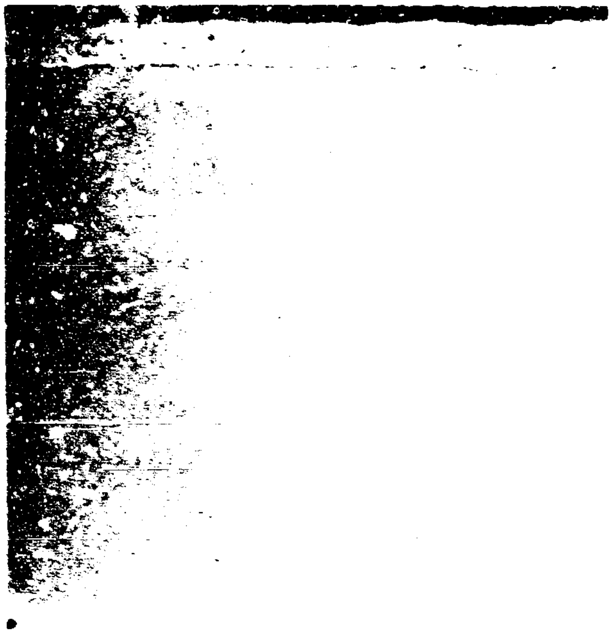
B-66 Alloy D-43 Alloy

Middle Edge Retort Position

Figure 40 Typical Cr-Ti Alloy Coatings Formed on B-66 and D-43 Alloys in 8 Hours at 2300°F Using a 60Cr-40Ti Alloy Pack - 7-1/2" Diameter x 18" High Retort 250X



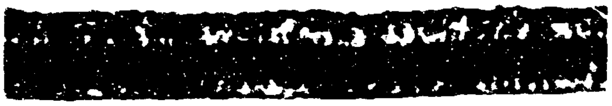
Top Center Retort Position



Middle Edge Retort Position

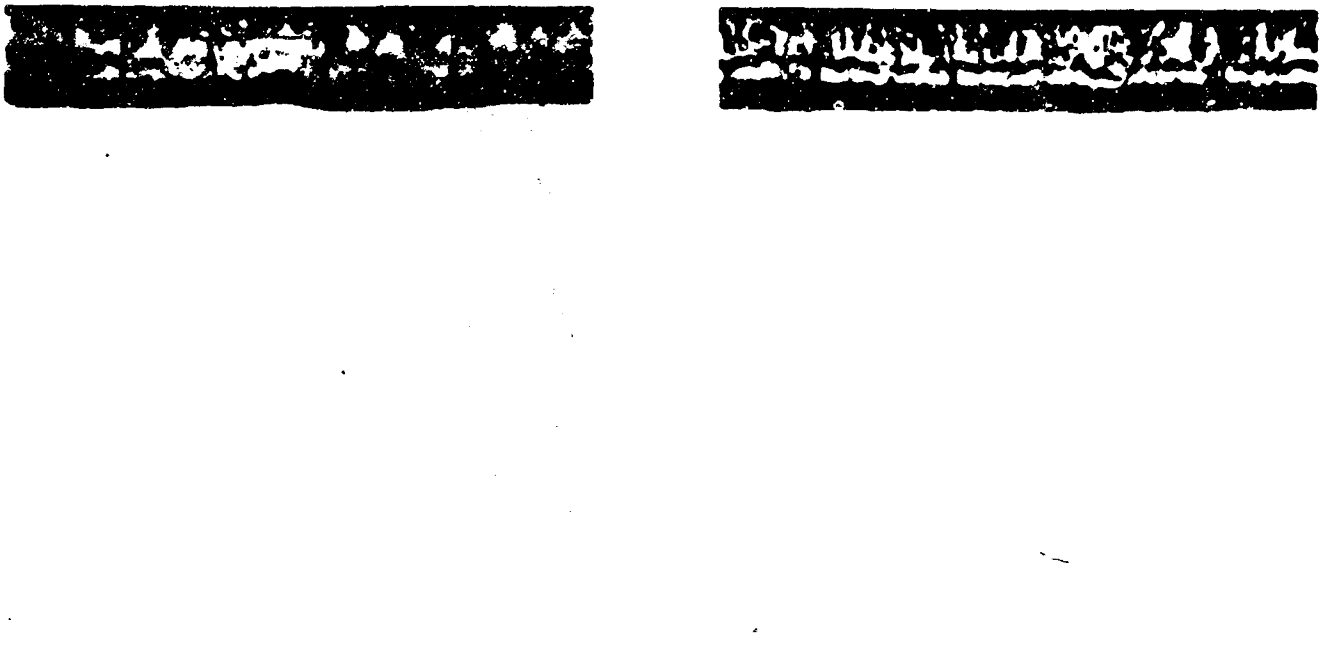
Figure 41 Typical Cr-Ti Alloy Coatings Formed on D-43 Alloy in 1[illegible] Hours at 2350°F Using a 60Cr-40Ti Alloy Pack - 7-1/2" Diameter x 18" High Retort 250X

Top Center Retort Position



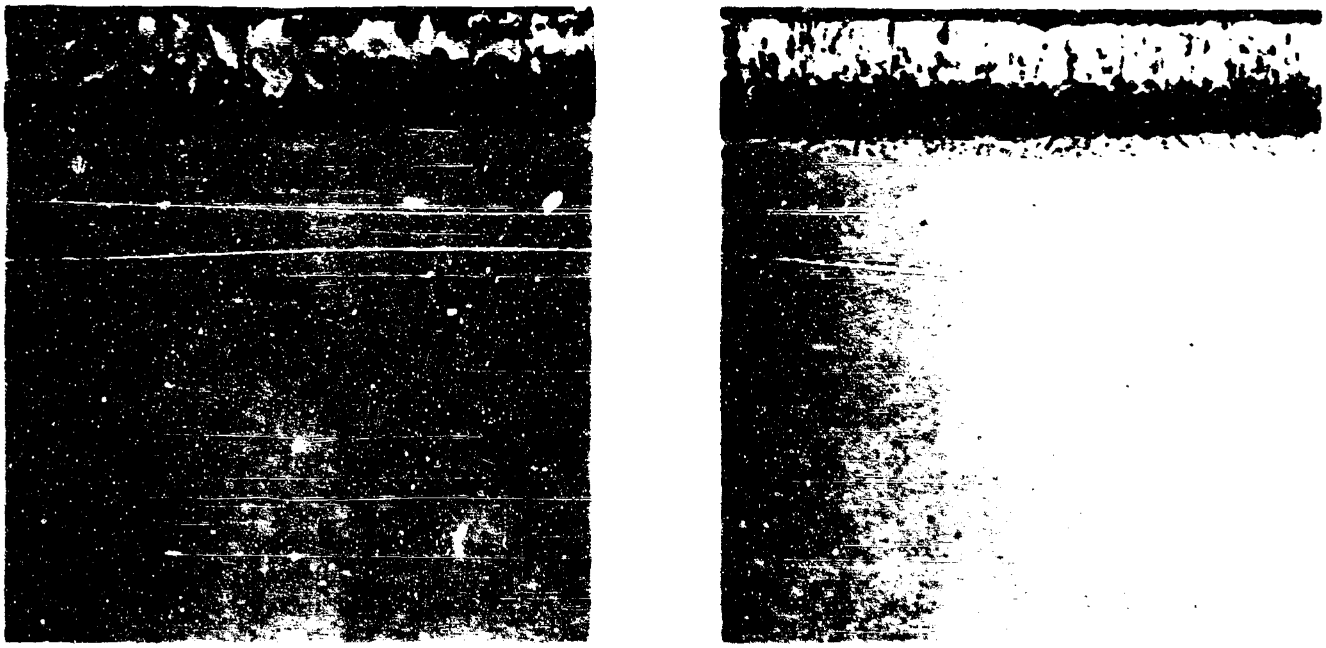
Middle Edge Retort Position

Figure 42 Typical Cr-Ti-Si Coatings Formed on D-43 Alloy in the 3" Diame
x 8" High Retort - Cr-Ti 8 Hours at 2300°F - Silicon 4 Hours a
2000°F 25



B-66 Alloy D-43 Alloy

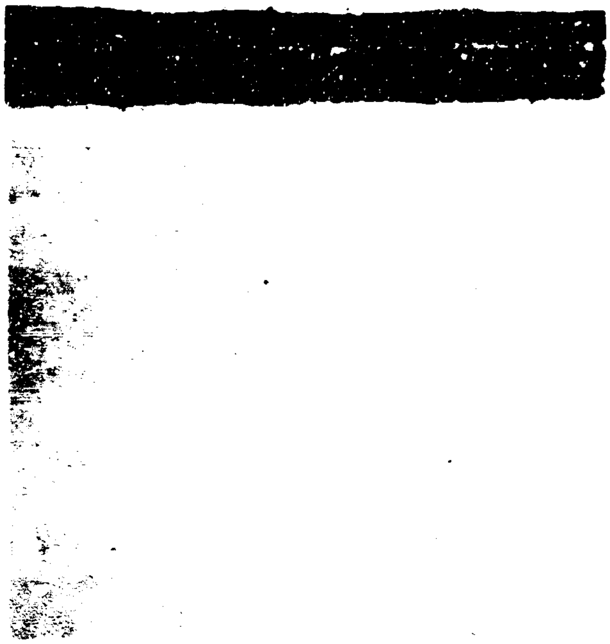
Top Center Retort Position



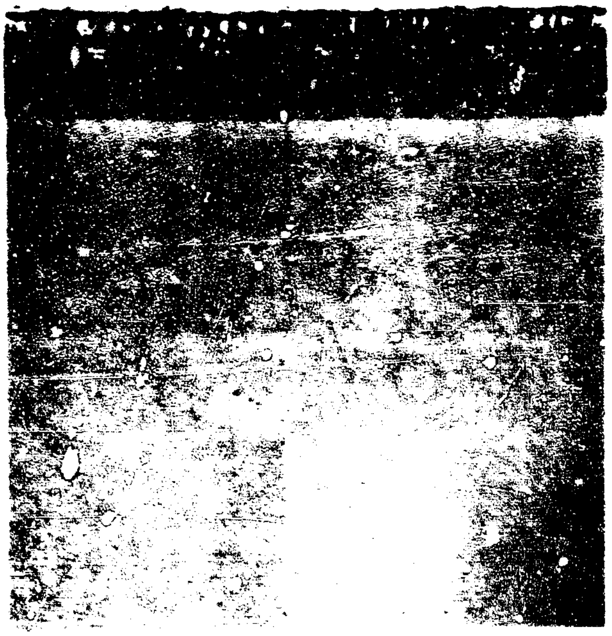
B-66 Alloy D-43 Alloy

Middle Edge Retort Position

Figure 43 Typical Cr-Ti-Si Coatings Formed on B-66 and D-43 Alloys in the 7-1/2" Diameter x 18" High Retort - Cr-Ti 8 Hours at 2300°F, Silicon 4 Hours at 2000°F

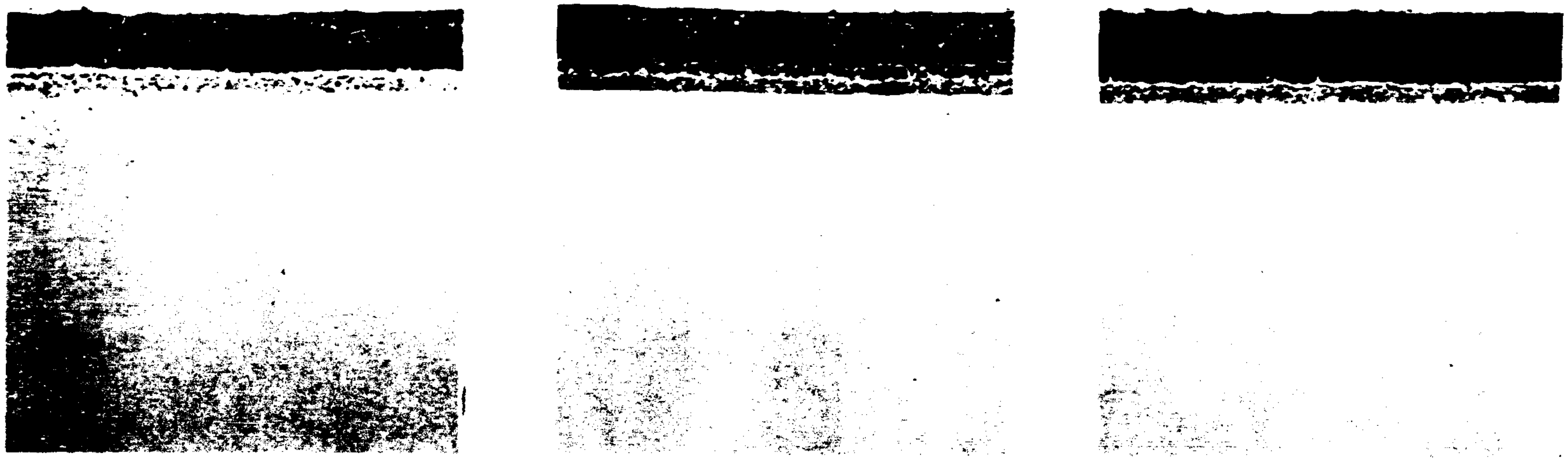


Top Center Retort Position



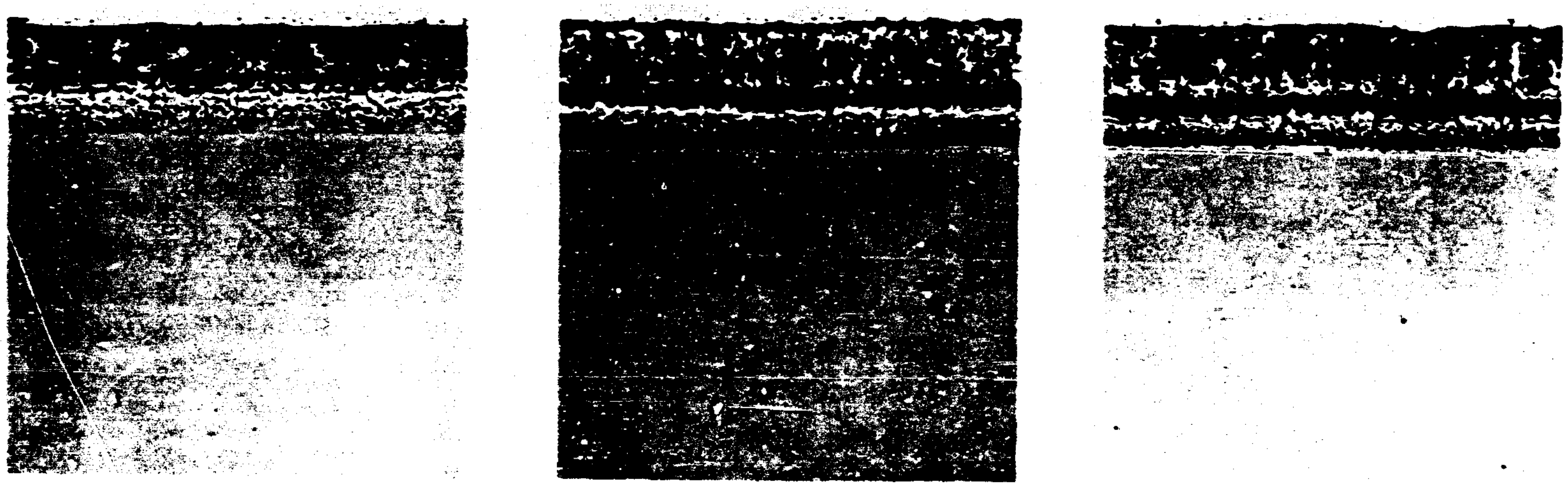
Middle Edge Retort Position

Figure 44 Typical Cr-Ti-Si Coatings Formed on D-43 Alloy in the 3" Diameter x 8" High Retort - Cr-Ti 8 Hours at 2300°F, Silicon 6 Hours at 2100°F 250X



Top Middle Bottom

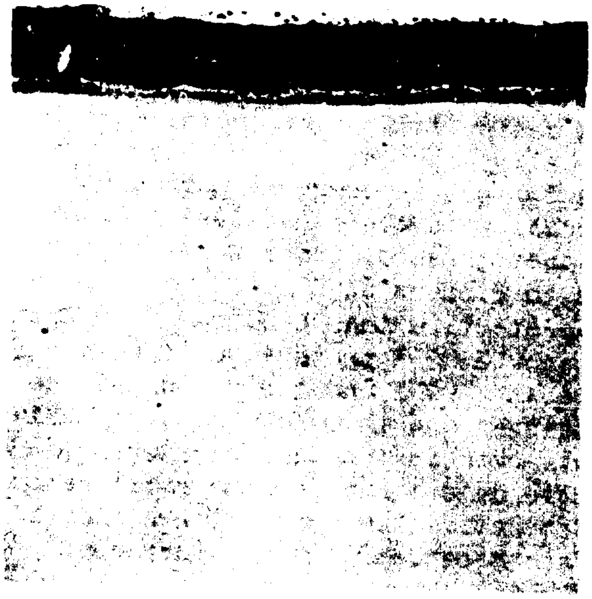
Center Retort Position



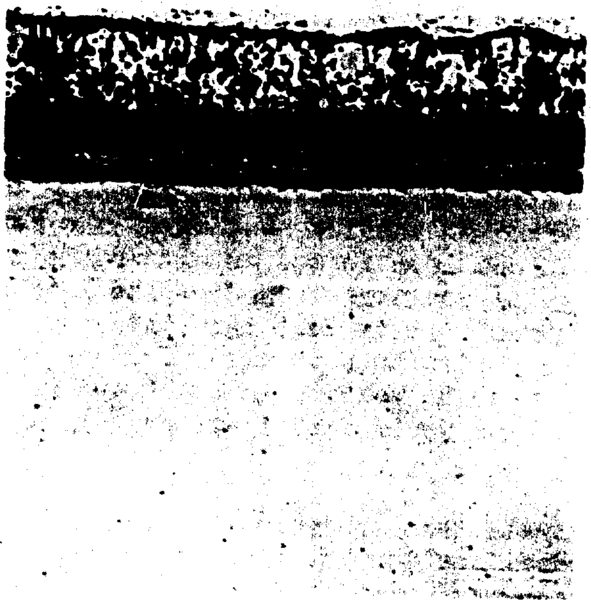
Top Middle Bottom

Edge Retort Position

Figure 45 Typical Cr-Ti-Si Coatings Formed on D-43 Alloy in the 7-1/2" Diameter x 18" High Retort - Cr-Ti 8 Hours at 2300°F, Silicon 6 Hours at 2100°F 250X



Top Center Retort Position



Middle Edge Retort Position

Figure 46 Typical Cr-Ti-Si Coatings Formed on D-43 Alloy in the 7-1/2" Diameter x 18" High Retort - Cr-Ti 10 Hours at 2350°F, Silicon 6 Hours at 2100°F 250X scatter diagrams. These diagrams are presented in Figures 47, 48 and 49. The variable exerting the greatest influence on 2500°F life was found to be vertical position in the retort, the top section giving rise to the least protective coating. Horizontal specimen position also exerted a significant influence, with the edge position having the superior oxidation life. Alloy composition was also important. Coupons fabricated from B-66 alloy were able to sustain longer exposure at 2500°F. Of interest is the fact that the silicon process parameters had less influence than any of the aforementioned factors. Note that these diagrams were compiled using only data obtained from coupons Cr-Ti coated in 8 hours at 2300°F. In general, coatings produced in the smaller retort were more protective than coatings formed in the 7-1/2" diameter furnace. Figures 50 and 51 show 2500°F protective life as a function of retort position for the 8 hour Cr-Ti cycle at 2300°F and the 6 hour silicon cycle at 2100°F. A rather wide range of life was observed due to batch-to-batch variation in the small retort. Much less variation was observed in the larger retort. However, it should be noted that the wider range of life determined for the small retort is primarily the result of many specimens being protective for longer times than in the larger furnace. Minimum life is not much different between the two furnaces.

No significant correlation between coating thickness and protective life at 2500°F was possible for the range of coatings obtained in this study. A slight trend to longer life with increasing thickness was observed, however, a greater range in thickness would be required to demonstrate this trend effectively. It is well known that very thin coatings are not as protective as thicker coatings. In analysing the oxidation life data, it was determined that two specimens, having essentially identical coating thickness, but applied in different positions in the retort, could have radically different protective capability. This was particularly true of specimens coated in the top of the retort in one run versus specimens coated in the middle or bottom of the retort in another run. This further substantiates the observation that coating composition, rather than coating thickness, is the controlling factor within the range of thickness investigated (1.5 to 2.5 mils). This composition effect, due to specimen position in the retort, is shown in Figures 52 and 53. The protective performance of coatings formed in the top section of the retort is poorer for a particular life requirement than coatings formed in either the middle or bottom positions. The greater protective life of coatings formed on the B-66 alloy sheet is apparent by comparing these two figures. It is felt that this may be a result of the greater depth of coating element diffusion in B-66 alloy for the same coating time and temperature. This results from the lower melting point of the B-66 alloy. A greater range of the diffusion zone thickness would facilitate determination of the contribution of this apparent effect.

These results demonstrate that specimen (or structure) position within the retort is a significant consideration in obtaining satisfactory coating performance. The alternative is an improvement in heat supply and heat transfer within the pack to decrease temperature variation. Although no great difference in protective life is associated with the two substrate compositions investigated, it may also be necessary to adjust coating process parameters to provide optimum life for particular substrate alloys of widely different composition.

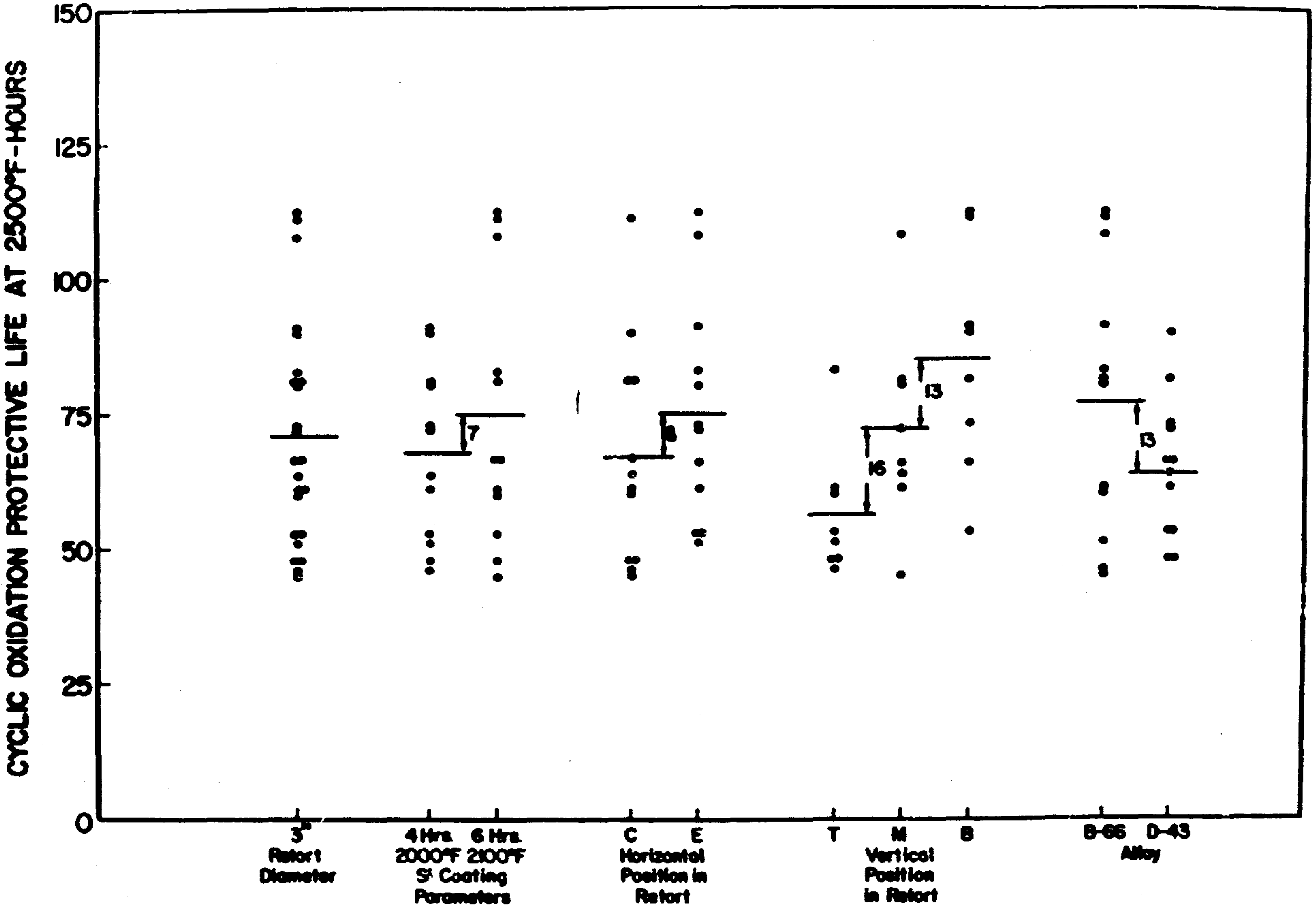


Figure 47 Scatter Diagrams Showing Variation in Cyclic Oxidation Protective Properties at 2500° F for Various Process Variables in the 3" Diameter x 8" High Retort

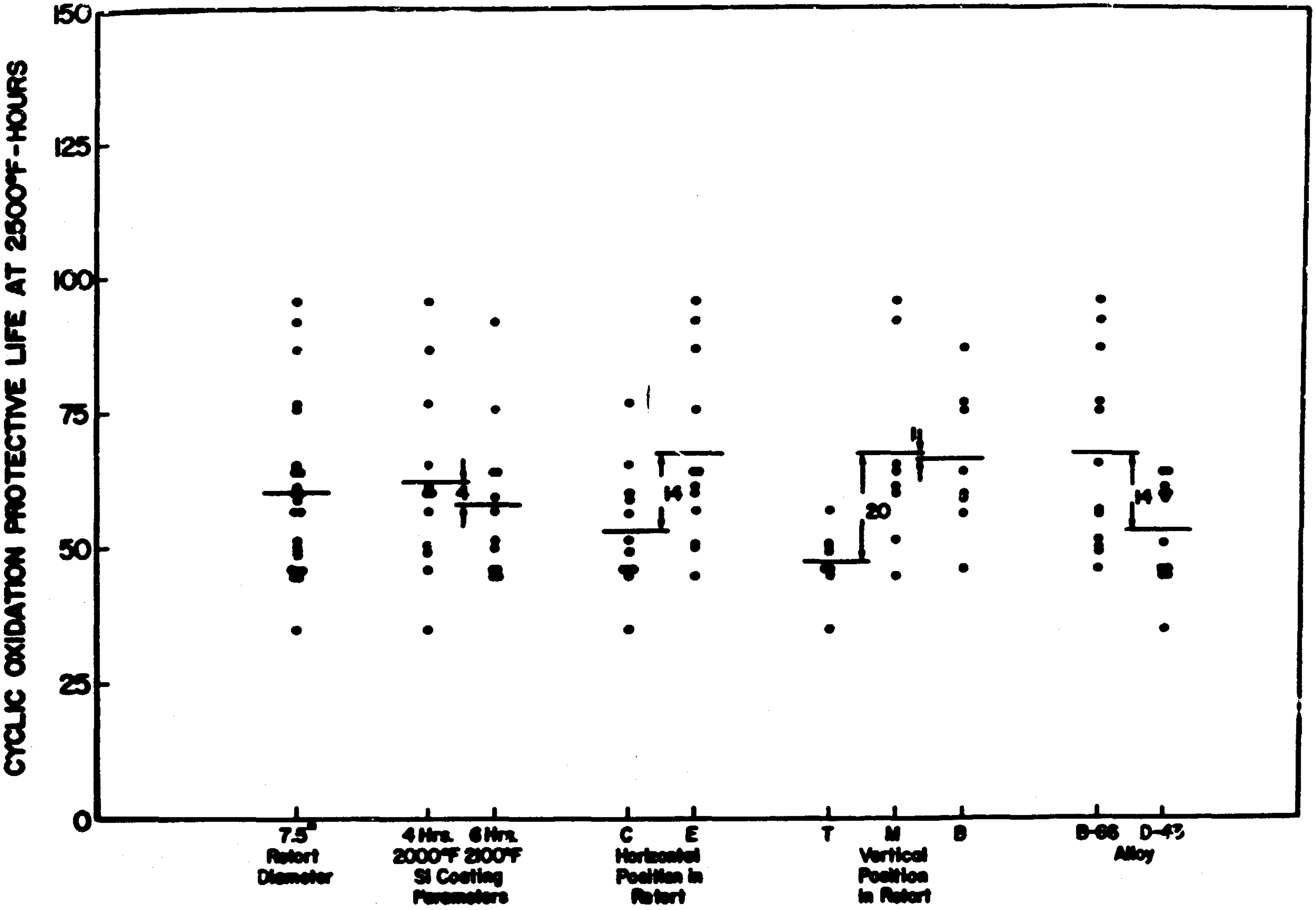


Figure 48 Scatter Diagrams Showing Variation in Cyclic Oxidation Protective Properties at 2500°F for Various Process Variables in the 7-1/2" Diameter x 18" High Retort

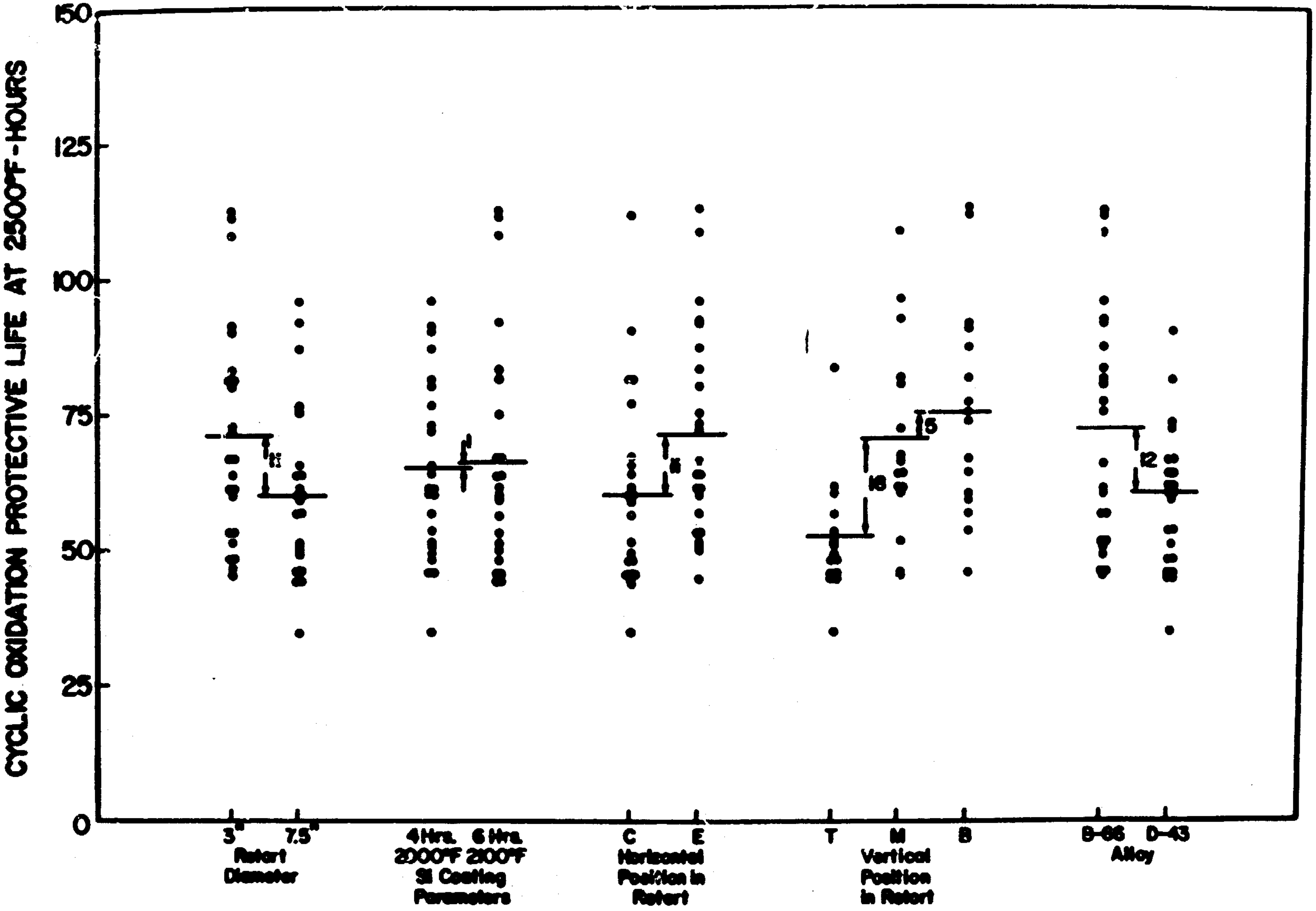


Figure 49 Scatter Diagrams Showing Variation in Cyclic Oxidation Protective Life at 2500°F for Various Process Variables and Two Retort Sizes

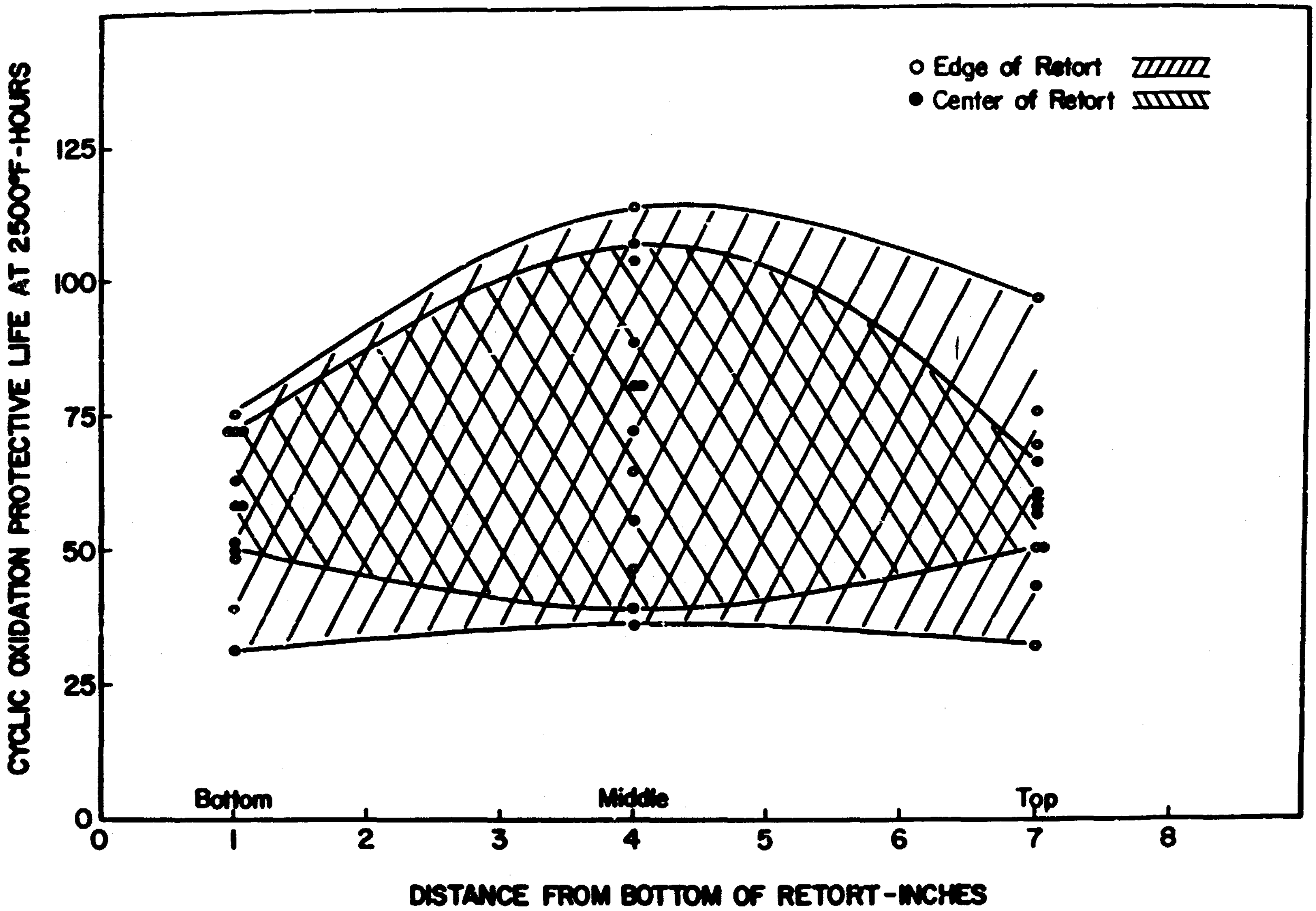


Figure 50 Relationship of Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy at 2500°F to Specimen Position in the Retort for the 3" Diameter x 8" High Retort

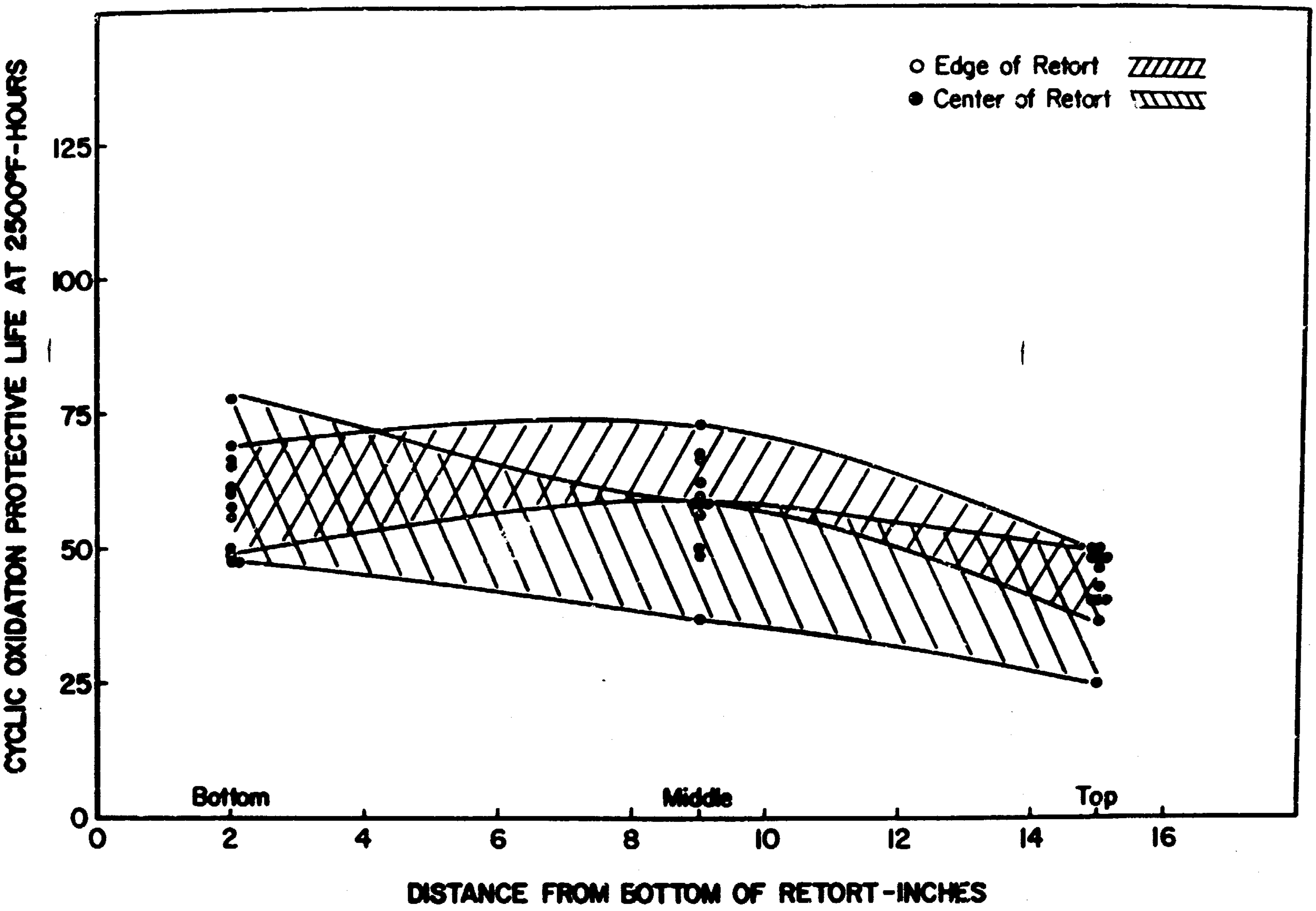


Figure 51 Relationship of Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy at 2500°F to Specimen Position in the Retort for the 7-1/2" Diameter x 18" High Retort

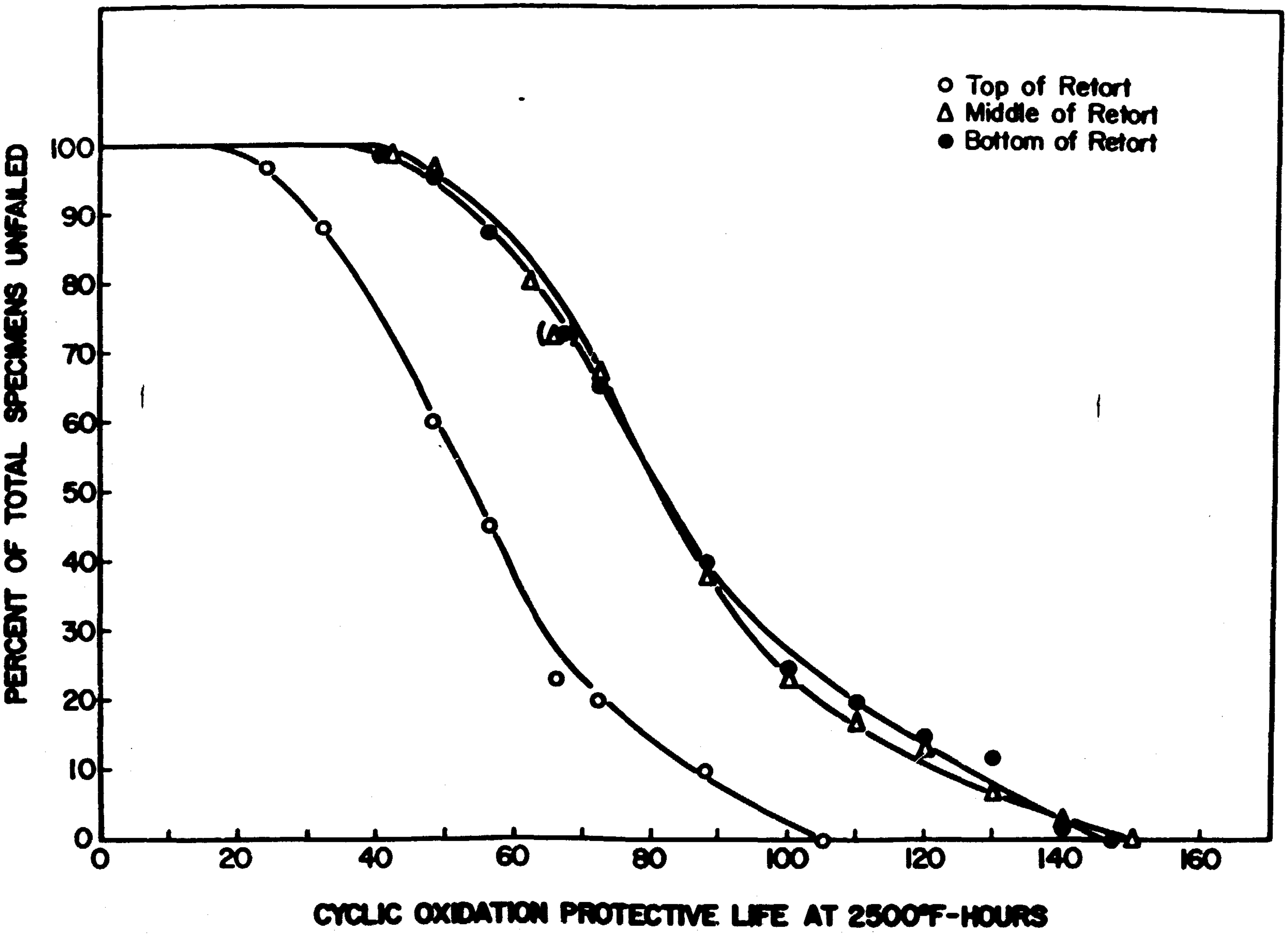


Figure 52 Cr-Ti-Si Coating Reliability at 2500°F for Coated B-66 Alloy as a Function of Vertical Position in the Retort

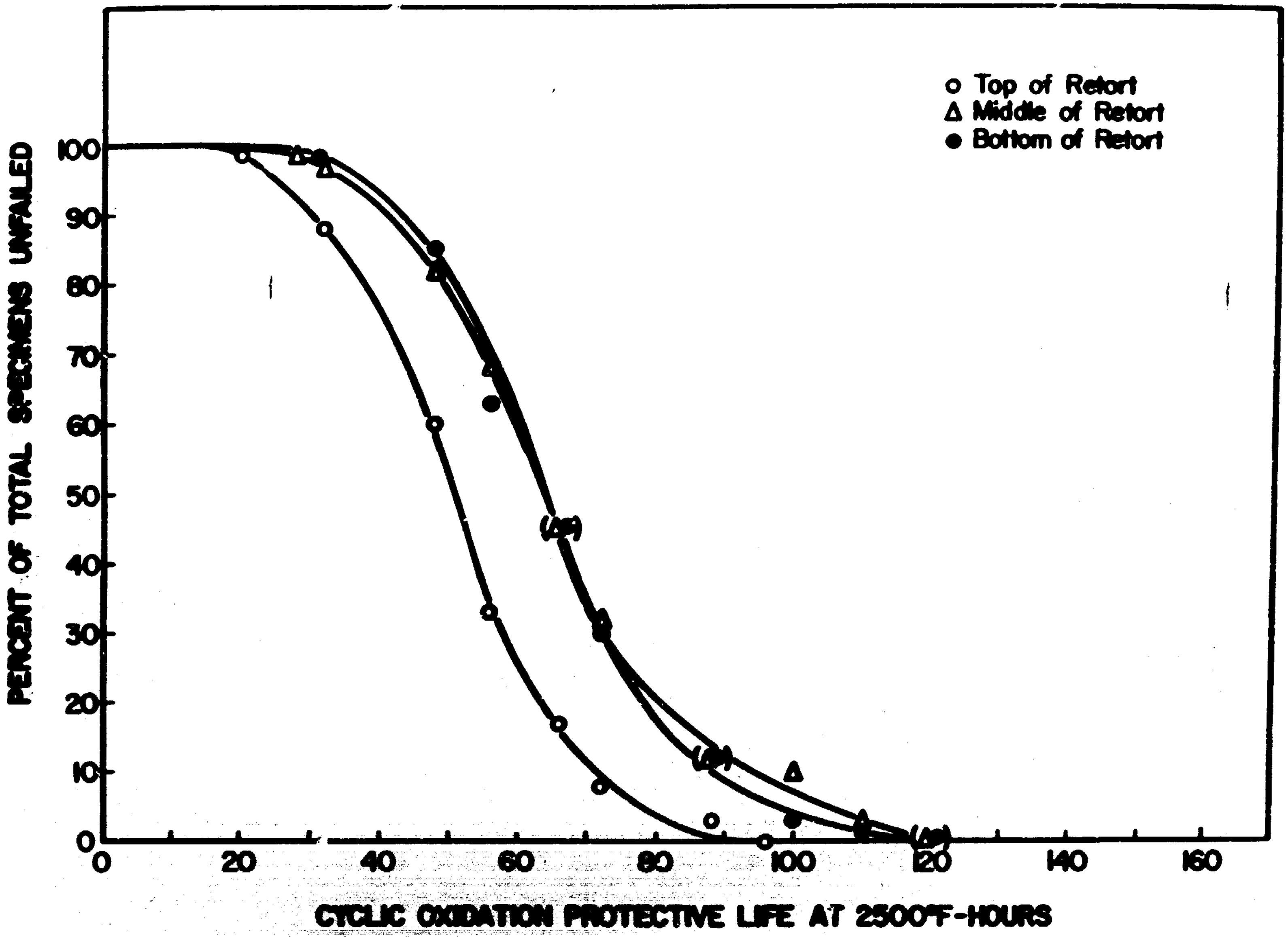


Figure 53 Cr-Ti-Si Coating Reliability at 2500°F for Coated D-43 Alloy as a Function of Vertical Position in the Retort

The cyclic oxidation data obtained for the 2700°F test temperature was not sufficiently varied to permit detailed analysis. However, it was determined that at 2700°F the coating thickness, for the range of thickness investigated, is not the sole life determining factor. Coating composition appears to be as much a factor in protective capability at 2700°F as it is at 2500°F. This is further substantiated by earlier development work where Cr-Ti-Si coatings processed to give higher chromium and lower titanium compositions gave significantly better performance in the 2700-2800°F range (10-20 hours). However, these same coatings suffered to a markedly greater degree in the 2000°F and below range. It, therefore, should be borne in mind that in this study with the process parameters selected and within the reproducibility limits attained, the same coating compositions were tested at 2000 and 2500°F as well as 2700°F.

A graphical presentation is made of the 2700°F protective life data for the two substrate compositions in Figures 54 and 55. In view of the fact that all test results fell within a relatively narrow time range the aforementioned compositional effect would have to be determined in order to select coating process parameters to give consistently better oxidation life at 2700°F. The vertical position in the retort is as much a factor at 2700°F as it was at 2500°F. Little difference between middle and bottom regions was found.

At 2500°F the B-66 alloy was found to give better oxidation protective life than D-43 alloy. Life at 2700°F was found to be higher for D-43 alloy than for B-66 alloy, indicating a dependence upon both coating thickness and diffusion rates.

7.2 Reliability Analysis

As previously mentioned, cyclic oxidation tests in air at 2000, 2500 and 2700°F at one atmosphere were employed to determine coating protective reliability. As shown in Figure 28, 7 samples of each alloy were taken from each retort position of each coating run and tested at 2000 (3 specimens), 2500 (3 specimens) and 2700°F (1 specimen). The cyclic oxidation life data are included in Tables 23 through 27. The cyclic oxidation tests were run until coating failure (defined as visual coating failure and growth of columbium oxide) was observed or until 150 hours of test time was accumulated. Tests were terminated at 150 hours in order to facilitate testing of all 2940 specimens.

At 2000°F 1080 1/2" x 1/2" (D-43 and B-66 alloy) Cr-Ti-Si coated specimens were tested. Only 16 specimens failed in less than 150 hours. All other specimens were removed from test after 150 hours without visible evidence of failure. Of the 16 specimens that failed the minimum life was 48 hours. On the basis of these data the reliability of the Cr-Ti-Si coating on D-43 and B-66 alloy specimens in the cyclic oxidation test at 2000°F can be assessed. The probability of a specimen lasting 150 hours at 2000°F is:

$$\text{Probability (P)} = \frac{\text{no. of specimens unfailed}}{\text{total no. of specimens tested}} \times 100 = \frac{1080-16}{1080} \times 100 = 98.5\%$$

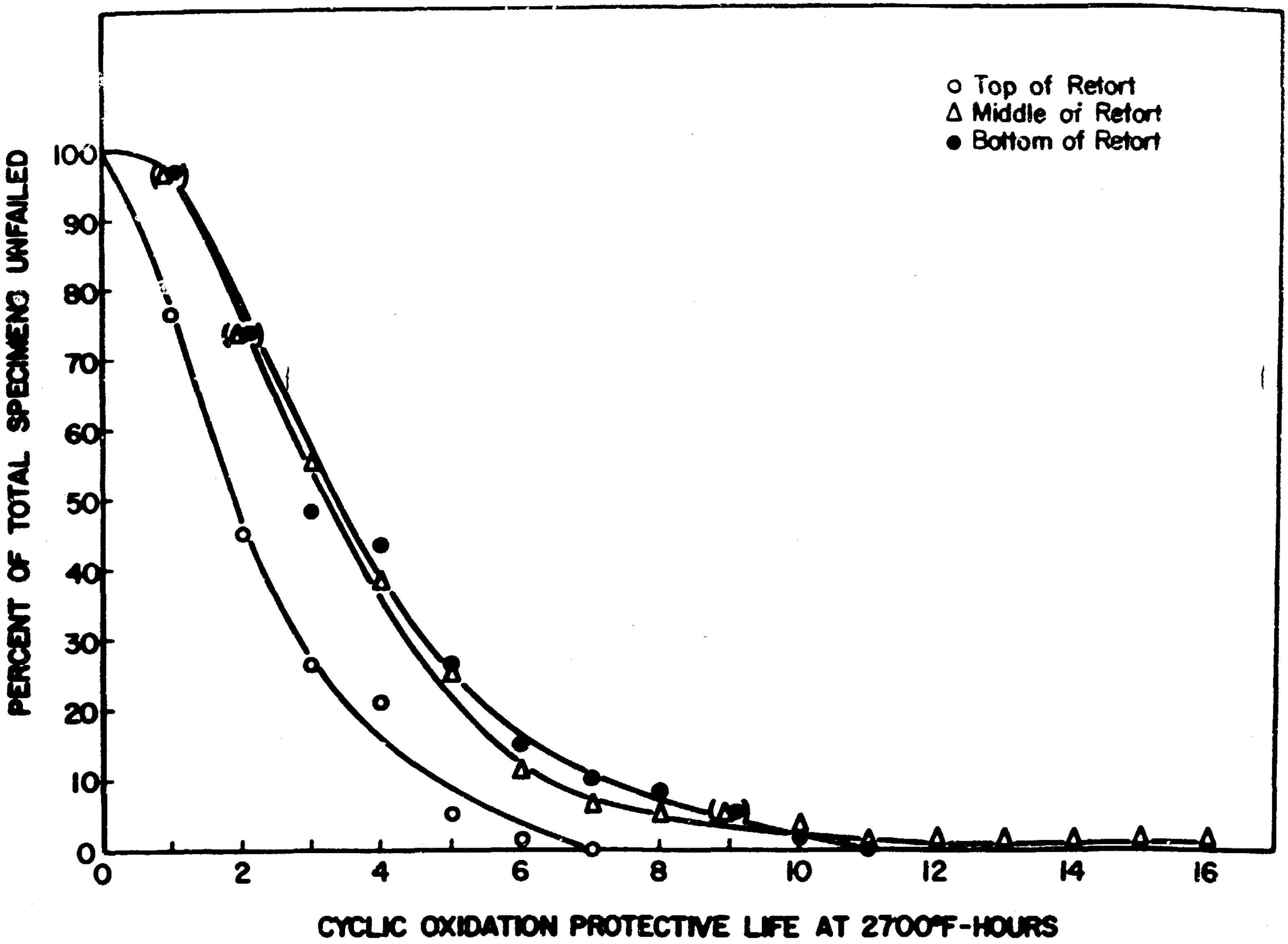


Figure 54 Cr-Ti-Si Coating Reliability at 2700°F for Coated B-66 Alloy as a Function of Vertical Position in the Retort

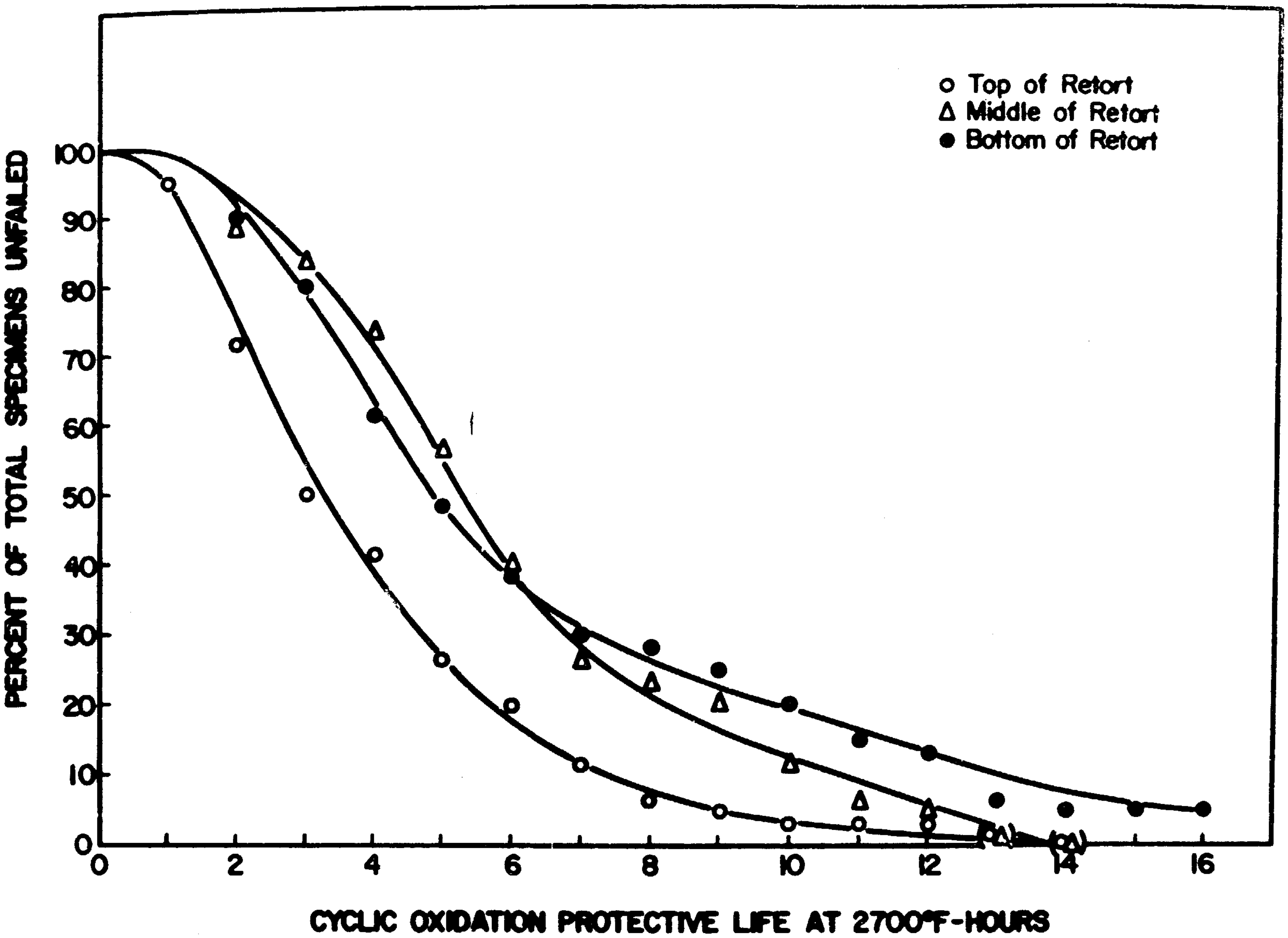


Figure 55 Cr-Ti-Si Coating Reliability at 2700°F for Coated D-43 Alloy as a Function of Vertical Position in the Retort

The confidence level on the probability can be obtained from a standard table of "Confidence Intervals for Proportions". The large size of the proportion $\left(\frac{1064}{1080}\right)$ gives an interval of ± 0.5% to the probability for a 99% confidence level. Therefore, any specimen has a 98.5 ± 0.5% probability at a 99% confidence level of having a 150 hour protective life at 2000°F.

The 2" x 2" test specimens fabricated from D-43 alloy were also oxidation tested at 2000°F. These specimens were included to demonstrate the uniformity of the Cr-Ti-Si coating as applied to a larger surface area piece. Two of the sixty 2" x 2" specimens failed in less than 150 hours. The minimum protective life was 72 hours. The reliability of the Cr-Ti-Si coating on the 2" x 2" specimens can be assessed in the same manner as for the 1/2" x 1/2" specimens above. The probability for 150 hours life at 2000°F is 96.5%. The 99% confidence interval for the proportion $\left(\frac{58}{60}\right)$ is ± 1.5%. The interval is larger for the 2" x 2" specimens since the number of tests is less and the proportion is correspondingly smaller. Therefore, a 96.5 ± 1.5% probability at a 99% confidence level exists for a 150 hour life for a 2" x 2" specimen at 2000°F.

A more comprehensive statistical analysis of the protective reliability of the Cr-Ti-Si coating on D-43 and B-66 alloy is possible at 2500°F since the majority of the test specimens failed in less than 150 hours.

The population of 2500°F oxidation data consists of a total of 1020 tests on 1020 specimens from 30 batches of approximately 34 specimens each.

In treating the protective life data for the 2500°F tests, the following considerations are made:

1) the two alloys are treated individually even though they were coated together

2) specimens of each alloy coated in the top section of both the 3" and 7-1/2" diameter retorts are treated separately from specimens coated in the middle and bottom sections

3) except in consideration of batch-to-batch variation, all batches of the same alloy whether from the 3" or 7-1/2" diameter retort are treated as one lot.

The two alloys are treated individually to indicate the effect of the substrate on coating reliability for the same process conditions. Based upon the results presented in the plots of Figures 54 and 55 it is apparent that specimens coated in the very top portion of the retorts consistently have different coating compositions with respect to specimens coated lower in the retorts for comparable thickness levels. It is, therefore, considered justifiable to treat such specimens separately. To gain an overall reliability assessment of the Cr-Ti-Si coating and the vacuum pack process relating both to current scale usage and future scale up, the test results of all specimens of a given alloy from 30 batches are treated statistically as a lot. This was done so that the net result incorporates the effects of different retort sizes (furnace sizes), different coating thicknesses and a range of practical process parameters.

As a first step in the analysis of the data, it is desirable to establish atistically the batch-to-batch variation of the 30 coating batches based upon the otective performance of the specimens in each batch. This is done by calculating d comparing the mean protective life and standard deviation for each batch. The lculations are made with the following equations:

For less than an infinite population -
μ (true mean) $\sim$ X (sample mean)
σ (true deviation) $\sim$ s (sample deviation)

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i = \frac{1}{N}\left(x_1 + x_2 + x_3 \cdots\cdots + x_N\right) \qquad (4)$$

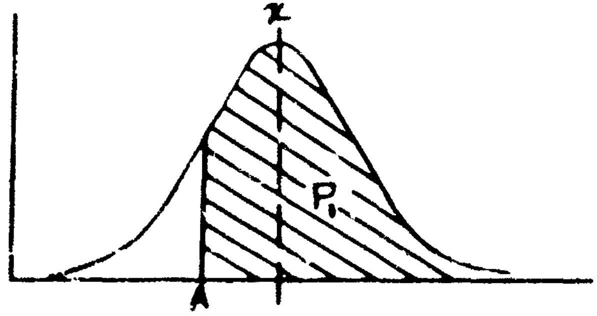
$$s = \sqrt{\frac{1}{N-1}\left[\sum_{i=1}^{N} x_i^2 - \frac{(\sum x_i)^2}{N}\right]} \qquad (5)$$

x_i = any specific test value
N = total number of tests

The calculated values for the mean 2500 and 2700°F protective life are tabu- ted for each batch in Table 28. The batch-to-batch variation for six batches is dicated by comparing the $\bar{x}$ values for each retort position from a given set of ocessing conditions. It is apparent, based on the mean life values, that some gree of batch-to-batch variation is present and is influencing the population read.

The protective reliability of the Cr-Ti-Si coating on D-43 and B-66 alloy ecimens is established by plotting a frequency polygon with each data lot and rmalizing it to a Gaussian distribution. Figures 56 through 63 show the frequency rsus life distribution for the two alloys in the top portion and the middle- ttom portion of the retorts. The mean ($\bar{x}$) and standard deviation (s) values lculated for the four distribution curves at 2500 and 2700°F are listed in ble 29.

Once the mean ($\bar{x}$) and standard deviation (s) are established, various protec- ve life probability levels can be calculated. This is done in the following nner:



1) the probability of any specimen reaching life A is given by the area under the curve represented by P_1

TABLE 28

Values of Mean Protective Life and Standard Deviation for Each Specimen Batch for 2500 and 2700°F Oxidation Tests

Alloy and Sample Lot	Batch No.	Processing Condition A(1)			Processing Condition B(1)			Processing Condition C(1)		
		$\bar{X}$	S	N	$\bar{X}$	S	N	$\bar{X}$	S	N
		Hours			Hours			Hours		
D-43 Alloy - Middle and Bottom Retort Position-2500°F Oxidation Test	1	64	27	12	64	16	21	69	9	22
	2	69	16	12	50	15	24	73	27	24
	3	88	20	12	63	25	18	64	22	24
	4	77	32	12	71	32	24	49	27	20
	5	70	22	12	74	23	24	76	26	24
	6	84	25	12	56	14	24	65	22	24
D-43 Alloy - Top Retort Position-2500°F Oxidation Test	1	47	28	6	58	23	11	50	2	7
	2	73	13	6	50	14	12	52	26	12
	3	53	10	6	41	20	9	48	13	12
	4	49	29	6	48	20	12	41	11	9
	5	69	19	6	49	17	12	55	18	12
	6	81	28	6	56	12	12	56	7	12
D-43 Alloy - Middle and Bottom Retort Position-2700°F Oxidation Test	1	8	4	4	4	1	8	3	1	8
	2	8	3	4	6	1	8	5	2	8
	3	5	1	4	6	2	8	6	2	8
	4	11	1	4	6	2	8	6	5	8
	5	10	6	4	8	4	8	8	4	8
	6	11	6	4	7	3	8	6	3	8
D-43 Alloy - Top Retort Position-2700°F Oxidation Test	1	5	0	2	2	0	4	2	1	4
	2	6	0	2	5	2	4	5	1	4
	3	3	0	2	4	1	4	6	3	4
	4	11	5	2	4	1	4	6	5	4
	5	6	2	2	5	4	4	5	4	4
	6	6	0	2	5	3	4	2	1	4

(1) Processing Condition A - Cr-Ti 10 hours at 2350°F, Silicon 6 hours at 2100°F
Processing Condition B - Cr-Ti 8 hours at 2300°F, Silicon 6 hours at 2100°F
Processing Condition C - Cr-Ti 8 hours at 2300°F, Silicon 4 hours at 2000°F

TABLE 28 (Continued)

Values of Mean Protective Life and Standard Deviation for Each Specimen Batch for 2500 and 2700°F Oxidation Tests

Alloy and Sample Lot	Batch No.	Processing Condition A(1)			Processing Condition B(1)			Processing Condition C(1)		
		$\bar{X}$	S	N	$\bar{X}$	S	N	$\bar{X}$	S	N
		Hours			Hours			Hours		
B-66 Alloy - Middle and Bottom Retort Position-2500°F Oxidation Test	1	89	28	12	72	33	21	78	28	20
	2	106	32	12	93	26	18	100	27	24
	3	86	11	12	80	29	21	75	27	24
	4	96	33	12	88	34	19	67	23	24
	5	90	17	12	53	25	14	82	40	24
	6	102	23	12	72	29	24	83	30	24
B-66 Alloy - Top Retort Position-2500°F Oxidation Test	1	51	14	6	41	24	12	37	16	12
	2	60	20	6	76	32	12	45	12	12
	3	51	2	6	64	35	12	57	17	12
	4	63	26	6	56	26	12	36	16	12
	5	78	23	6	61	29	12	66	22	12
	6	57	14	6	60	19	12	60	18	12
B-66 Alloy - Middle and Bottom Retort Position-2700°F Oxidation Test	1	5	1	4	3	1	8	2	1	8
	2	4	1	4	5	1	8	4	1	8
	3	11	5	4	4	1	8	5	3	8
	4	7	1	4	4	1	8	5	3	8
	5	4	1	4	4	2	8	6	4	8
	6	3	1	4	3	1	8	4	1	8
B-66 Alloy - Top Retort Position-2700°F Oxidation Test	1	5	0	2	2	0	4	2	1	4
	2	4	0	2	3	2	4	2	0	4
	3	5	3	2	4	2	4	3	2	4
	4	4	1	2	3	1	4	2	1	4
	5	4	1	2	3	1	4	3	2	4
	6	3	0	2	3	1	4	4	1	4

(1) Processing Condition A - Cr-Ti 10 hours at 2350°F, Silicon 6 hours at 2100°F
Processing Condition B - Cr-Ti 8 hours at 2300°F, Silicon 6 hours at 2100°F
Processing Condition C - Cr-Ti 8 hours at 2300°F, Silicon 4 hours at 2000°F

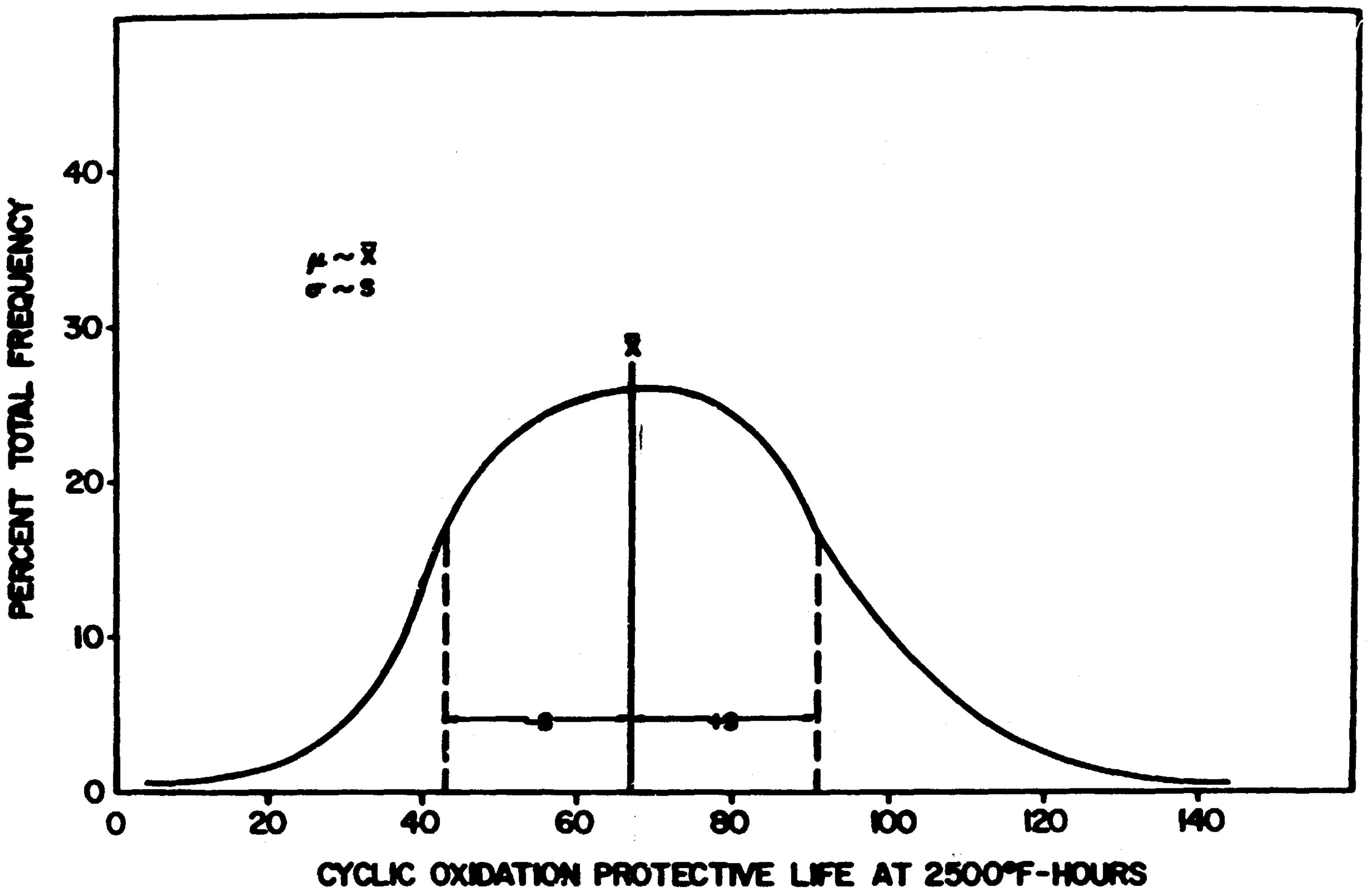


Figure 56 Frequency Distribution Curve for 2500° F Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy - Middle and Bottom Retort Positions

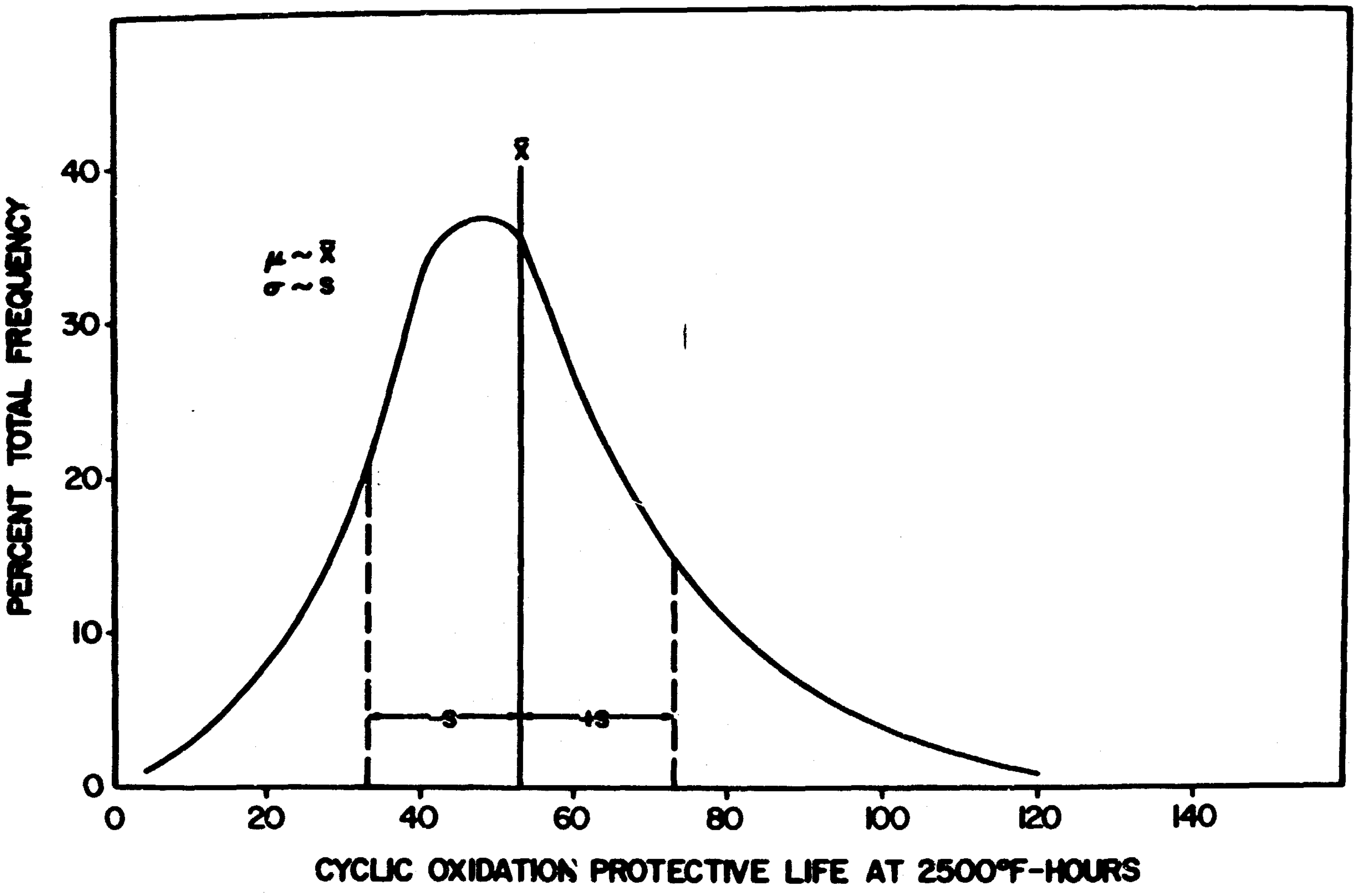


Figure 57 Frequency Distribution Curve for 2500°F Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy - Top Retort Position

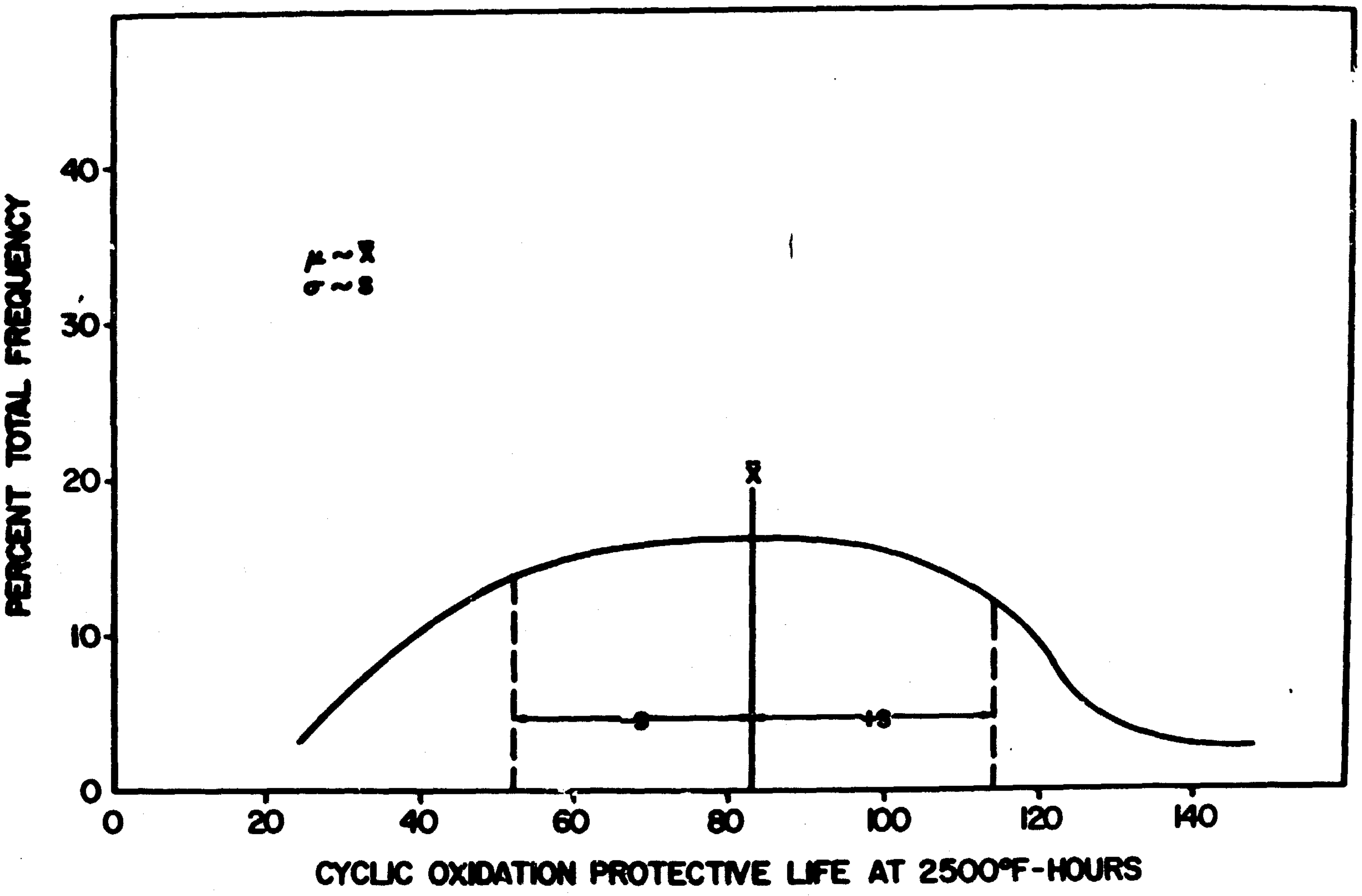


Figure 58 Frequency Distribution Curve for 2500°. Oxidation Protective Life of Cr-Ti-Si Coated B-66 Alloy - Middle and Bottom Retort Position

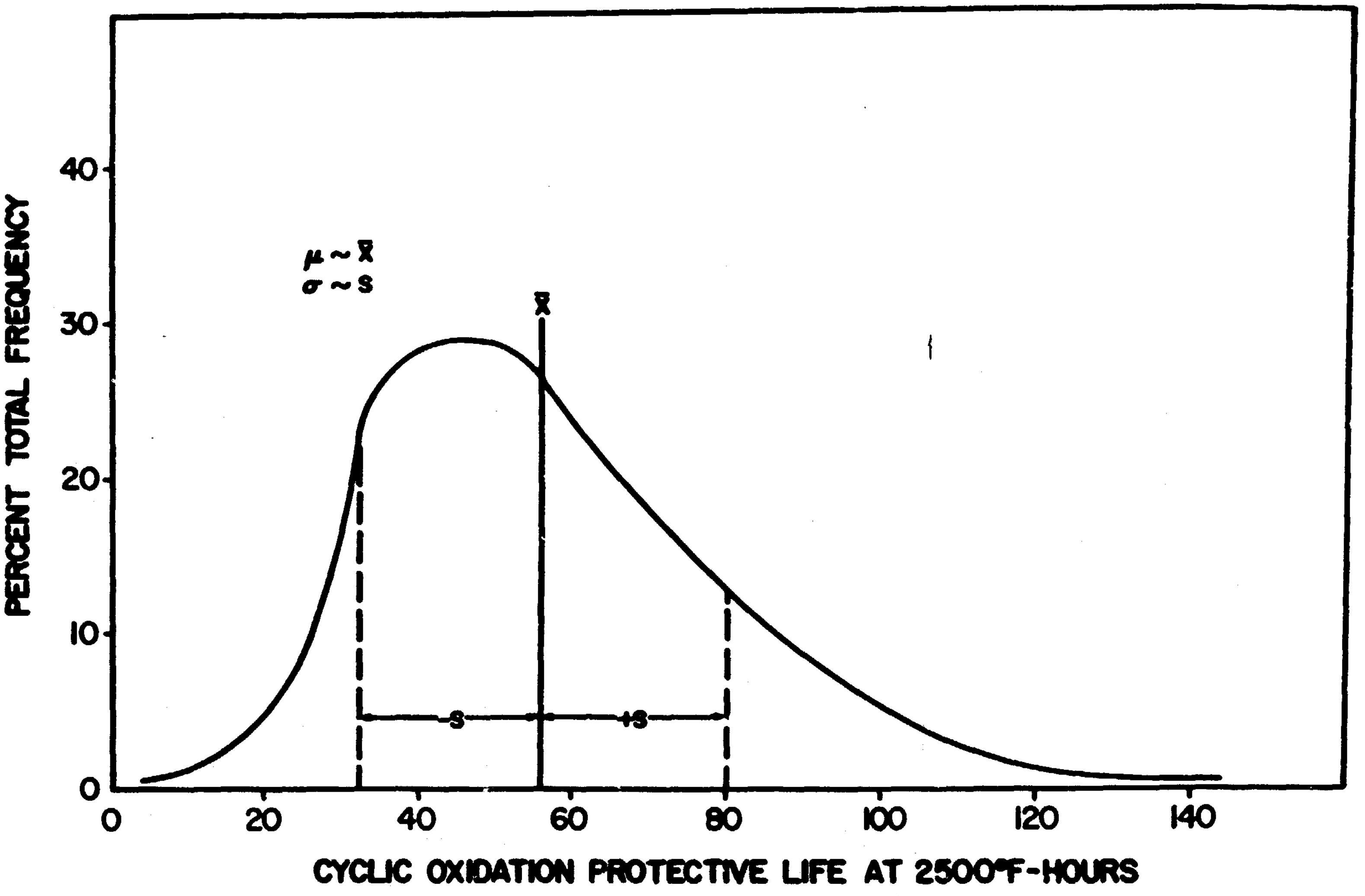


Figure 59 Frequency Distribution Curve for 2500° F Oxidation Protective Life of Cr-Ti-Si Coated B-66 Alloy - Top Retort Position

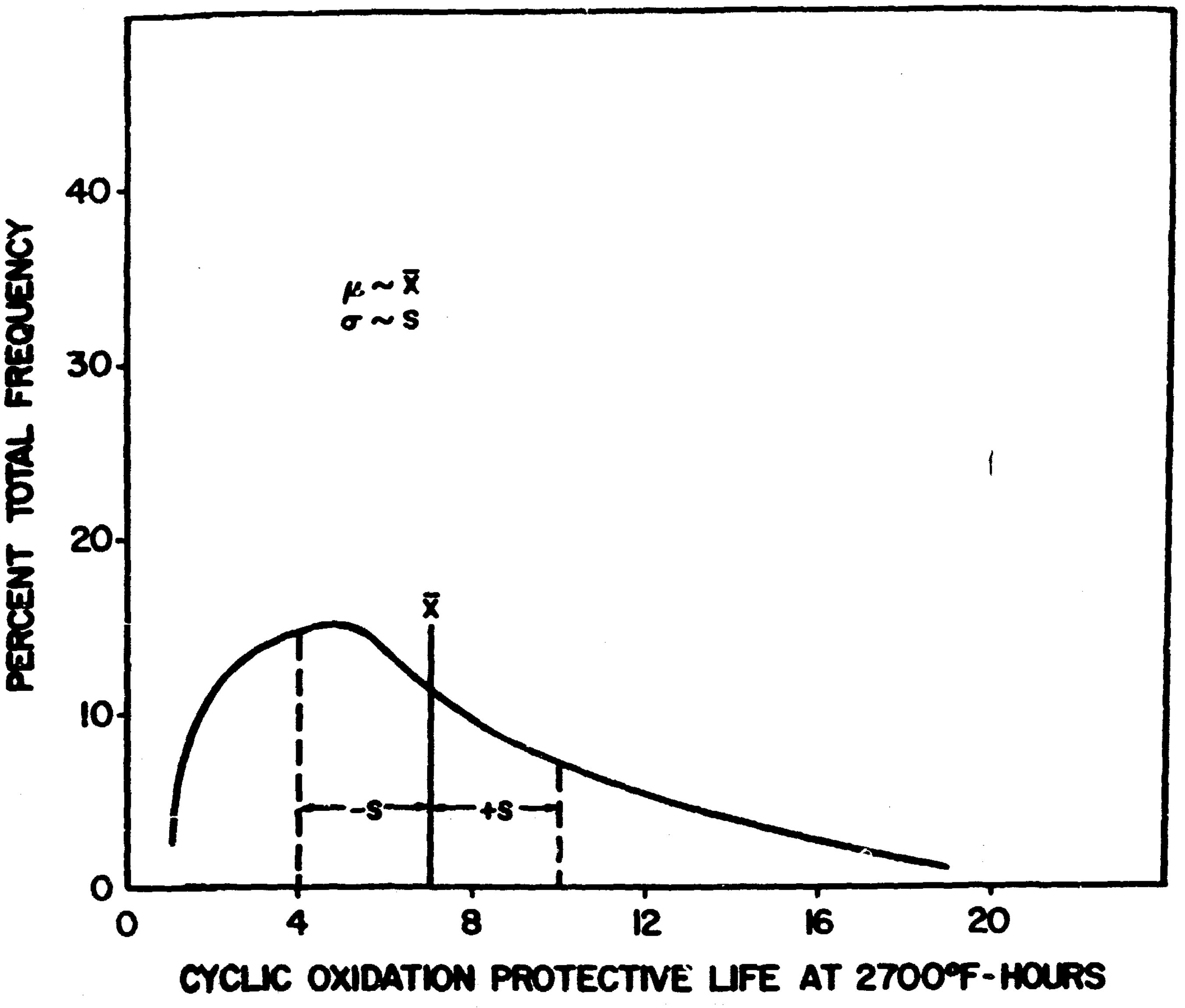


Figure 60 Frequency Distribution Curve for 2700°F Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy - Middle and Bottom Retort Positions

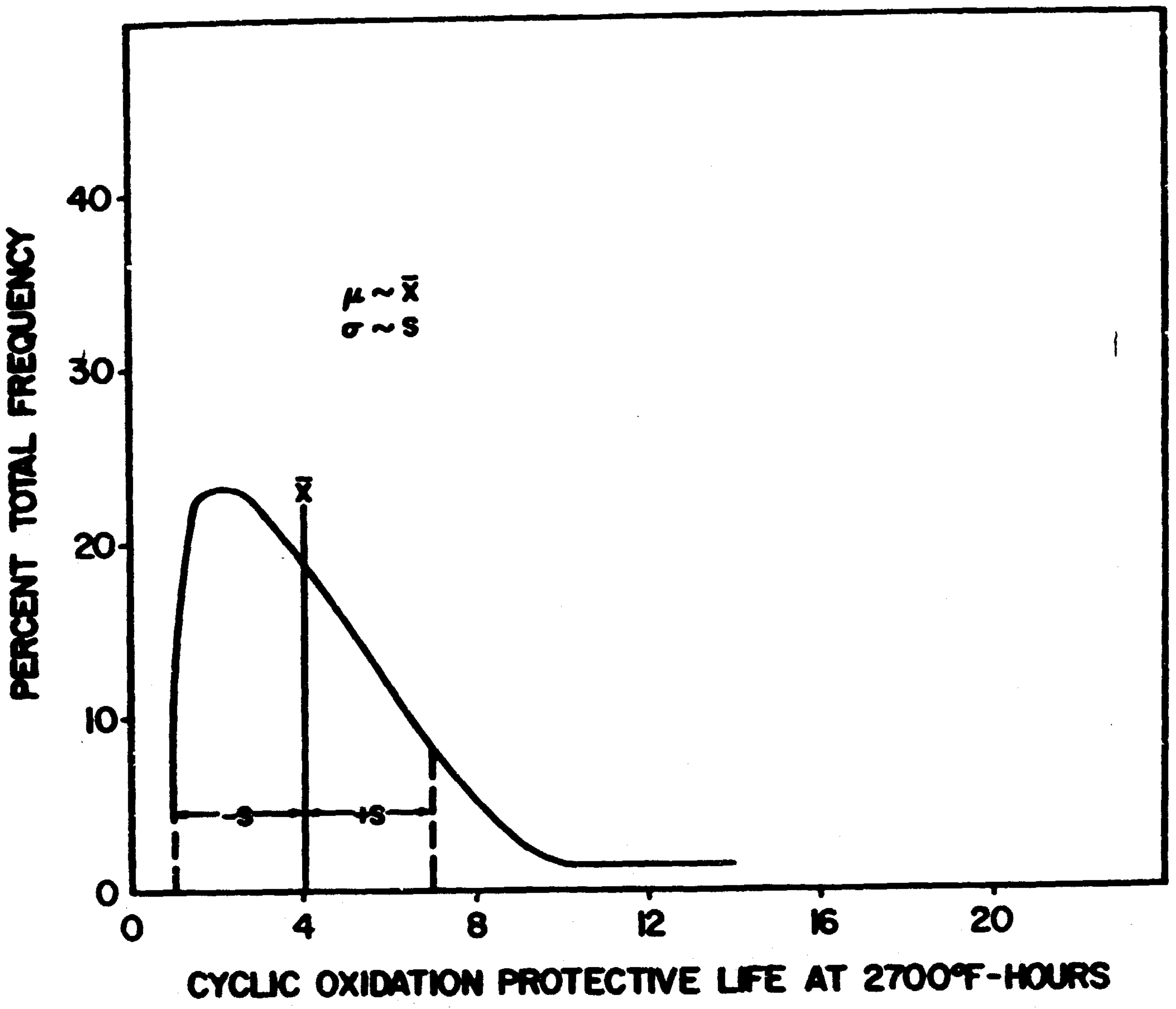


Figure 61 Frequency Distribution Curve for 2700°F Oxidation Protective Life of Cr-Ti-Si Coated D-43 Alloy - Top Retort Position

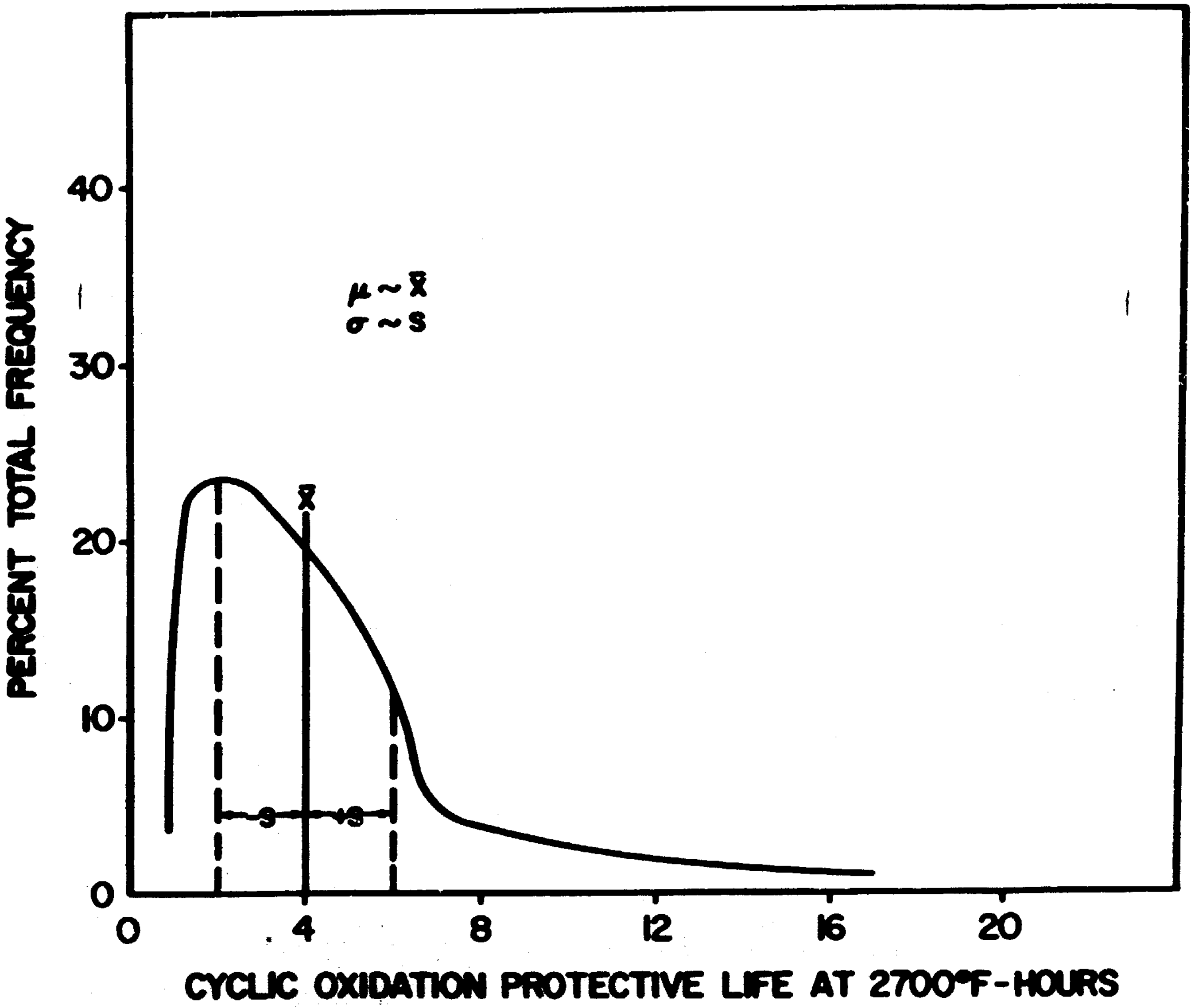


Figure 62 Frequency Distribution Curve for 2700°F Oxidation Protective Life of Cr-Ti-Si Coated B-66 Alloy - Middle and Bottom Retort Positions

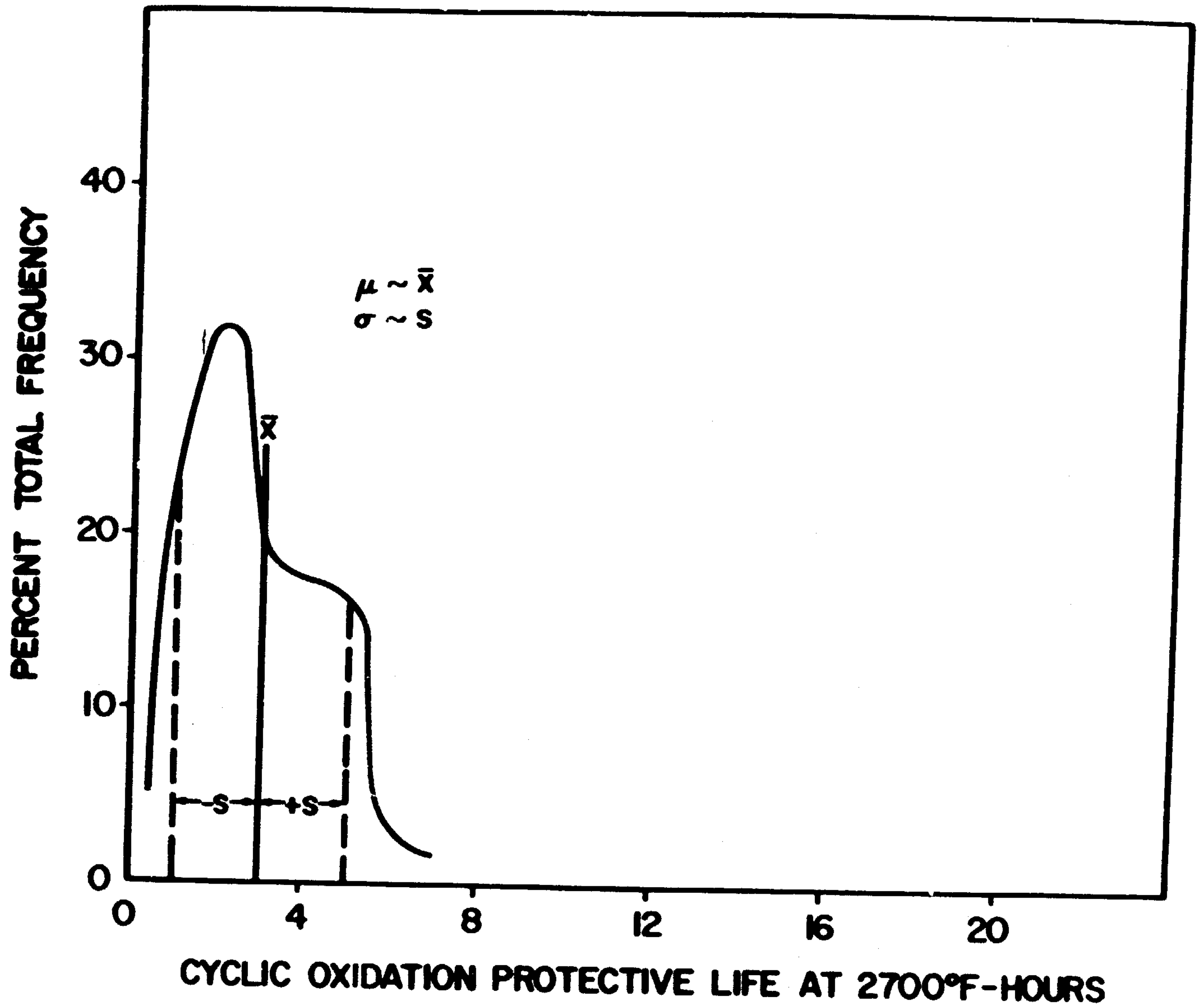


Figure 63 Frequency Distribution Curve for 2700°F Oxidation Protective Life of Cr-Ti-Si Coated B-66 Alloy - Top Retort Position

TABLE 29

Summary of the Mean Protective Life and Standard Deviation for 2500 and 2700°F Oxidation Tests

Middle and Bottom Retort Positions

Alloy	Oxidation Test Temperature-°F	$\bar{X}$	S	N
D-43	2500	67	24	345
D-43	2700	7	3	120
B-66	2500	83	31	326
B-66	2700	4	2	120

Top Retort Position

Alloy	Oxidation Test Temperature-°F	$\bar{X}$	S	N
D-43	2500	53	20	168
D-43	2700	4	3	60
B-66	2500	56	24	180
B-66	2700	3	1	60

2) the life at A is determined by

$$\bar{x} - K(s) = A \quad (\bar{x} + K(s) = A \text{ if } A \text{ were to the right of } \bar{x}) \tag{6}$$

where the value of K for P_1 is obtained from a table of "Percentiles of Normal Distribution"

3) at this point P_1 and A are known, the level of confidence of P_1 is determined by establishing the confidence interval for $\bar{x}$ by

$$\bar{x} \pm K_c \left(\frac{s}{\sqrt{N}}\right) \tag{7}$$

where N is the total number of tests involved and K_c corresponds to the percentile value of the desired confidence level (99% confidence level - K = 2.33)

4) the true mean (μ) for an infinite population will lie within the confidence interval established for $\bar{x}$ and the upper and lower probability limits are set by the values of K given from

$$\left[\bar{x} + K_c \frac{s}{\sqrt{N}}\right] - K_a(s) = A \tag{8}$$

and

$$\left[\bar{x} - K_c \frac{s}{\sqrt{N}}\right] - K_b(s) = A \tag{9}$$

or solved to

$$K_a = \frac{\left[\bar{x} + K_c\left(\frac{s}{\sqrt{N}}\right)\right] - A}{s} \tag{10}$$

$$K_b = \frac{\left[\bar{x} - K_c\left(\frac{s}{\sqrt{N}}\right)\right] - A}{s} \tag{11}$$

5) the percentile values corresponding to K_a and K_b fall above and below P_1, respectively, and establish the probability limits for P_1 at the desired level of confidence for a given life value of A.

Table 30 presents the reliability analysis of the 2500°F protective life data for Cr-Ti-Si coated D-43 and B-66 alloys in terms of protective life probability at a 99% confidence level. A similar reliability analysis of the 2700°F protective life data for the two Cr-Ti-Si coated alloys in terms of protective life probability at a 99% confidence level is given in Table 31.

TABLE 30

Cr-Ti-Si Coating Protective Reliability for Cyclic Oxidation at 2500°F

99% Confidence Level

Cr-Ti-Si Coated D-43 Alloy

Middle and Bottom Retort Positions		Top Retort Position	
Probability	Life-Hours	Probability	Life-Hours
97.5±0.5%	20	97.5±1%	14
95±1%	28	95±2.5%	20
90±2%	36	90±3.5%	27
75±4%	51	75±6%	39

Cr-Ti-Si Coated B-66 Alloy

Middle and Bottom Retort Positions		Top Retort Position	
Probability	Life-Hours	Probability	Life-Hours
97.5±0.5%	22	97.5±1%	9
95±1%	32	95±1.5%	17
90±2%	43	90±3%	25
75±4%	62	75±3.5%	30

TABLE 31

Cr-Ti-Si Coating Protective Reliability for Cyclic Oxidation at 2700°F

99% Confidence Level

Cr-Ti-Si Coated D-43 Alloy

Middle and Bottom Retort Positions		Top Retort Position	
Probability	Life-Hours	Probability	Life-Hours
97.5±1%	1	75±11%	2
95±2%	2		
90±3%	3		
75±6%	5		

Cr-Ti-Si Coated B-66 Alloy

Middle and Bottom Retort Positions		Top Retort Position	
Probability	Life-Hours	Probability	Life-Hours
95±3.5%	1	90±1.5%	1
90±4.5%	2	75±7%	2
75±7%	3		

The values for protective reliability represent the probability of obtaining a given protective life at 2500 or 2700°F from any B-66 or D-43 alloy piece Cr-Ti coated utilizing the process parameters included in this study. It should be noted that the life-hour expectancy listed in the tables for a given probability level applies to coatings processed using a relatively wide variation in process condition The batch-to-batch variation, previously noted, is factored into the values for protective reliability. It should also be noted that the coatings utilized in this stu were selected to be reasonably protective over the temperature range from below 2000 to 2700°F. This required some sacrifice of protective properties at both high and low temperatures in order to achieve better overall performance for this wide range of test temperatures. Improvement of protective capability at a particular test temperature could be achieved by adjustment of the process parameters and associated coating composition.

8. REDUCED PRESSURE OXIDATION STUDIES

In many applications involving coated columbium alloys, such as high altitude re-entry vehicles, components will be subjected to elevated temperature exposures at gas pressures below one atmosphere. Very little data are presently available concer ing the effect of reduced pressure oxidation on the protective capabilities of refractory metal coatings. Limited data have been obtained from work carried out at Lockheed involving testing of silicide coated molybdenum under reduced pressure conditions simulating those of a radiation cooled leading edge structure of a hypothetical glide re-entry vehicle(4). This work and similar studies initiated by other organizations indicate conclusively that cyclic oxidation properties at one atmosphere are not alone sufficient criteria for the evaluation of refractory metal coating protection for aerospace applications. Degradation of silicide coating protective capabilities has been produced by low pressure exposure, resulting from the deterioration of the normally protective glassy SiO_2 layer by the volatization of silicon monoxide (SiO).

The primary objective of this phase of the program was that of elucidating the protective properties and stability of the Cr-Ti-Si coating for a range of reduced pressure-elevated temperature exposure conditions.

The program was originally planned to include low pressure exposure temperature of 2500 and 2600°F and pressure levels (air) of from 10^{-2} to 50 mm. However, initia test results indicated the range of pressures of primary interest to be 10^{-2} to 5 mm Thus, the program was modified to provide a comparison of the effects of the followi variables:

a) exposure pressures of 10^{-2}, 10^{-1} and 5 mm

b) exposure temperatures of 2500 and 2600°F

c) exposure times of 1, 2 and 4 hours

d) initial specimen conditions of (1) as coated, (2) pre-oxidized 1 hour at 2500°F at 1 atmosphere and (3) pre-oxidized 4 hours at 2000°F at 1 atmosphere.

Visual inspection and metallographic examination of representative specimens exposed to the reduced pressure environment were employed to determine the effect of exposure. In addition, cyclic post-oxidation tests at 1800 and 2500°F were utilized to determine the post-oxidation protective characteristics of specimens exposed at reduced pressure as compared to the cyclic oxidation protective properties of as coated specimens.

The low pressure facility constructed for this work is shown in cross section in Figure 64. The horizontal high purity alumina tube (2.0" I.D.) is externally heated by four globar elements. Water cooled copper fixturing is attached to each end of the refractory tube with wax vacuum seals. A vacuum tight push rod assembly is attached to one end of the vacuum chamber for manipulating a high purity alumina specimen tray in and out of the hot zone. The hot zone is 12" overall length and permits uniform heating of a 6" long specimen boat. Temperature measurements are made with an optical pyrometer through a sight port and correlated with measurements within the tube using a Pt-Pt-10% Rh thermocouple. A McLeod type vacuum gage is utilized for pressure measurements. This unit has been evacuated to approximately 1 micron pressure (10^{-3} mm) at 2600°F. The design of this furnace permits simultaneous testing of several coated coupons, and has provisions for thermal cycling for visual inspection. At the higher operating pressures air is bled through the system and the gas flow rates metered.

Initially, difficulty with the test apparatus was encountered because of cracking of the refractory alumina tubes. This problem was discussed with the refractory tube suppliers, and as a result several modifications were made in the furnace hearth and tube support designs. In addition to design modifications, Mullite MV-30 tubes (supplied by McDanel Refractory Porcelain Co.) were installed to replace the high purity alumina tubes. The apparatus was successfully operated at pressures to 10^{-3} mm (1 micron) up to 2600°F. One mullite tube cracked after several hours operation; a second was installed and successfully operated in excess of 100 hours. However, excessive tube breakage was again encountered with the present apparatus, and it was concluded that additional testing was not economically feasible. All testing was completed, with the exception of tests scheduled at 2600°F, at 5 mm pressure. It is felt that the test apparatus can be improved to eliminate the tube breakage problem.

Cr-Ti-Si coated D-14 columbium alloy sheet was utilized exclusively for this portion of the investigation. The coupons were Cr-Ti-Si coated in five separate batches. All coupons, however, were coated by utilizing identical coating parameters. The coating was applied from a 50Cr-50Ti pack in 8 hours at 2300°F using 0.5 w/o KF activation and a pressure of 1.5 mm (blanked off system). The silicon cycle involved 4 hours at 2050°F using 1.0 w/o KF activation and a system pressure of 10^{-2} mm.

At 2500°F a wide range of pressures were investigated. These included 10^{-2}, 10^{-1} , 1, 5 and 50 mm utilizing exposure times of 1, 2 and 4 hours. As coated specimens were exposed at each pressure level, and in addition pre-oxidized specimens (1 hour at 2500°F - one atmosphere and 4 hours at 2000°F - one atmosphere) were exposed at 10^{-2} , 10^{-1} and 5 mm. The testing conducted at 2600°F included

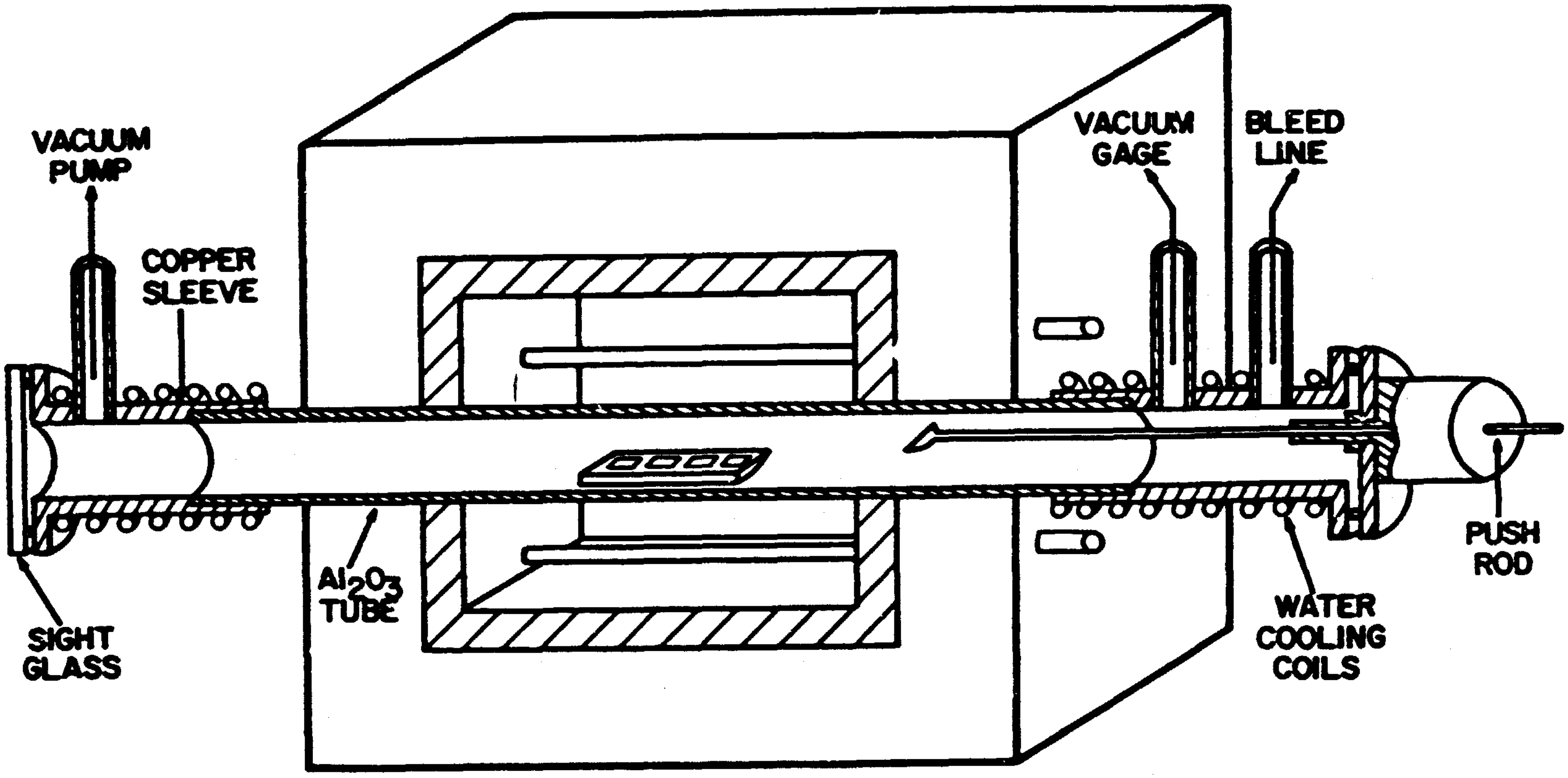


Figure 64 Cross Sectional Drawing of Globar Heated Reduced Pressure Exposure Furnace - Approximately 1/5X

only pressures of 10^{-2} and 10^{-1} mm. All three specimen starting conditions were evaluated at each pressure. Of prime importance is the fact that there were no instances of visible coating failure and associated growth of columbium oxide on any of the specimens exposed to the high temperature-reduced pressure environments.

Five specimens were exposed at each indicated time for each set of test parameters. One specimen from each low pressure exposure group was sectioned for metallographic examination, two specimens were post-oxidation tested at 1800°F and two specimens were post-oxidation tested at 2500°F in air at one atmosphere.

Operating pressures of 10^{-2} and 10^{-1} mm were obtained by controlling the pumping rate to the system. The higher operating pressures of 1, 5 and 50 mm were obtained with a controlled air bleed into the system. Air flow rates required to produce the desired operating pressures were metered and values for mass flow obtained for air entering the system at room temperature and constant pressure. These values are listed in Table 32. Considering the expansion of the air in the furnace hot zone at 2500°F, the average air velocity in this portion of the tube would be increased by a factor of approximately five. The mass flow of air through the tube was obviously quite low at these pressures.

Post-oxidation tests used to evaluate the extent of change in the coating protective life resulting from the low pressure exposure were conducted in the same manner as for evaluation of one atmosphere protective life. Specimens were cycled from the test temperature to room temperature once each hour for 8 hours followed by 16 hours of static exposure for each 24 hour period with testing continued until the first external evidence of coating failure was observed. A globar heated box furnace with a slowly moving air atmosphere was used for all oxidation tests at one atmosphere. Cr-Ti-Si coated specimens similar to those exposed to reduced pressures were cyclic oxidation tested for baseline data for evaluation of the effect of the reduced pressure exposure on the protective capability of the coating. Table 33 lists the results of the post-oxidation tests conducted on all specimens exposed to low pressure environments.

8.1 Summary of Low Pressure Behavior

Exposure of as coated specimens at 10^{-2} mm at 2500°F did not cause loss of protective capability at 1800°F. 2500°F exposure at 10^{-1} mm of specimens preoxidized 4 hours at 2000°F likewise did not effect the 1800°F one atmosphere protective capability of the coating. This was also true of all conditions involving exposure at 2500°F at pressures greater than 10^{-1} mm. Pre-oxidized specimens exposed at 2500°F at 10^{-2} mm sufferend some loss of low temperature capability. As coated and pre-oxidized (1 hour at 2500°F at one atmosphere only) specimens exposed at 10^{-1} mm also showed some loss of 1800°F one atmosphere protective life. All exposure conditions investigated at 2600°F caused loss of subsequent 1800°F one atmosphere protective capability of the Cr-Ti-Si coating.

Some degradation of the 2500°F one atmosphere protective life was apparent for all reduced pressure exposure conditions at 2500°F involving pressures of less than 5 mm. Serious loss of 2500°F one atmosphere protective properties resulted

TABLE 32

Mass Flow of Air in Reduced Pressure Test Facility

Pressure	CFH	CFS	lbs/sec.	ft/sec. (2500° F)
1 mm	10	2.8×10^{-3}	0.22×10^{-3}	0.12
5 mm	15	4.4×10^{-3}	0.35×10^{-3}	0.22
10 mm	22	5.8×10^{-3}	0.47×10^{-3}	0.26
50 mm	28	7.1×10^{-3}	0.57×10^{-3}	0.36
100 mm	32	8.6×10^{-3}	0.69×10^{-3}	0.40

TABLE 33

Cyclic Oxidation Protective Life (Air) for Cr-Ti-Si Coated D-14 Alloy After Exposure to Elevated Temperature - Reduced Pressure Environments

Pre-Oxidation Exposure			Low Pressure Exposure			Post Oxidation Protective Life at 1 Atmosphere - Hours	
Temperature °F	Time Hours	Pressure mm.	Temperature °F	Time Hours	Pressure mm.	1800°F	2500°F
none			none			*200,200	104,104
none			none			200,200	72,80
none			none			200,200	117,148
none			2500	1	10^{-2}	200,200	124,140
none			2500	2	10^{-2}	200,200	96,117
none			2500	4	10^{-2}	200,200	4,6
2500	1	760	2500	1	10^{-2}	200,200	56,56
2500	1	760	2500	2	10^{-2}	48,200	3,3
2500	1	760	2500	4	10^{-2}	5,144	2,78
2000	4	760	2500	1	10^{-2}	200,200	8,31
2000	4	760	2500	2	10^{-2}	200,200	14,31
2000	4	760	2500	4	10^{-2}	200,200	8,14
none			2500	1	10^{-1}	200,200	96,96
none			2500	2	10^{-1}	200,200	4,76
none			2500	4	10^{-1}	4,24	4,4
2500	1	760	2500	1	10^{-1}	200,200	48,96
2500	1	760	2500	2	10^{-1}	24,53	5,48
2500	1	760	2500	4	10^{-1}	24,72	5,5
2000	4	760	2500	1	10^{-1}	200,200	48,56
2000	4	760	2500	2	10^{-1}	200,200	48,48
2000	4	760	2500	4	10^{-1}	200,200	8,56
none			2500	1	1	200,200	31,79
none			2500	2	1	200,200	70,96
none			2500	4	1	200,200	4,96

* Indicates test discontinued at 200 hours - no visible external evidence of coating failure

TABLE 33 (Continued)

Cyclic Oxidation Protective Life (Air) for Cr-Ti-Si Coated D-14 Alloy After Exposure to Elevated Temperature - Reduced Pressure Environments

Pre-Oxidation Exposure			Low Pressure Exposure			Post Oxidation Protective Life at 1 Atmosphere - Hours	
Temperature °F	Time Hours	Pressure mm.	Temperature °F	Time Hours	Pressure mm.	1800°F	2500°F
none			2500	1	5	*200,200	71,79
none			2500	2	5	200,200	70,70
none			2500	4	5	200,200	70,70
2500	1	760	2500	1	5	200,200	96,117
2500	1	760	2500	2	5	200,200	98,117
2500	1	760	2500	4	5	200,200	77,117
2000	4	760	2500	1	5	200,200	96,120
2000	4	760	2500	2	5	200,200	80,124
2000	4	760	2500	4	5	200,200	24,120
none			2500	1	50	200,200	120,144
none			2500	2	50	200,200	104,120
none			2500	4	50	200,200	144,169
none			2600	1	10^{-2}	5,8	48,50
none			2600	2	10^{-2}	8,24	8,8
none			2600	4	10^{-2}	8,8	2,2
2500	1	760	2600	1	10^{-2}	5,5	2,2
2500	1	760	2600	2	10^{-2}	5,8	2,2
2500	1	760	2600	4	10^{-2}	8,8	1,1
2000	4	760	2600	1	10^{-2}	5,8	4,6
2000	4	760	2600	2	10^{-2}	5,5	3,48
2000	4	760	2600	4	10^{-2}	8,48	3,3

* Indicates test discontinued at 200 hours - no visible external evidence of coating failure

TABLE 33 (Continued)

Cyclic Oxidation Protective Life (Air) for Cr-Ti-Si Coated D-14 Alloy After Exposure to Elevated Temperature - Reduced Pressure Environments

Pre-Oxidation Exposure			Low Pressure Exposure			Post Oxidation Protective Life at 1 Atmosphere - Hours	
Temperature °F	Time Hours	Pressure mm.	Temperature °F	Time Hours	Pressure mm.	1800°F	2500°F
none			2600	1	10^{-1}	5,5	6,8
none			2600	2	10^{-1}	5,8	2,6
none			2600	4	10^{-1}	4,8	2,2
2500	1	760	2600	1	10^{-1}	*200,200	31,31
2500	1	760	2600	2	10^{-1}	144,200	48,49
2500	1	760	2600	4	10^{-1}	24,28	3,3
2000	4	760	2600	1	10^{-1}	5,8	31,31
2000	4	760	2600	2	10^{-1}	5,76	2,3
2000	4	760	2600	4	10^{-1}	- -	- -

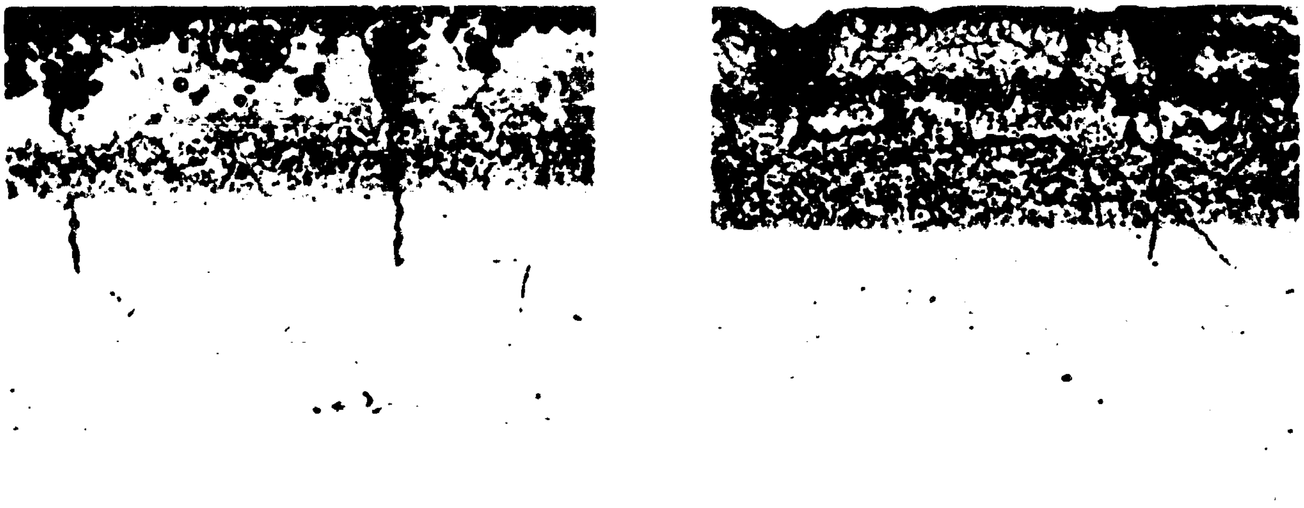
* Indicates test discontinued at 200 hours - no visible external evidence of coating failure

from exposure of as coated specimens for 4 hours at 10^{-2} mm at 2500°F. Exposure for less than 4 hours at this pressure caused only a minor decrease in protective life. Oxidation at one atmosphere prior to exposure at 10^{-2} mm at 2500°F resulted in serious loss of 2500°F protective properties. Exposure at 2600°F at 10^{-2} mm or at either 2500 or 2600°F at 10^{-1} mm caused loss of 2500°F one atmosphere protection regardless of initial specimen condition. Reduced pressure exposure at 1 mm at 2500°F also caused a reduction in 2500°F one atmosphere protective properties, although less serious than exposure at 10^{-1} mm at 2500°F. Exposure to reduced pressure environments at 2500°F at pressures of 5 and 50 mm caused no reduction of 2500°F one atmosphere protective characteristics. In fact, an apparent improvement in the high temperature protective capability of the Cr-Ti-Si coating was observed as a result of exposure at 50 mm.

8.2 Low Pressure Behavior at 10^{-2} mm

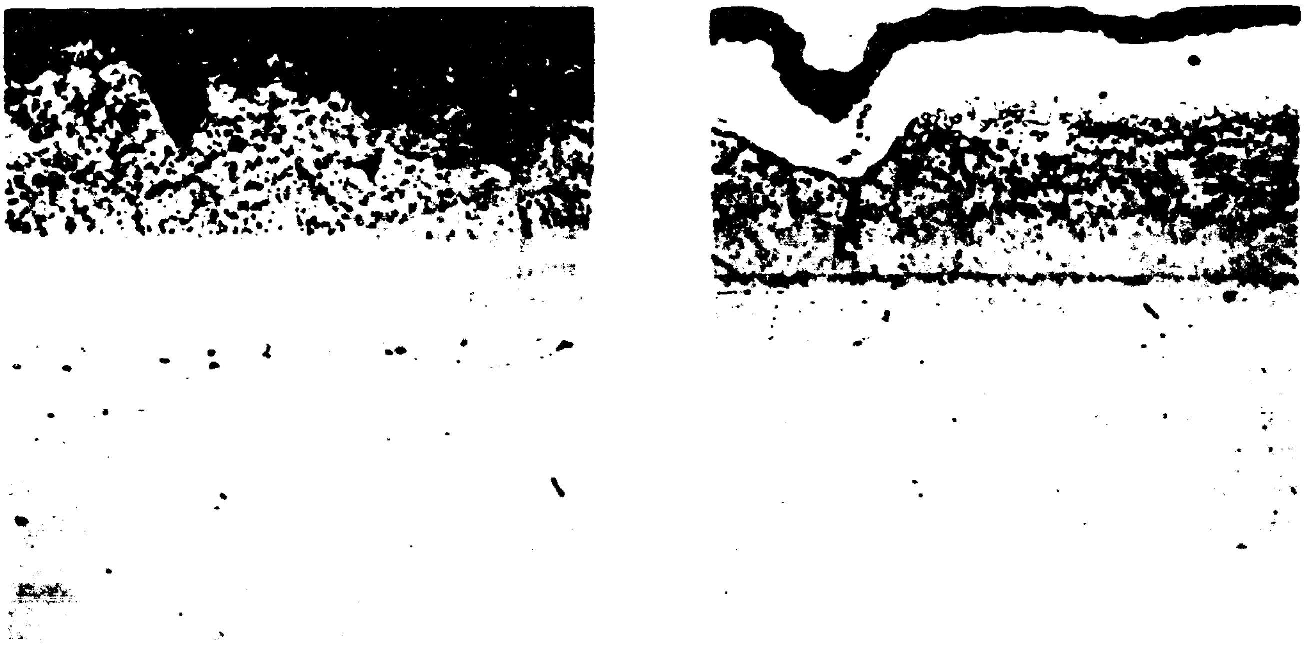
Figure 65 shows photomicrographs of the Cr-Ti-Si coated specimens exposed for 1 and 4 hours at 10^{-2} mm (2500°F) in comparison with similar specimens exposed at one atmosphere at 2500°F. A relative change in coating microstructure is readily observed after the 1 hour exposure. Recessions in the coating surface are noted after exposure at both pressures, however, at one atmosphere these pockets became filled with a protective oxide layer. This figure, at 500X, compares the changes that occur in coating structure during exposure in air at one atmosphere and at 10^{-2} mm for 4 hours at 2500°F. All other photomicrographs of specimens exposed to the reduced pressure environments are shown at 250X. The gradual formation of the distinctive layer in the outer surface of the coating of as coated specimens exposed at 10^{-2} (2500°F) is shown again in Figure 66. This layer is thought to be titanium silicide resulting from chromium depletion of the coating. The oxide which formed on these specimens upon subsequent post-oxidation was yellowish-brown in color, characteristic of the oxide which forms on titanium silicide. Chromium loss during the reduced pressure exposure was evidenced as a deposit of green chromium oxide on the walls of clean alumina boats during exposure. In general, the coating thickness was relatively unchanged by this particular reduced pressure exposure. The major microstructural change was the formation of the distinct surface depletion layer. The finger-like recessions which are apparent in the coating microstructure are observed macroscopically as a craze crack pattern on the specimen surface, in the absence of any appreciable oxide surface layer. Figure 67 is a photograph of this crack pattern. This condition apparently is caused by preferential volatilization of the coating constituents (probably chromium) from these localized recesses.

A coupon weight loss of approximately 6 mg/hour occurred during exposure (2500°F) at 10^{-2} mm, and it was obvious that the coating was depleted of a considerable quantity of chromium. Chromium vaporization from the coating apparently continued for up to 4 hours during the reduced pressure oxidation treatment. Chromium was, in fact, evaporated in small amounts from the Cr-Ti-Si coating at one atmosphere during oxidation testing at 2500°F and above. For increasing exposure times at low pressure, decreasing quantities of chromium were observed to be lost from the coatings during oxidation test at one atmosphere at 2500°F. The weight changes recorded for low pressure exposure at 2500°F are presented graphically in



1 Hour - 2500°F
1 Atmosphere

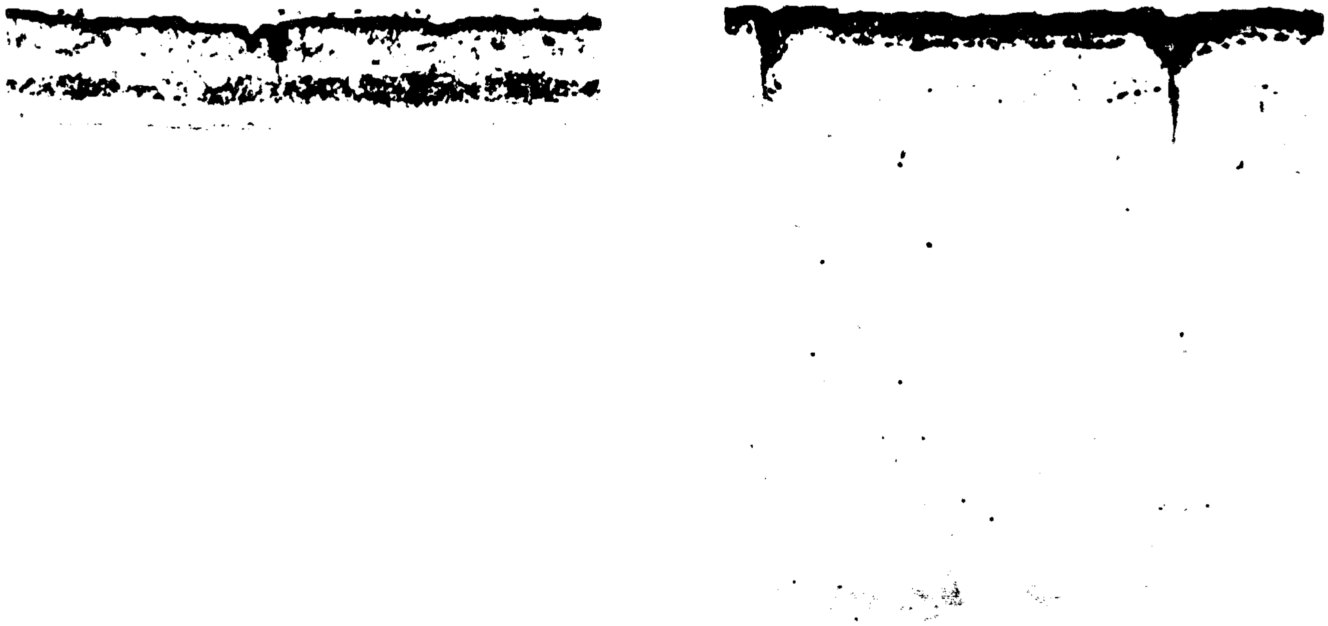
1 Hour - 2500°F
10^{-2} mm



4 Hours - 2500°F
1 Atmosphere

4 Hours - 2500°F
10^{-2} mm

Figure 65 Cr-Ti-Si Coated D-14 Alloy After 1 and 4 Hour Exposures in Air at 2500°F, at Both 1 Atmosphere and 10^{-2} mm 500X

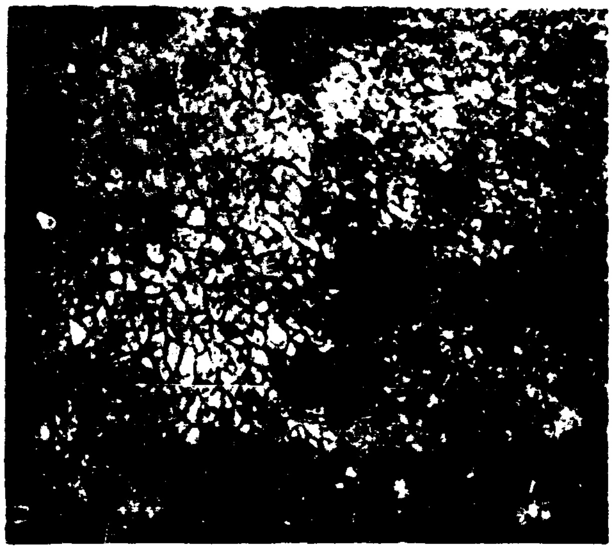


1 Hour - 2500°F
10^{-2} mm

2 Hours - 2500°F
10^{-2} mm

4 Hours - 2500°F
10^{-2} mm

Figure 66 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hour Exposures in Air at 2500°F at 10^{-2} mm 250X



4 Hours - 2500° F - 10^{-2} mm 10X

4 Hours - 2500° F - 10-2 mm Polarized Light 100X

Figure 67 Cr-Ti-Si Coated D-14 Alloy After 4 Hours Exposure in Air at 2500° F at 10^{-2} mm Showing Surface Craze Cracking

Figure 68. Figure 69 shows the weight changes recorded for low pressure exposure at 2600° F.

The specimen weight loss of 6 mg/hour reported above corresponds to approximately 1.8 mg/cm^2/hour based on the total specimen area (1/2" x 1/2" x 0.040") or approximately five percent of the total weight of the coating per hour. During these tests only one side of the specimen was entirely exposed, the opposite face being in contact with the alumina boat. The exact value of the coating weight loss per unit area was therefore somewhat greater than the above value for the exposed surfaces.

Figures 70 and 71 show photomicrographs of specimens oxidized at 2500° F for 1 hour and 2000° F for 4 hours (one atmosphere) and subsequently exposed at 2500° F at 10^{-2} mm. Both pre-oxidation exposure conditions caused a reduction in the low temperature protective properties as compared to as coated specimens exposed at the same conditions. Of the two pre-oxidation conditions, the 1 hour treatment at 2500° F caused the greater reduction in 1800° F protective capability. Both pre-oxidation treatments resulted in more serious loss of 2500° F protective properties than direct exposure of as coated specimens. A comparison of these microstructures with those in Figure 66 shows the presence of a heavy surface oxide layer on the specimens pre-oxidized at 2500° F before the low pressure exposure and a thinner oxide on specimens pre-oxidized at 2000° F. The coating remaining on the pre-oxidized specimens is seen to be much thinner than on as coated specimens exposed at 10^{-2} mm at 2500° F. The oxide layer formed on the surface of the coatings during pre-oxidation is obviously not completely removed by the low pressure exposure treatment. Some contamination is visible in the substrate of pre-oxidized specimens, particularly those pre-oxidized at 2500° F and exposed 4 hours at 10^{-2} mm (2500° F). The oxide surface layer is no doubt the source of oxygen which ultimately diffuses into the substrate at 2500° F. Vaporization of coating elements, notably chromium, apparently renders the coating permeable to small amounts of oxygen. The pre-oxidation treatment involving 1 hour at 2500° F greatly reduced the specimen weight loss (Figure 68) during subsequent low pressure exposure compared to the as coated initial specimen condition. Apparently the formation of a dense glassy layer during the 2500° F pre-oxidation treatment served to lower the rate of chromium vaporization from the coatings. The oxide formed at 2000° F was not dense enough to slow the loss of chromium, thus the weight loss for this starting condition during low pressure exposure approximated that recorded for as coated specimens.

Figures 72 and 73 are photomicrographs of coupons which were post-oxidation tested at 1800 and 2500° F (one atmosphere) after previous 10^{-2} mm oxidation at 2500° F. At 1800° F a protective oxide is observed to have formed at one atmosphere on the chromium depleted surface layer of the specimen exposed at 10^{-2} mm. This oxide provided protection equivalent to that of the oxide formed on the as coated Cr-Ti-Si coating, based on the time limit of the test. However, at 2500° F this unidentified depleted layer exhibited relatively poor protection as compared to the as coated specimen. Deterioration of the coating is observed after 6 hours oxidation at one atmosphere on an individual coupon after a 4 hour exposure at 2500° F and 10^{-2} mm. Only slight degradation of the one atmosphere 2500° F protective life

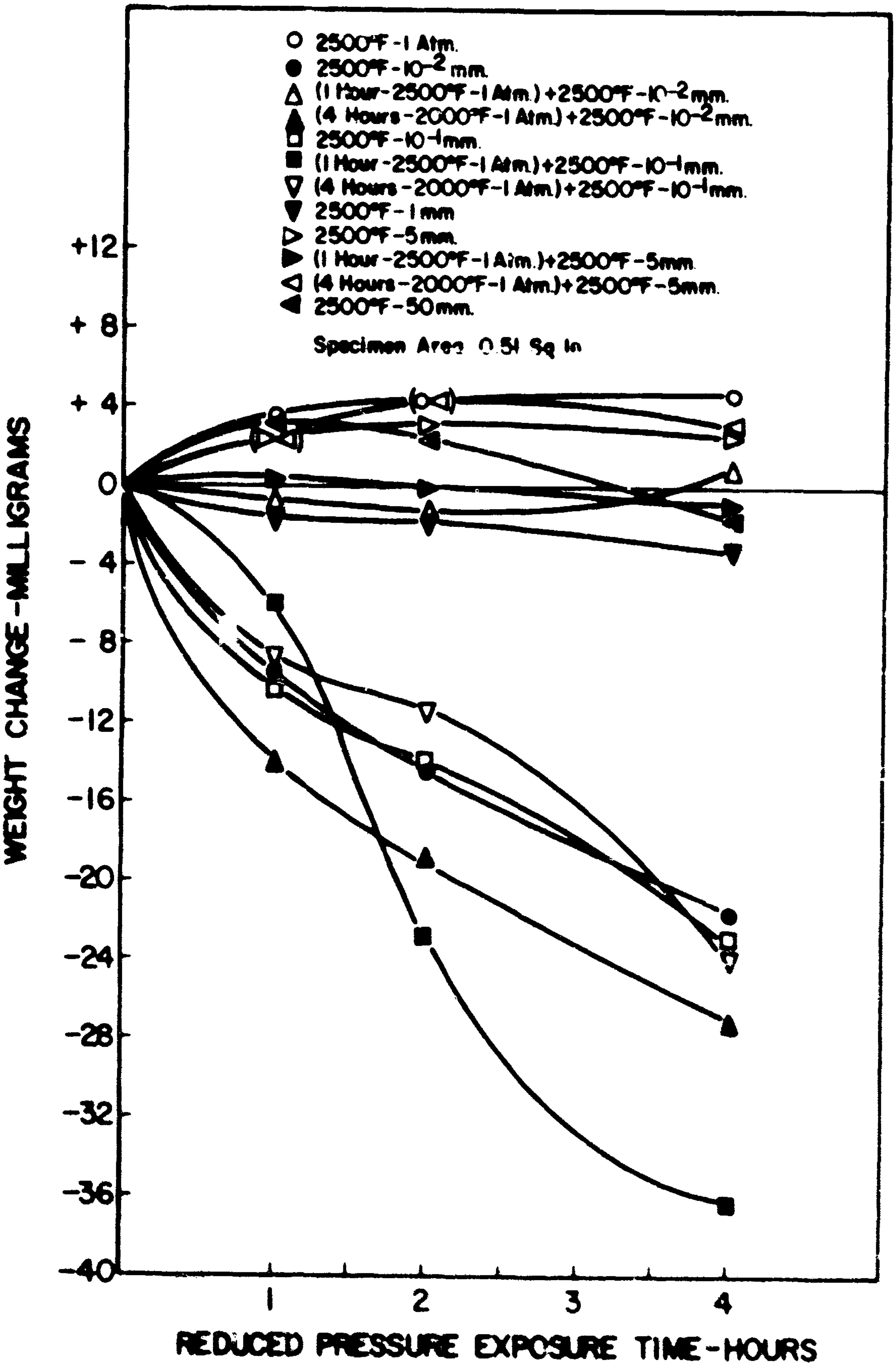


Figure 68 Weight Change of Cr-Ti-Si Coated D-14 Alloy as a Function of Time for Various Reduced Pressure Treatments at 2500°F

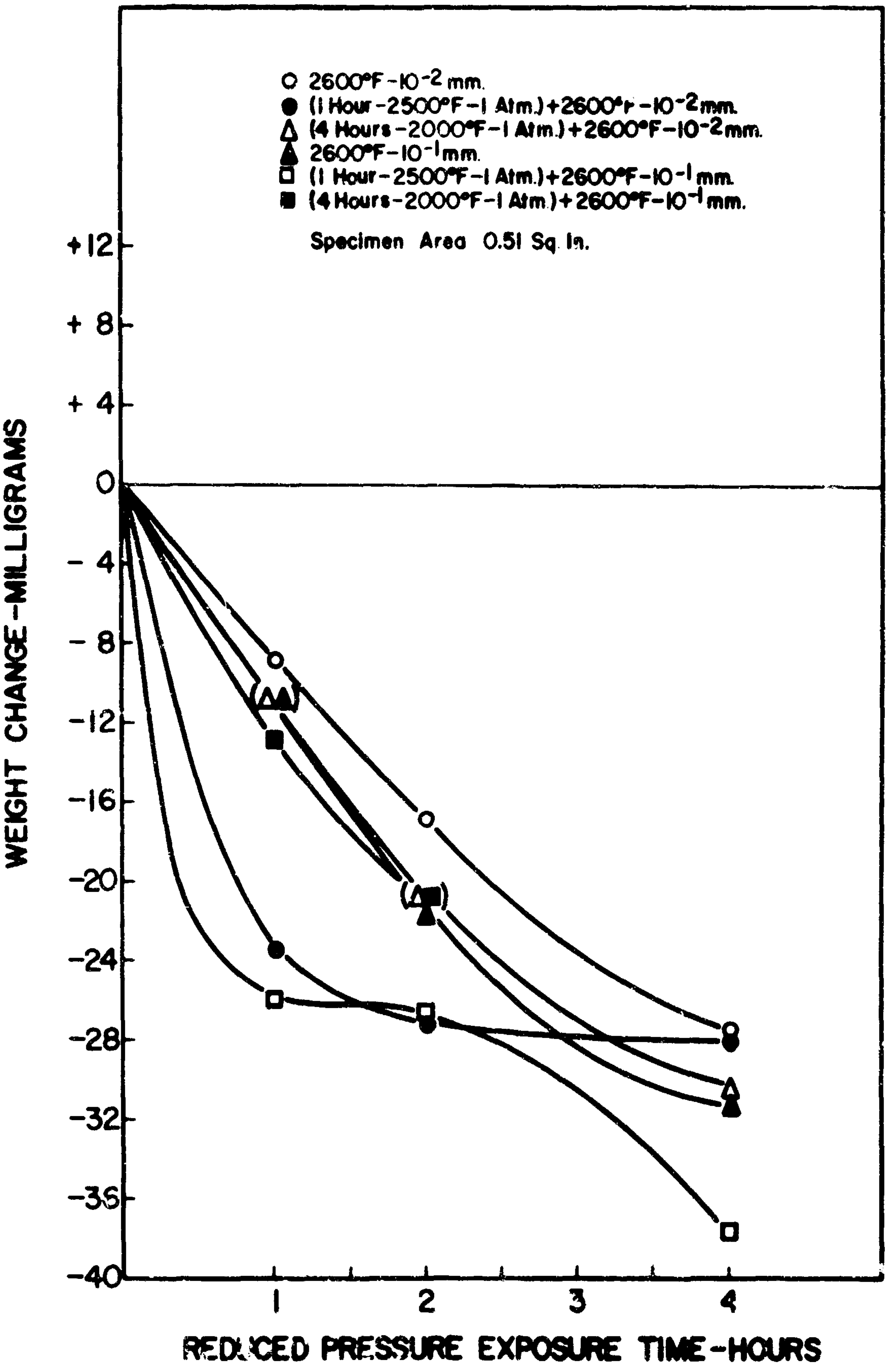
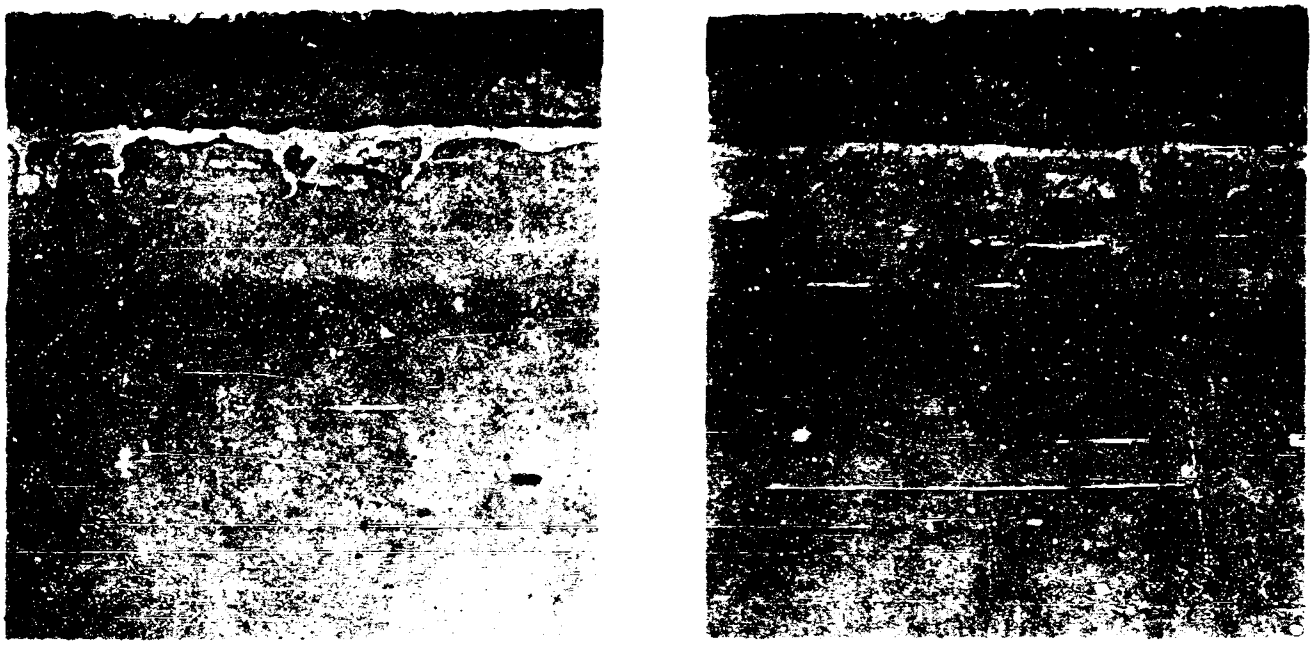


Figure 69 Weight Change of Cr-Ti-Si Coated D-14 Alloy as a Function of Time for Various Reduced Pressure Treatments at 2600°F

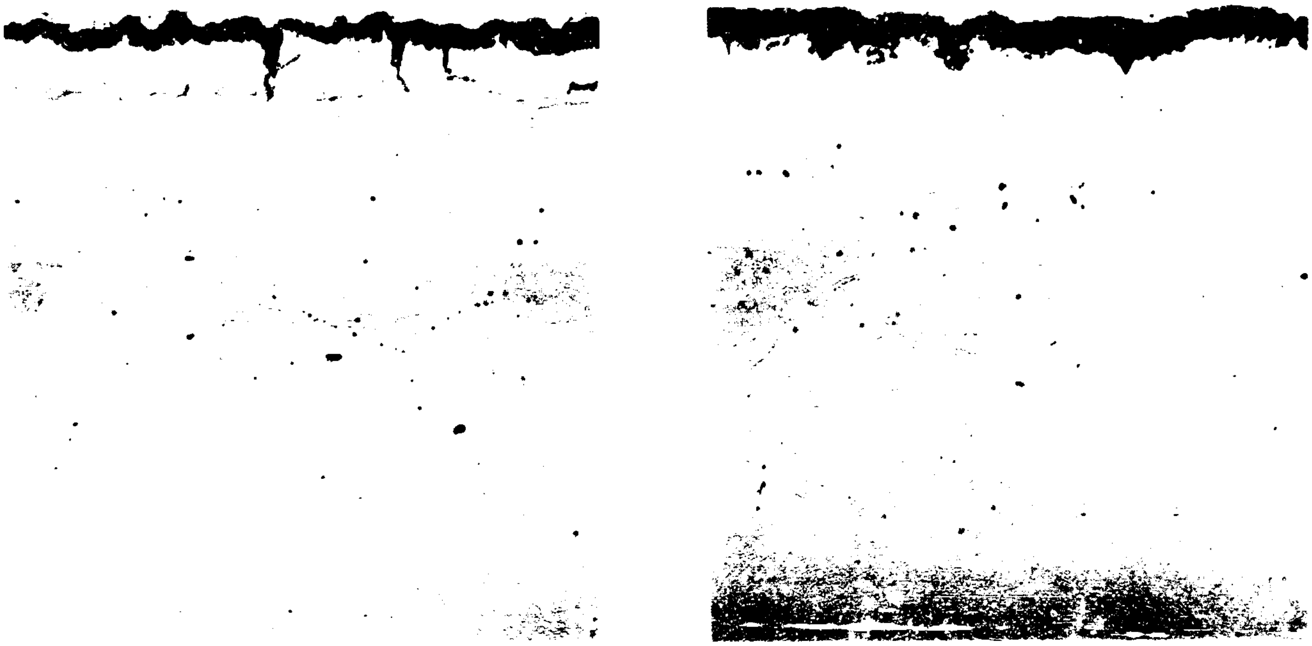


1 Hour - 2500°F - 1 Atm
1 Hour - 2500°F - 10^{-2} mm

1 Hour - 2500°F 1 Atm
2 Hours - 2500°F - 10^{-2} mm

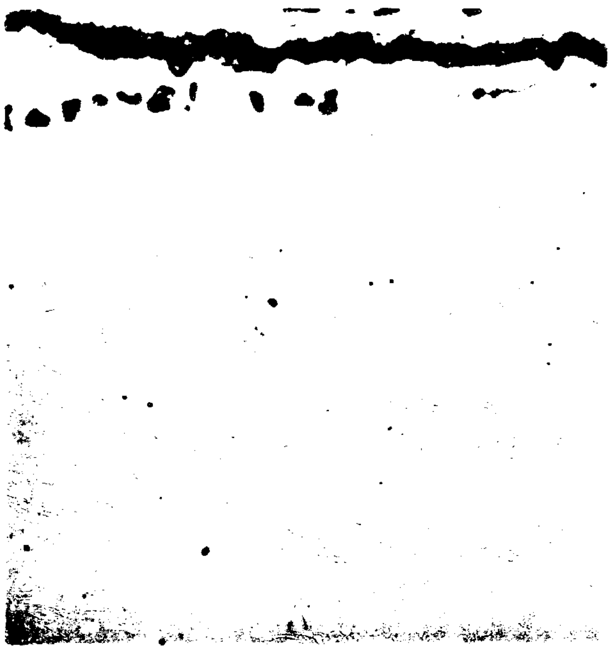
1 Hour - 2500°F - 1 Atm
4 Hours - 2500°F - 10^{-2} mm

Figure 70 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2500°F at 1 Atmosphere and Exposure in Air at 2500°F for 1, 2 and 4 Hours at 10^{-2} mm 250X



4 Hours - 2000°F - 1 Atm
1 Hour - 2500°F - 10^{-2} mm

4 Hours - 2000°F - 1 Atm
2 Hours - 2500°F - 10^{-2} mm



4 Hours - 2000°F-1 Atm
4 Hours - 2500°F - 10^{-2} mm

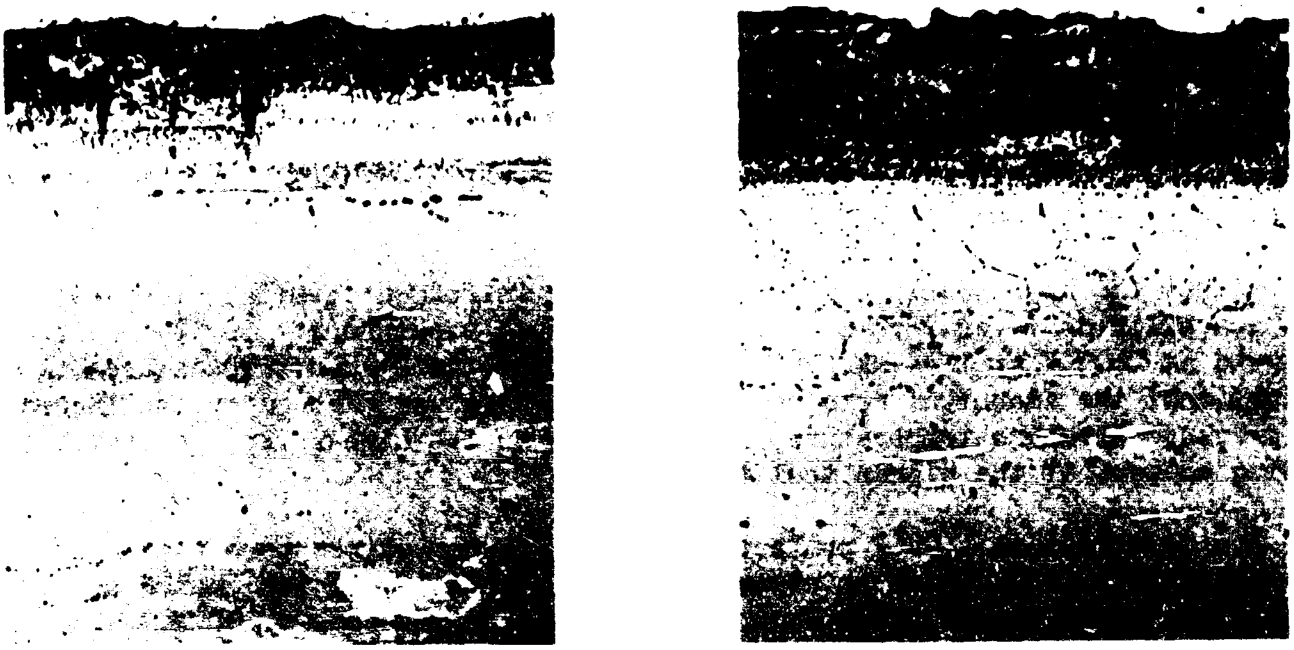
Figure 71 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2000°F at 1 Atmosphere and Exposure in Air at 2500°F for 1, 2 and 4 Hours at 10^{-2} mm 250X

1 Hour - 2500°F - 10^{-2} mm
+
200 Hours - 1800°F - 1 Atm

4 Hours - 2500°F-10^{-2} mm
+
200 Hours - 1800°F - 1 Atm

200 Hours - 1800°F - 1 Atm

Figure 72 Cr-Ti-Si Coated D-14 Alloy After 1800°F Oxidation in Air of As Coated and Reduced Pressure Exposed (2500°F) Specimens 250X



1 Hour - 2500°F - 10^{-2} mm
+
65 Hours 2500°F - 1 Atm

4 Hours - 2500°F - 10^{-2} mm
+
6 Hours - 2500°F - 1 Atm

104 Hours - 2500°F - 1 Atm

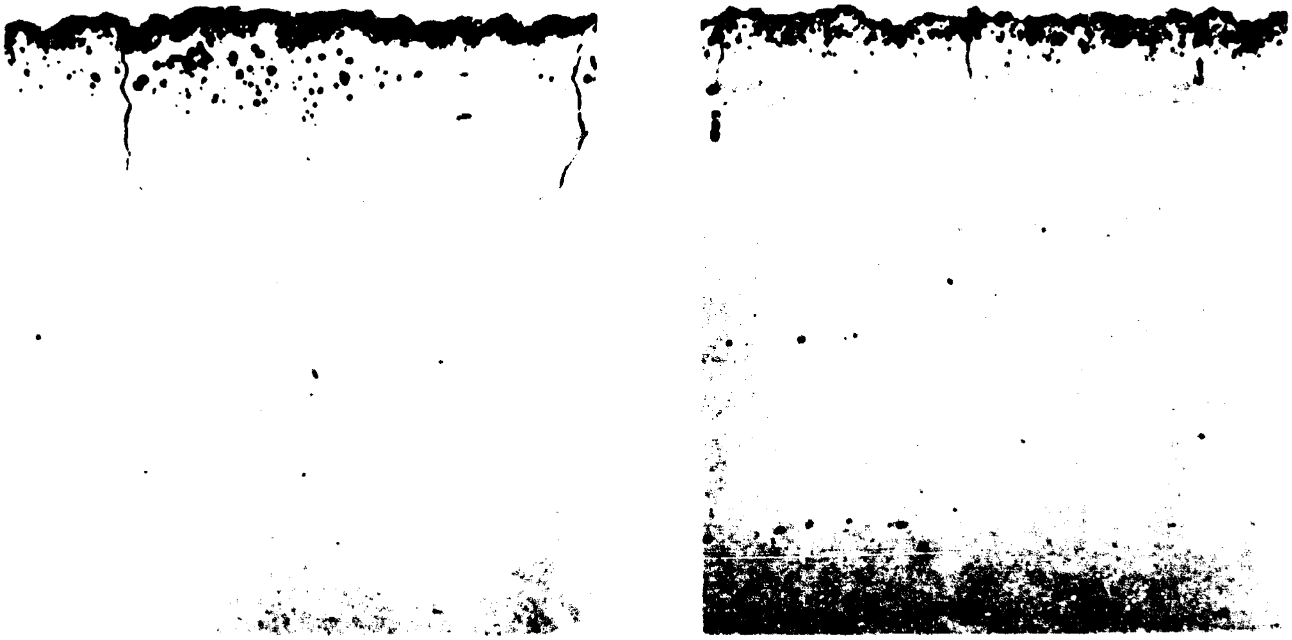
Figure 73 Cr-Ti-Si Coated D-14 Alloy After 2500°F Oxidation in Air at Both One Atmosphere and at 10^{-2} mm 250X resulted from the 1 and 2 hour low pressure treatments, apparently because of the less significant alteration in the coating composition.

Figures 74, 75 and 76 depict the microstructure of the Cr-Ti-Si coating after exposure at 10^{-2} mm at 2600°F. All three initial specimen conditions are represented. A similarity between the as coated material exposed at 10^{-2} mm at 2600°F and at 2500°F is obvious. No appreciable surface oxide layer is formed at either temperature. The titanium silicide layer formed during low pressure exposure at 2500°F, while also observed at 2600°F at 10^{-2} mm, is less distinct at the higher temperature. It is evident that the amount of retained silicide coating was reduced by the increase in low pressure exposure temperature; no doubt due to the higher vapor pressure of the coating elements at the higher test temperature.

The reduction in 2500°F protective capability (one atmosphere post-oxidation) attributed to reduced pressure exposure at 10^{-2} mm at 2500°F (as coated specimens) was greatly magnified as the exposure temperature was increased 100°F. Whereas, the low temperature (1800°F) protective properties were unaffected by the 2500°F exposure, a drastic reduction in 1800°F one atmosphere protective capability occurred at a reduced pressure test temperature of 2600°F. This was, in fact, true for all specimens exposed at 2600°F at 10^{-2} mm. The photomicrographs of the pre-oxidized specimens exposed at 2600°F at 10^{-2} mm accentuate the Cr-Ti-Si coating behavior observed at this pressure level at 2500°F. While there was essentially no difference in the protective capability of the coating exposed at 2600°F and 10^{-2} mm with regard to initial specimen condition, there was a significant difference in microstructure. Pre-oxidation at 2500°F at one atmosphere resulted in a substantial reduction in retained coating thickness. Large voids were observed at the coating-base metal interface and substantial substrate contamination, beneath the titanium enriched diffusion zone, was noted. Pre-oxidation at 2000°F at one atmosphere, on the other hand, did not significantly alter the microstructure from that observed for as coated specimens exposed to these conditions. Apparently, at the higher pre-oxidation temperature the amount of oxygen which reacts with the coating to form the SiO_2 layer at one atmosphere is sufficiently greater than that reacted at 2000°F to account for the difference in microstructural effects.

8.3 Low Pressure Behavior at 10^{-1} mm

Figure 77 shows Cr-Ti-Si coated specimens exposed 1, 2 and 4 hours at 2500°F at 10^{-1} mm. A surface oxide layer is observed to have formed at this pressure, increasing in thickness with increasing exposure time. The amount of retained silicide coating was significantly decreased by this exposure treatment. An appreciable amount of internal contamination is observed after 2 and 4 hours exposure, indicating a substantial loss in the protective characteristics of the coating. The severity of coating degradation resulting from exposure at 10^{-1} mm as compared with exposure at 10^{-2} mm is most probably due to the fact that at 10^{-2} mm insufficient oxygen is present to cause formation of a protective oxide layer. At 10^{-2} mm the principal mechanism involved in microstructural changes is chromium evaporation. At 10^{-1} mm, however, sufficient oxygen is present in the atmosphere to permit reaction with the silicide layer. Degradation then results from vaporization of

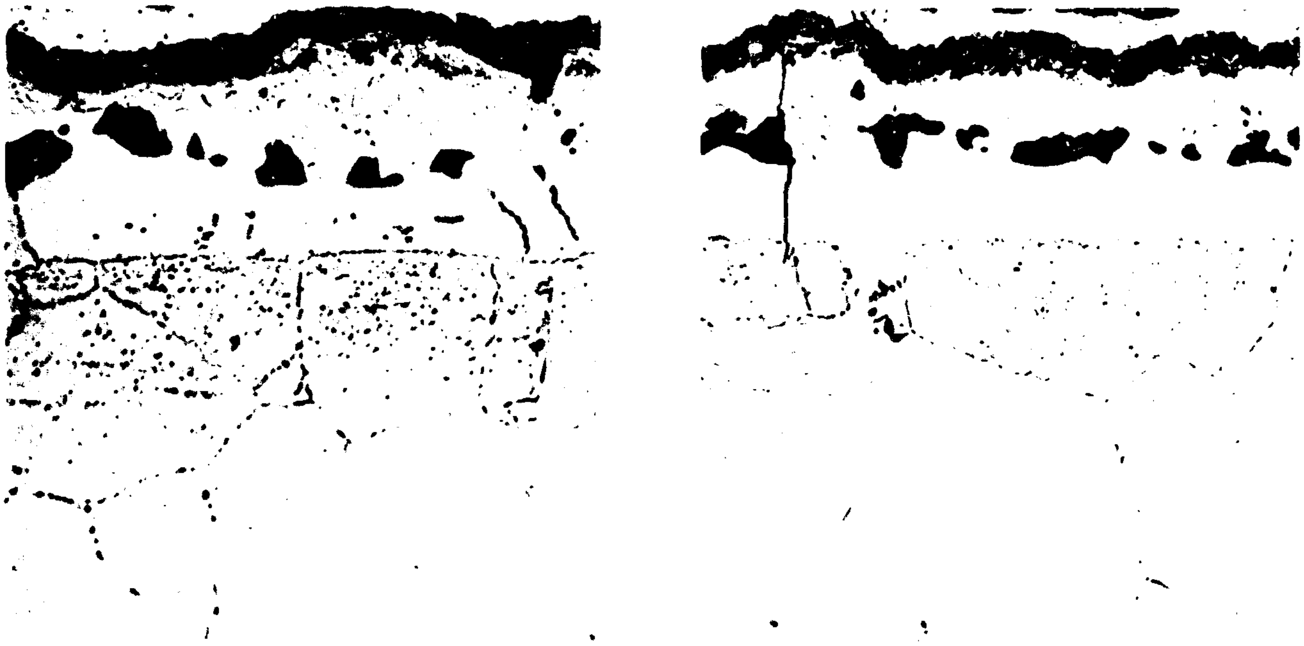


1 Hour - 2600°F
10^{-2} mm

2 Hours - 2600°F
10^{-2} mm

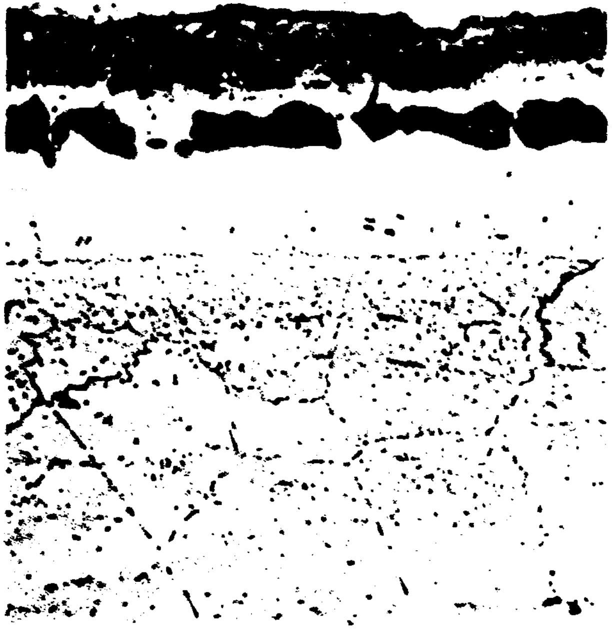
4 Hours - 2600°F
10^{-2} mm

Figure 74 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hour Exposures in Air at 2600°F at 10^{-2} mm 250X



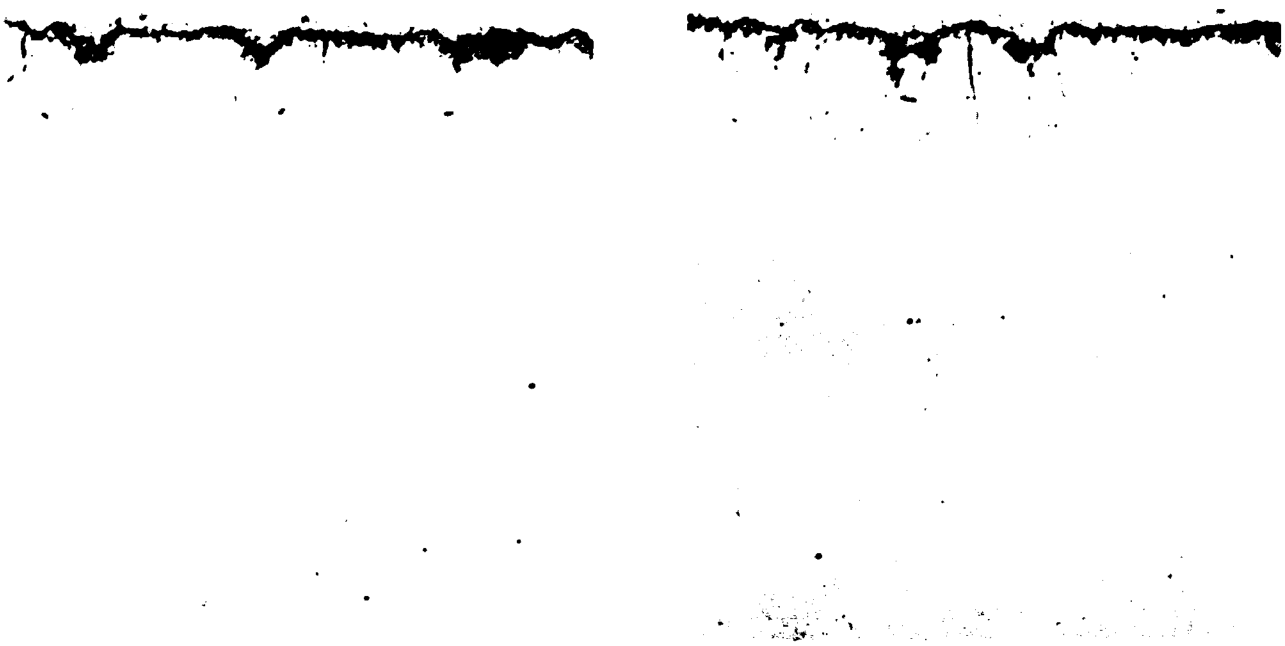
1 Hour - 2500°F - 1 Atm
1 Hour - 2600°F - 10-2 mm

1 Hour - 2500°F - 1 Atm
2 Hours - 2600°F - 10-2 mm



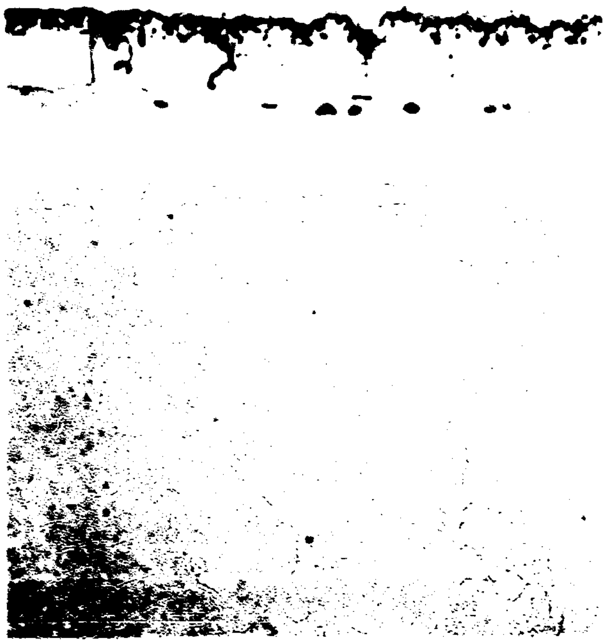
1 Hour - 2500°F - 1 Atm
4 Hours - 2600°F - 10-2 mm

Figure 75 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2500°F at 1 Atmosphere and Exposure in Air at 2600°F for 1, 2 and 4 Hours at 10^{-2} mm 250X



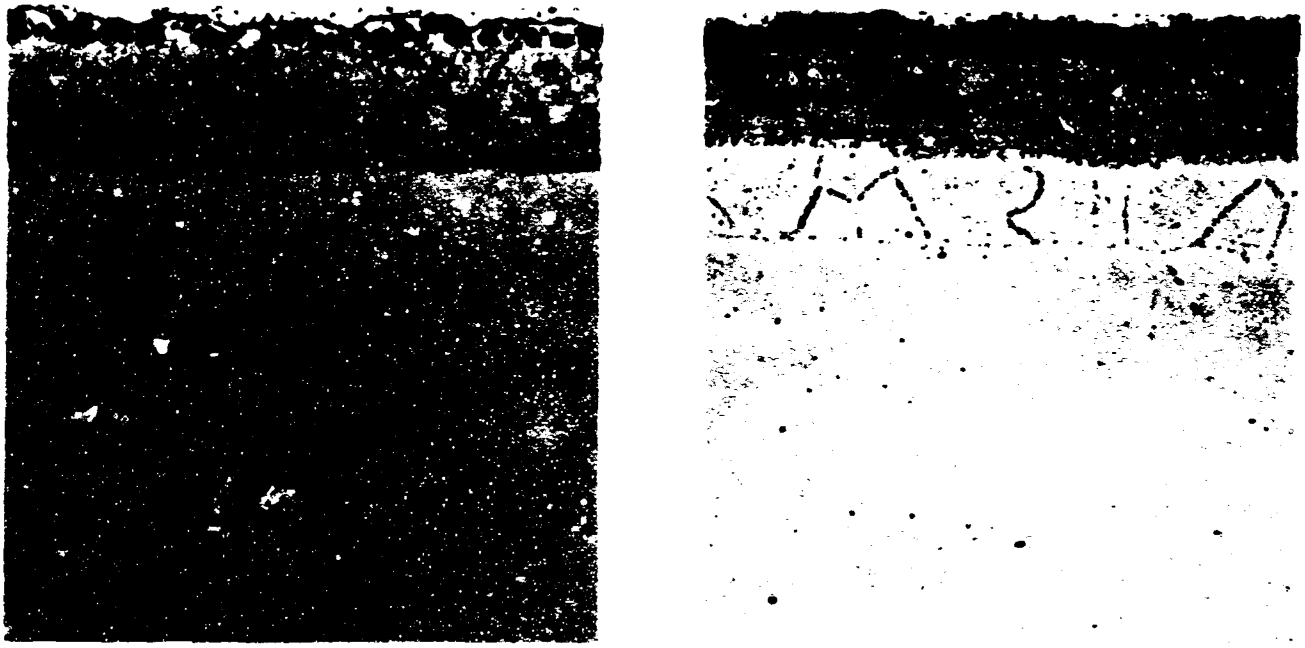
4 Hours - 2000°F - 1 Atm
1 Hour - 2600°F - 10^{-2} mm

4 Hours - 2000°F - 1 Atm
2 Hours - 2600°F-10^{-2} mm



4 Hours - 2000°F - 1 Atm
4 Hours - 2600°F - 10^{-2} mm

Figure 7c Cr-Ti-Si Coated [illegible]-14 Alloy After Pre-Oxidation in Air at 2000°F at 1 Atmosphere and Exposure in Air at 2600°F for 1, 2 and 4 Hours at 10^{-2} mm 250X



1 Hour - 2500°F
10^{-1} mm

2 Hours - 2500°F
10^{-1} mm

4 Hours - 2500°F
10^{-1} mm

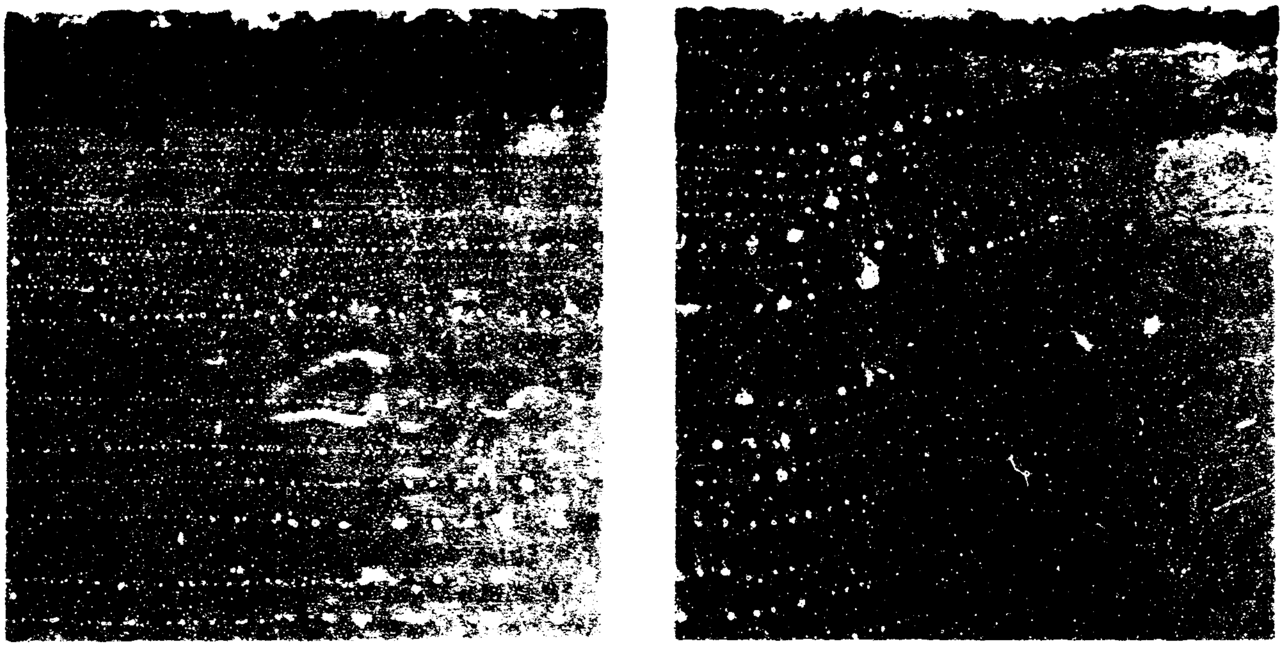
Figure 77 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hour Exposures in Air at 2500°F at 10^{-1} mm 250X

the silicon monoxide (SiO) in addition to loss of chromium. In a dynamic system such as utilized for these tests surface reaction products would be removed, allowing continuous formation and volatilization of SiO and thus a continuous loss of the silicide layer.

One group of specimens was pre-oxidized at 2500°F (one atmosphere) for 1 hour prior to exposure at 10^{-1} mm at 2500°F. Figure 78 shows photomicrographs of these specimens after 1 and 2 hours exposure to the reduced pressure environment. This pre-treatment did not significantly alter the reduction of the post-oxidation protective properties of the coating. Microstructurally there was no essential difference between specimens which were pre-oxidized and those which were not. An adherent glassy surface layer was formed on the specimens during the one atmosphere oxidation treatment. However, the mechanism of coating degradation by volatilization of SiO and chromium appeared to be unaffected by this pre-treatment. A second group of specimens were pre-oxidized at 2000°F (one atmosphere) for 4 hours prior to exposure (2500°F) at 10^{-1} mm and photomicrographs of these specimens, after reduced pressure exposure, are shown in Figure 79. Again, there was little microstructural difference after low pressure exposure between the pre-oxidized specimens and those which were not. No glassy surface layer was formed at this lower pre-oxidation temperature. The protective capability of this group of coupons was nearly identical (or slightly improved) as compared to specimens directly exposed in the as coated condition.

Weight losses of specimens which were directly exposed at 10^{-1} mm were comparable with those observed at 10^{-2} mm, although different effects on the coating microstructure were noted. Deviations in weight loss measurements may be readily attributed to oxygen pick-up during exposure. Examination of the microstructure of specimens exposed at 10^{-1} mm clearly shows evidence of oxygen pick-up (Figure 77), whereas specimens exposed at 10^{-2} mm (Figure 66) do not indicate substantial contamination. A considerably greater weight loss was incurred with specimens exposed at 10-1 mm after pre-oxidation for 1 hour at 2500°F at one atmosphere. This may be associated with vaporization of SiO from the glassy surface layer which was formed during pre-oxidation. In addition, spalling of the surface oxide layer was observed upon cooling the specimens to room temperature. The weight changes recorded for coupons pre-oxidized at 2000°F (one atmosphere) were equivalent to those recorded for as coated material exposed at 10^{-1} mm at 2500°F.

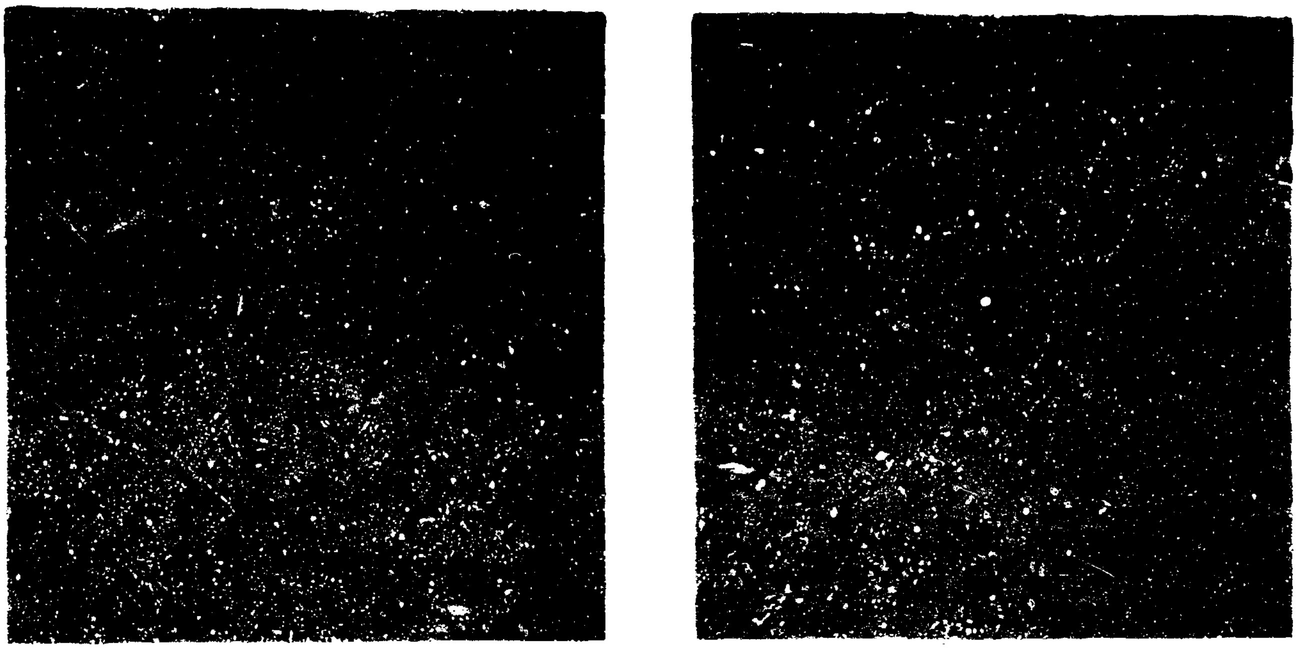
Figures 80, 81 and 82 are photomicrographs of coupons exposed at 2600°F at 10^{-1} mm, both in the as coated condition and after pre-oxidation at one atmosphere. Exposure of as coated specimens under these conditions resulted in serious loss of both low and high temperature one atmosphere protective characteristics. Microstructurally, a surface oxide layer was observed, increasing in thickness with increasing exposure time. Also, voids were observed at the coating-base metal interface probably resulting from (a) chromium vaporization at the surface and (b) rapid chromium diffusion to the surface. Specimens pre-oxidized at 2500°F at one atmosphere showed a characteristic dense surface oxide layer (glassy), increasing in thickness with increasing low pressure exposure time. The protective capability of coatings exposed to this pre-oxidation treatment was superior to as coated



1 Hour - 2500°F - 1 Atm
1 Hour - 2500°F - 10^{-1} mm

1 Hour - 2500°F - 1 Atm
2 Hours - 2500°F - 10^{-1} mm

Figure 78 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2500° F at 1 Atmosphere and Exposure in Air at 2500°F for 1 and 2 Hours at 10^{-1} mm 250X

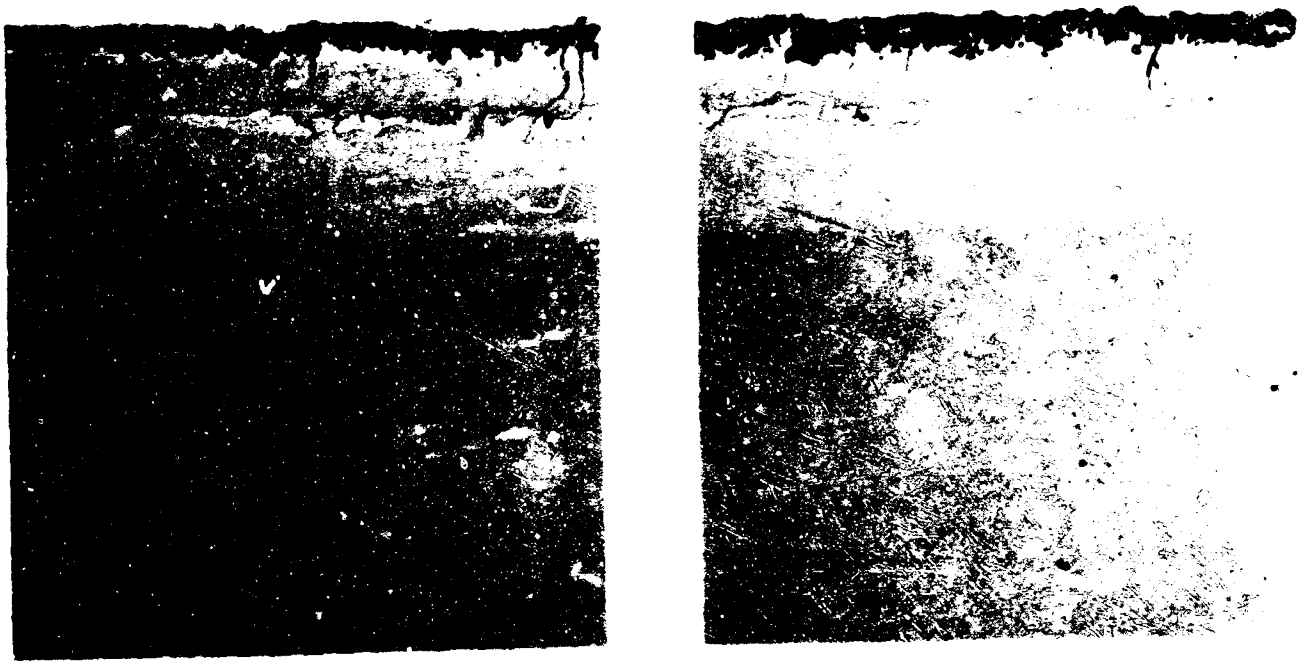


4 Hours - 2000°F - 1 Atm
1 Hour - 2500°F - 10^{-1} mm

4 Hours - 2000°F - 1 Atm
2 Hours - 2500°F - 10^{-1} mm

4 Hours - 2000°F - 1 Atm
4 Hours - 2500°F - 10^{-1} mm

Figure 79 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2000°F at 1 Atmosphere and Exposure in Air at 2500°F for 1, 2 and 4 Hours at 10^{-1} mm 250X

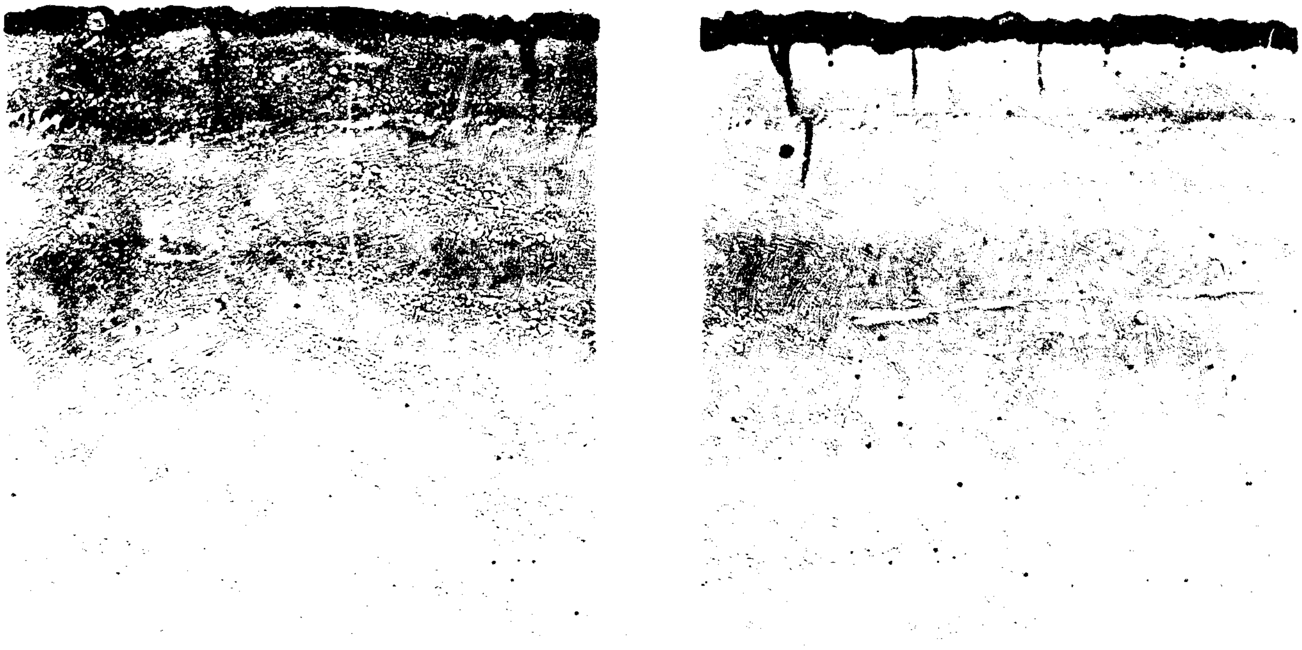


1 Hour - 2600°F
10^{-1} mm

2 Hours - 2600°F
10^{-1} mm

4 Hours - 2600°F
10^{-1} mm

Figure 80 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hours Exposures in Air at 2600°F at 10^{-1} mm 250X

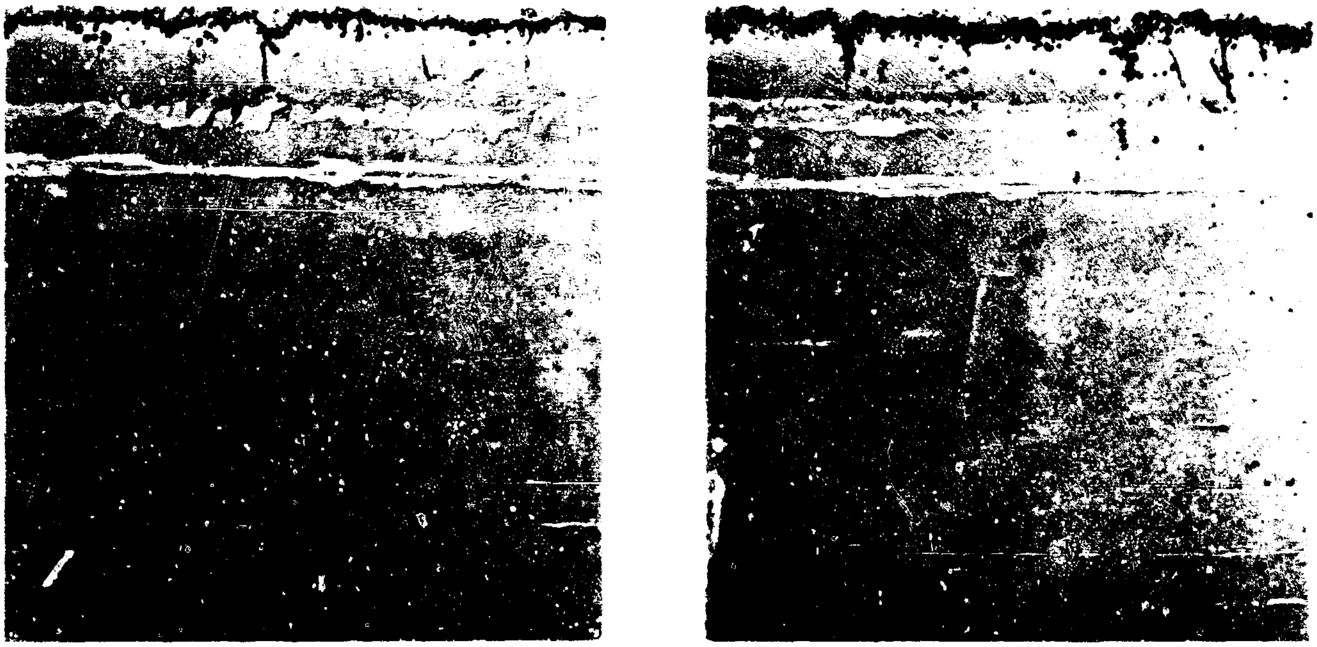


1 Hour - 2500°F - 1 Atm
1 Hour - 2600°F - 10^{-1} mm

1 Hour - 2500°F - 1 Atm
2 Hours - 2600°F - 10^{-1} mm

1 Hour - 2500°F - 1 Atm
4 Hours - 2600°F - 10^{-1} mm

Figure 81 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2500°F at 1 Atmosphere and Exposure in Air at 2600°F for 1, 2 and 4 Hours at 10^{-1} mm 250X



4 Hours - 2000°F - 1 Atm
1 Hour - 2600°F - 10^{-1} mm

4 Hours - 2000°F - 1 Atm
2 Hours - 2600°F - 10^{-1} mm

Figure 82 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2000°F at 1 Atmosphere and Exposure in Air at 2600°F for 1 and 2 Hours at 10^{-1} mm 250X specimens exposed to the same reduced pressure condition. Apparently the formation of the dense adherent surface oxide layer effectively reduced the rate of chromium loss from the coating, thereby reducing the degradation effect of the low pressure exposure.

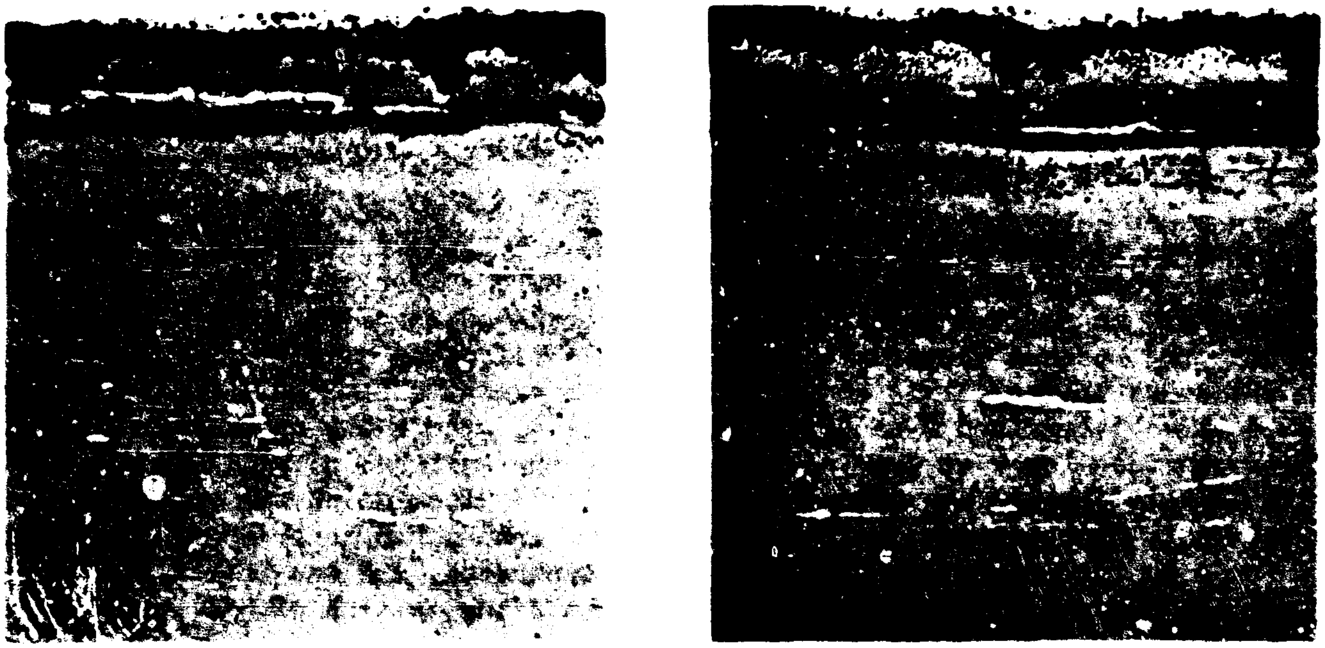
The weight changes corresponding to this series of exposures nearly approximates the weight changes recorded at 10^{-2} mm. At both pressures (10^{-1} and 10^{-2} mm) the greatest weight loss was sustained by specimens pre-oxidized at 2500°F. Pre-exposure at 2000°F did not significantly alter the weight loss pattern from the as coated specimen starting condition.

8.4 Low Pressure Behavior at 1, 5 and 50 mm

Exposure at 2500°F at 1 mm (Figure 83) did not cause loss of 1800°F one atmosphere protective properties. Some loss of one atmosphere protective capability at 2500°F was observed, no doubt primarily due to the decreased chromium content of the coating following the reduced pressure treatment. Volatilization of SiO would be expected at 1 mm pressure; in fact, this should result upon exposure at 2500°F at all pressures below 2 mm as determined from equilibrium data(5). There was no obvious formation of a glassy surface layer at 1 mm, substantiating the evidence of volatilization of SiO. A white porous deposit was observed on the specimen face which was adjacent to the alumina boat after exposure at 1 mm pressure. Perkins has reported a similar condensate found in the colder regions of his test apparatus, and has identified it as silicon and amorphous silica resulting from the decomposition of SiO in the absence of oxygen(5).

Figures 84, 85, 86 and 87 show photomicrographs of specimens exposed at 5 and 50 mm at 2500°F. A much less significant alteration in coating microstructure was observed at these higher pressures. A glassy adherent oxide surface layer was formed at both test pressures. No appreciable difference in microstructure exists between specimens exposed at these two pressures. Weight change measurements were comparable for specimens exposed at 5 and 50 mm and specimens exposed at one atmosphere. However, it is significant that in all cases the weight change of specimens exposed in air was positive and in all instances greater than observed for specimens exposed at any reduced pressure indicating some loss of coating constituents due to volatilization.

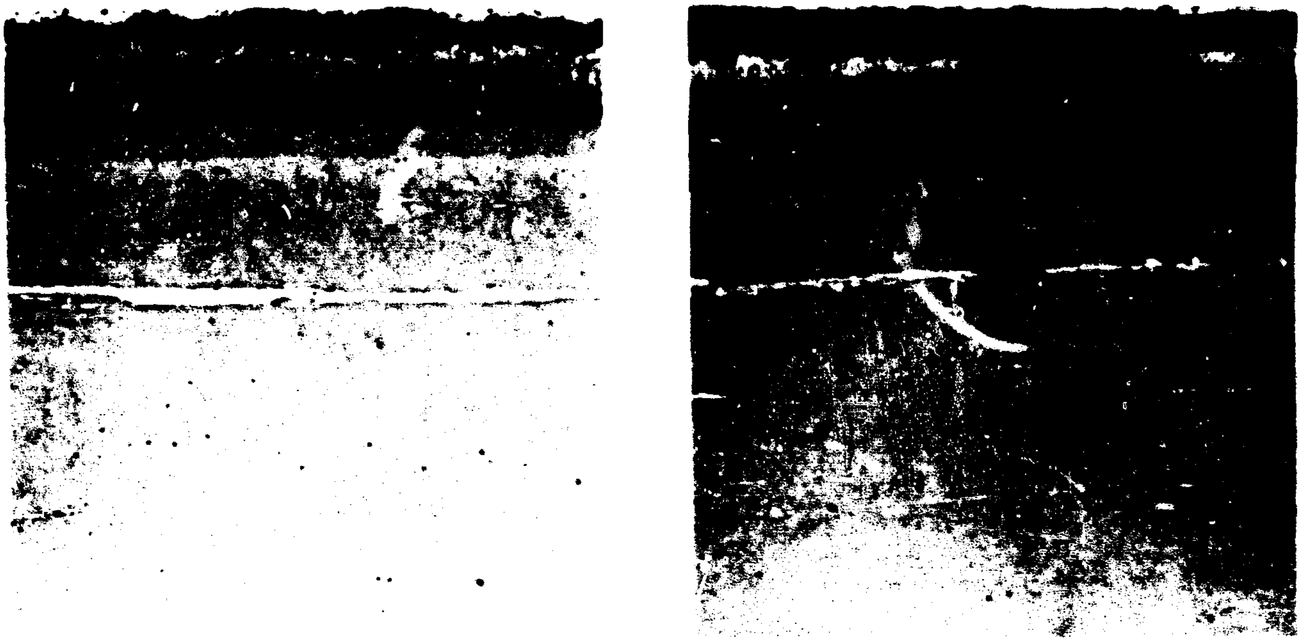
Substantially more internal contamination was observed in the substrates of coated specimens pre-oxidized at 2500°F and one atmosphere prior to exposure at 5 mm as compared with material directly exposed at 5 mm. Also, exposure at 50 mm resulted in increased internal penetration as compared with the 5 mm exposure of as coated specimens. This contamination has not been observed in the substrates of Cr-Ti-Si coated coupons oxidized at one atmosphere at 2500°F for comparable times, while it has been observed to varying degrees at all reduced pressure levels. Microstructural and protective capability differences between material exposed to reduced pressure (5-50 mm range) as compared with material exposed only at one atmosphere are minimal. However, all data indicate that the Cr-Ti-Si coating is somewhat permeable with respect to oxygen at all reduced pressures studied.



1 Hour - 2500°F
1 mm

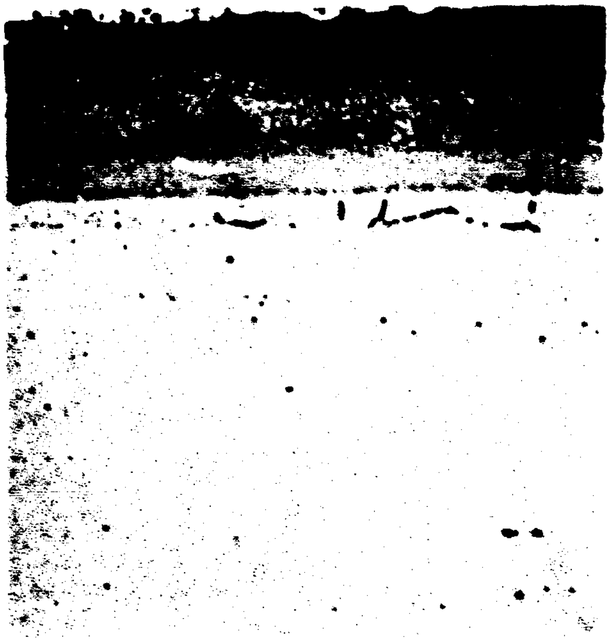
4 Hours - 2500°F
1 mm

Figure 83 [illegible] Coated D-14 Alloy After 1 and 4 Hour Exposures in [illegible] 2500°F at 1 mm 250X



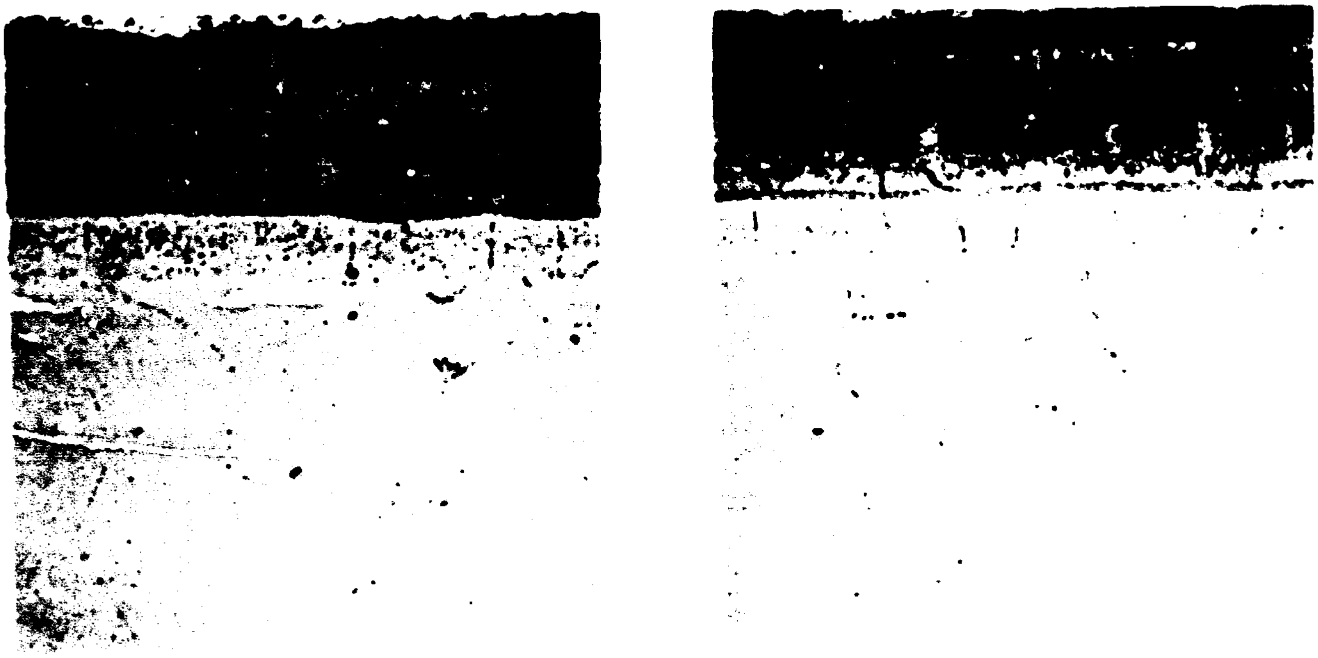
1 Hour - 2500°F
5 mm

2 Hours - 2500°F
5 mm



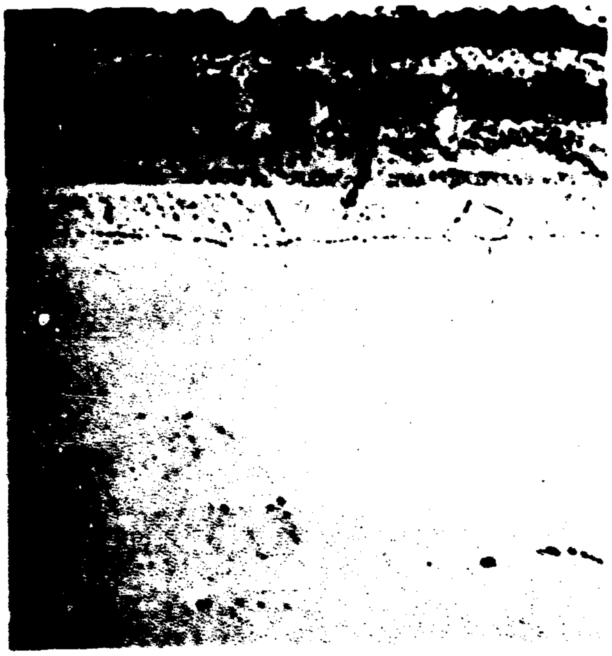
4 Hours - 2500°F
5 mm

Figure 84 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hour Exposures in Air at 2500°F at 5 mm 250X



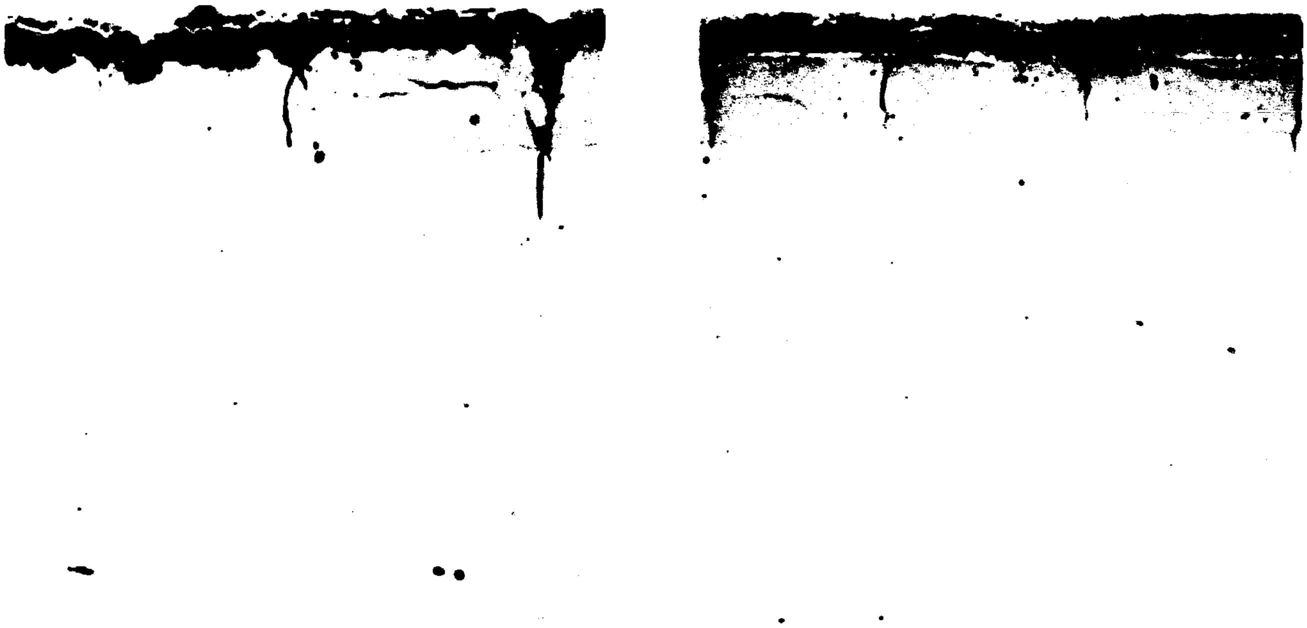
1 Hour - 2500°F - 1 Atm
1 Hour - 2500°F - 5 mm

1 Hour - 2500°F - 1 Atm
2 Hours - 2500°F - 5 mm



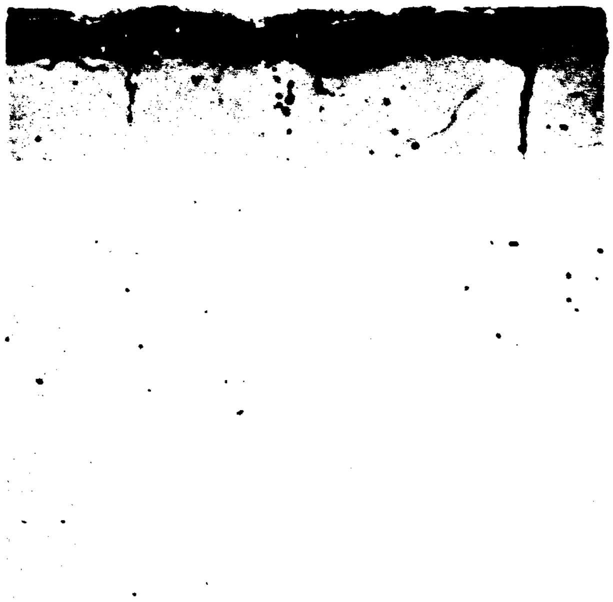
1 Hour - 2500°F - 1 Atm
4 Hours - 2500°F - 5 mm

Figure 85 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2500°F at 1 Atmosphere and Exposure in Air at 2500°F for 1, 2 and 4 Hours at 5 mm 250X



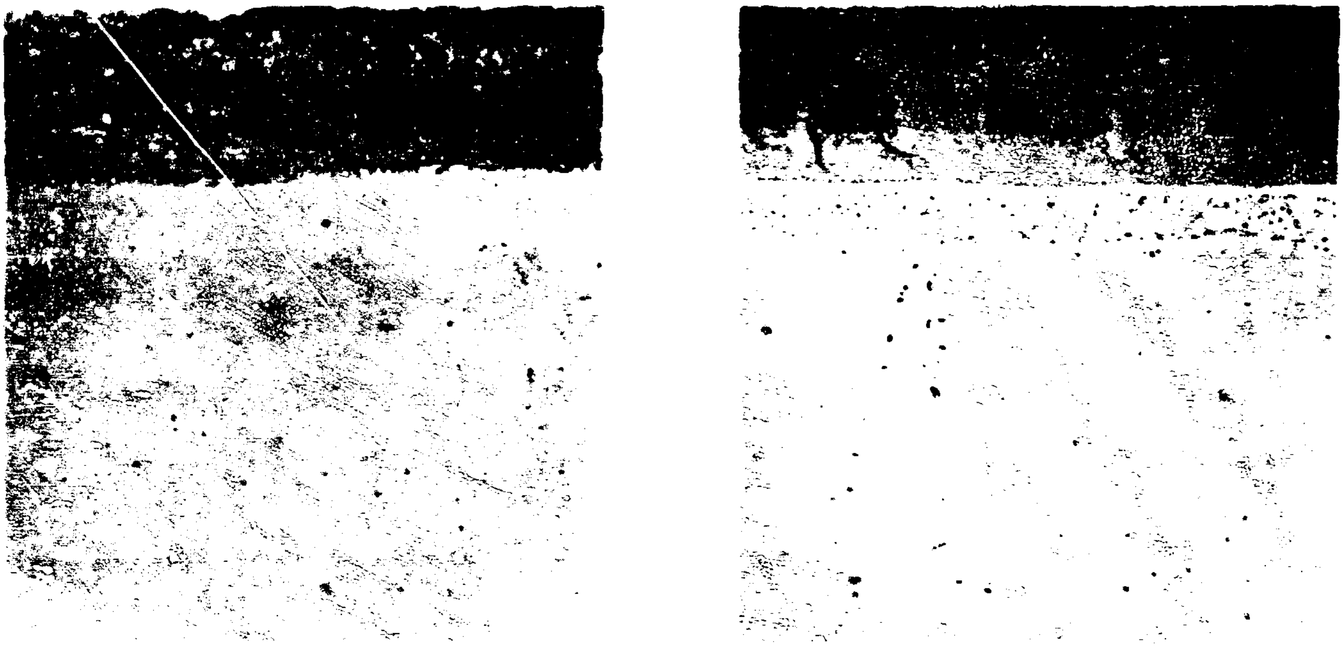
4 Hours - 2000°F - 1 Atm
1 Hour - 2500°F - 5 mm

4 Hours - 2000°F - 1 Atm
2 Hours - 2500°F - 5 mm



4 Hours - 2000°F - 1 Atm
4 Hours - 2500°F - 5 mm

Figure 96 Cr-Ti-Si Coated D-14 Alloy After Pre-Oxidation in Air at 2000°F at 1 Atmosphere and Exposure in Air at 2500°F for 1, 2 and 4 Hours at 5 mm 250X



1 Hour - 2500°F
50 mm

2 Hours - 2500°F
50 mm

4 Hours - 2500°F
50 mm

Figure 87 Cr-Ti-Si Coated D-14 Alloy After 1, 2 and 4 Hour Exposures in Air at 2500°F at 50 mm 250X

8.5 Analysis of Low Pressure Behavior

Although the phenomena of substrate contamination and loss of the Cr-Ti-Si coating resulting from low pressure exposure has not been thoroughly analysed thermodynamically, an explanation is theorized. In the simplest case, the basic reactions which occur at the coating surface between the surrounding atmosphere and the Cr-Ti-Si coating outer layer are:

$$Si + O_2 \rightleftharpoons SiO_2 \qquad (12)$$

$$2Si + O_2 \rightleftharpoons 2SiO\uparrow \qquad (13)$$

$$2SiO\uparrow + O_2 \rightleftharpoons 2SiO_2 \qquad (14)$$

Since exposure at one atmosphere at 2500°F does not cause internal contaminati it is felt that equation (12) applies and that the resulting glassy protective layer (SiO_2 or modified SiO_2) is thermodynamically stable. Penetration of oxygen into th substrate is blocked by the reaction with the silicide layer for form stable SiO_2 and the slow diffusion through the silicide layer.

Exposure of the Cr-Ti-Si coating at reduced pressures, even though sufficient oxygen is present to form SiO_2, results in varying degrees of internal contaminatio This is apparently due to the thermodynamic instability of SiO_2 at low pressures according to the following composite equation:

$$Si + O_2 \longrightarrow SiO_2 \rightleftharpoons SiO\uparrow + [O] \qquad (15)$$

Apparently the SiO_2 layer decomposes to some degree to form SiO (gas) and oxygen. The SiO is removed and the oxygen diffused through the silicide layer and into the substrate. Evaporation of chromium at a relatively fast rate during reduced pressu exposure (as compared with one atmosphere exposure) may cause microscopic voids or channels to form within the silicide layer. The presence of inter-connected voids (channels) would reduce the effective coating thickness and the distance required for oxygen diffusion into the substrate. Assuming the above to be true, the degree of internal contamination would be dependent upon both the rate and amount of SiO_2 decomposing and the extent of micro-porosity within the coating silicide layer.

A reduction in the system pressure (50 to 5 mm range) would obviously decrease the amount of available oxygen and thus reduce the rate of SiO_2 formation on specime exposed in the as coated condition. The supply of atomic oxygen would also decreas resulting in less internal contamination, even though the extent of micro-porosity due to chromium vaporization should increase. The use of the pre-oxidation treatme would contribute to increased internal contamination, since the source of oxygen from the decomposition of SiO_2 would be increased. This is consistent with what is observed metallographically.

Further reductions in system pressure to 1 mm or less would, in the instance c as coated material, restrict the amount of oxygen available for reaction with silic thus causing formation of SiO (Eq. 13) rather than SiO_2 (Eq. 12) resulting in the observed coating recession (SiO removed). Again, pre-oxidation at one atmosphere would only provide an SiO_2 layer which apparently decomposes, thus increasing the degree of internal contamination.

In an oxygen poor atmosphere, such as exists at 10^{-2} mm, the reaction between the silicide and oxygen proceeds at a significantly reduced rate and the primary observed microstructural change results from chromium vaporization. The slight amount of internal contamination which was observed after 4 hours exposure (initial condition - as coated) at 10^{-2} mm probably resulted from the presence of microscopic voids in the coating.

At a pressure of 10^{-1} mm where the coating performance was poorest, all the factors contributing to the destruction of the protective characteristics of the coating were additive. These factors were:

a) rapid volatilization of chromium

b) instability of SiO_2 - increasing SiO formation and internal contamination

c) competing reaction of oxygen and silicon to form SiO directly - increasing silicon loss from the coating leaving a non-protective oxide scale.

Pre-oxidation at one atmosphere again provided an SiO_2 layer which, upon decomposition, provided a source of atomic oxygen resulting in increased internal contamination. However, at an exposure temperature of 2500°F the dense oxide layer formed during pre-oxidation at 2500°F acted to restrict chromium vaporization and associated reduction of coating thickness, apparently by acting as a barrier layer. The oxide formed at the lower pre-oxidation temperature did not restrict coating element vaporization.

This phenomena suggests that less degradation of the Cr-Ti-Si coating during low pressure exposure could be achieved by utilization of some effective surface barrier layer.

Weight change determinations were made during post-oxidation at one atmosphere of specimens exposed at reduced pressures. In general an initial weight increase was recorded for approximately 4 hours oxidation at both 1800 and 2500°F and thereafter the specimen weight stabilized until failure occurred. This initial increase must be associated with oxygen pick-up. In the few instances where initial weight losses were recorded, spalling of the surface oxide scale was observed.

.6 Low Pressure Exposure Study at 2800 and 3000°F

Several Cb-752 alloy specimens were Cr-Ti-Si coated for reduced pressure oxidation testing at elevated temperatures. These specimens were fabricated from a small amount of Cb-752 alloy sheet supplied by the Air Force. These specimens were heated by self resistance to 2800 and 3000°F for 1 and 2 hours in a water cooled chamber maintained at 1 mm pressure. Chamber pressure was controlled by throttling the pumping system rather than the use of a controlled leak. Thus, the system was essentially static at 1 mm. The specimen temperature was measured with an optical pyrometer, utilizing both surface emittance and sight glass temperature correstions. The emittance correction was based on the observed melting point (at 1 mm pressure) of columbium oxide. Comparative optical temperatures were simultaneously determined on coated and uncoated Cb-752 surfaces, utilizing a specimen on which the coating had been removed from half the surface. It was observed that at approximately 2800-3000°F the emittance of the oxidized-uncoated columbium alloy surface was nearly equivalent to that of the oxidized Cr-Ti-Si coating. Additional Cb-752 alloy coupons were also Cr-Ti-Si coated for comparative exposures at one atmosphere at 2800 and 3000°F in an air furnace.

At 3000°F and 1 mm pressure a melting reaction of the oxide product was observed with the resistance heated-coated columbium alloy substrate. Specimens exposed under these conditions failed in less than 1/2 hour upon subsequent one atmosphere exposure at 2500°F in an air furnace. Loss of chromium during exposure under these conditions contributes to the formation of a non-protective oxide scale which is not protective at 2500°F at one atmosphere. No coating failures and apparently no oxide melting occurred within 2 hours oxidation of similarily coated coupons exposed directly at one atmosphere at 3000°F in an air furnace. Figure 88 shows the structure of the Cr-Ti-Si coating on Cb-752 alloy in the as coated condition. Figure 89 shows this material after 1 and 2 hour exposures at 3000°F both at one atmosphere and at 1 mm pressure. The coating remained intact for 2 hours exposure at one atmosphere; however, it is apparent that severe oxide penetration occurred within the time limit of the test. A very heavy surface oxide scale formed during this exposure. Thus the coating prevented visible columbium oxide growth but did not completely prevent oxygen leakage. Exposure at 1 mm at 3000°F caused complete coating failure and permitted oxygen penetration completely through the substrate.

At 2800°F and 1 mm pressure localized areas apparently melted or spalled from the coating surface after 1 and 2 hours of reduced pressure exposure. Upon 2500°F post-oxidation these pre-exposed coatings were still protective after 7 hours of cyclic oxidation. However, the tests were terminated due to oxide growth from the end sections of the specimens damaged by the electrode grips during reduced pressure testing. The cyclic oxidation protective life of this Cr-Ti-Si coating on Cb-752 alloy, exposed directly at one atmosphere, ranged from 4 to 10 hours at 2800°F. Figure 90 shows these coatings after 1 and 2 hour exposures at 2800°F at both one atmosphere and 1 mm. The coatings were not significantly affected by exposure at one atmosphere, the major microstructural change being the formation of a glassy surface oxide layer. One hour exposure at 1 mm also caused little microstructural change; however, 2 hours exposure resulted in loss of nearly all of the coating through vaporization and oxide formation with substantial oxygen penetration into the substrate.

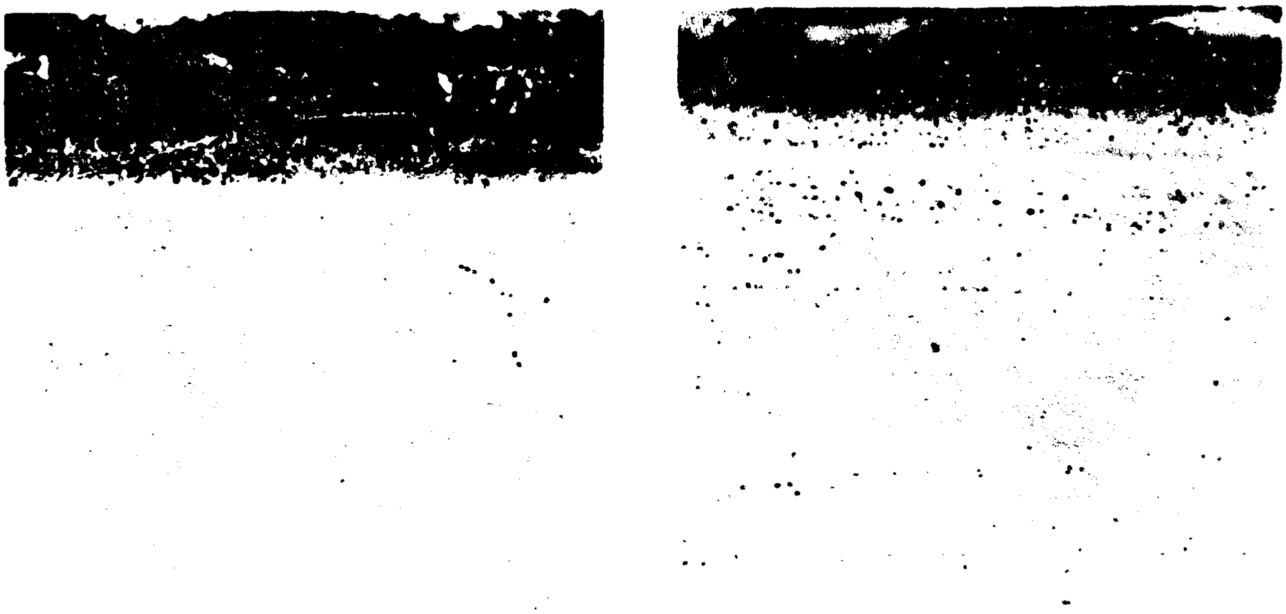
9. APPLICATIONS OF THE Cr-Ti-Si COATING

9.1 Application of the Cr-Ti-Si Coating to Simple Joint Configurations

Practical application of columbium alloy materials to aerospace systems must

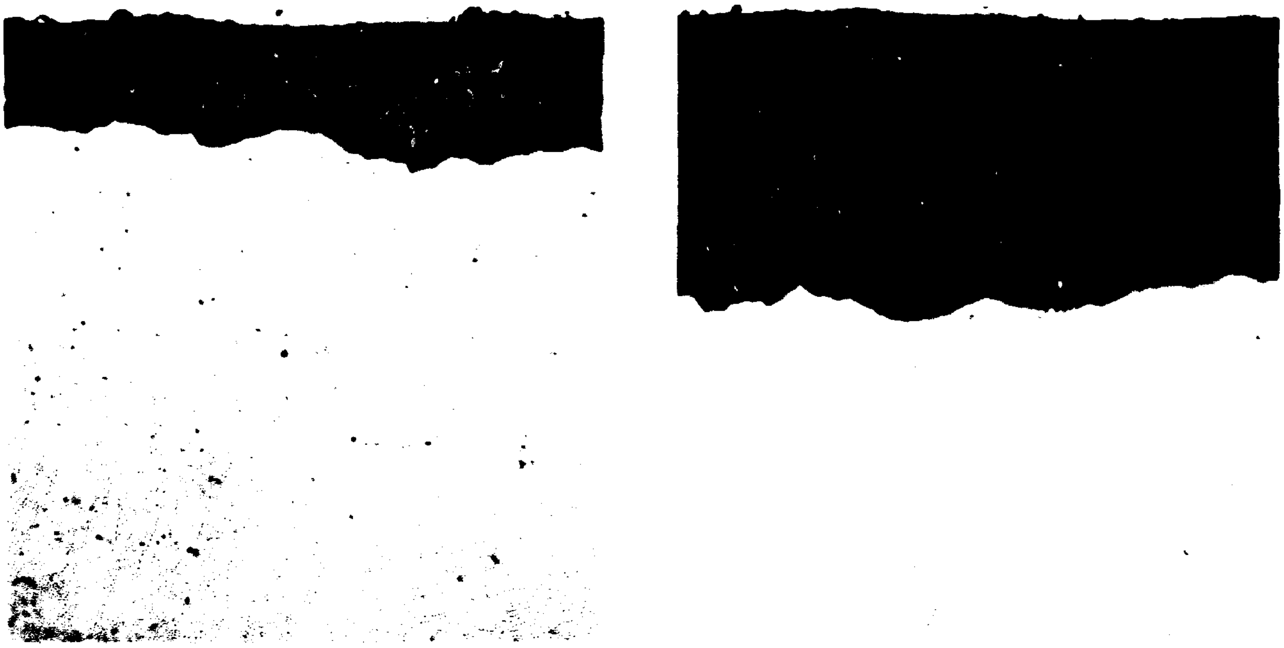
As Coated

Figure 88 Cr-Ti-Si Coated Cb-752 Alloy 250X



1 Hour - 3000°F
1 Atm

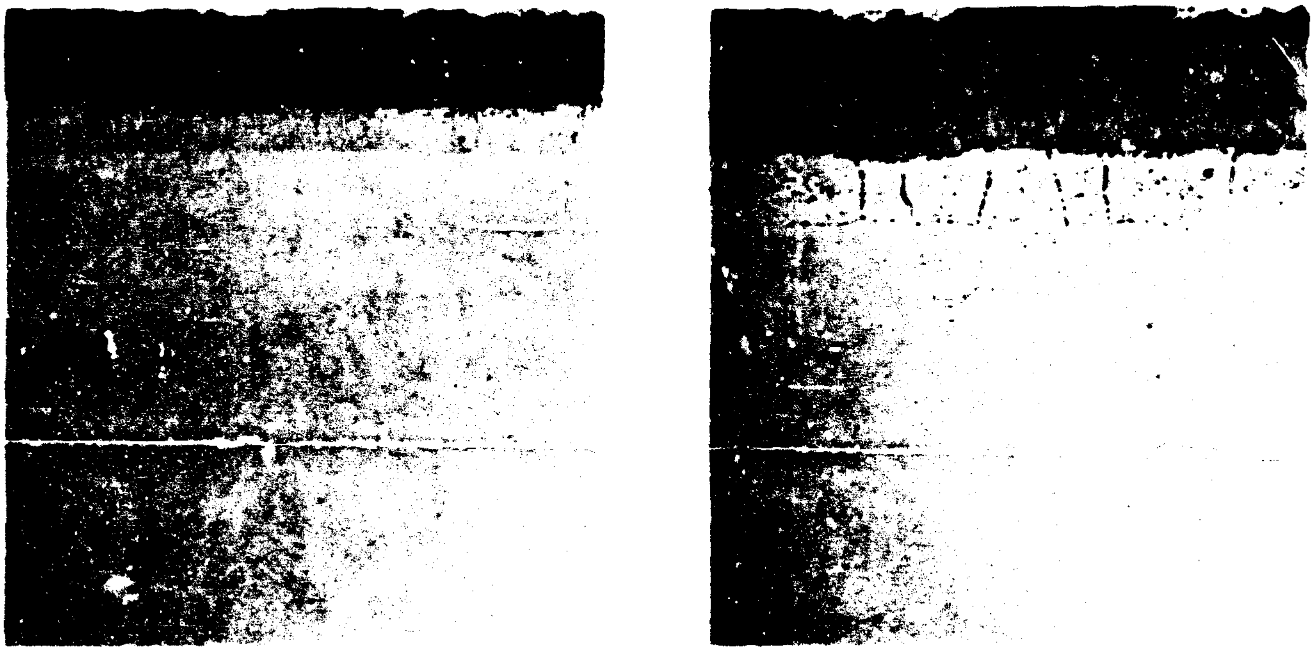
2 Hours - 3000°F
1 Atm



1 Hour - 3000°F
1 mm

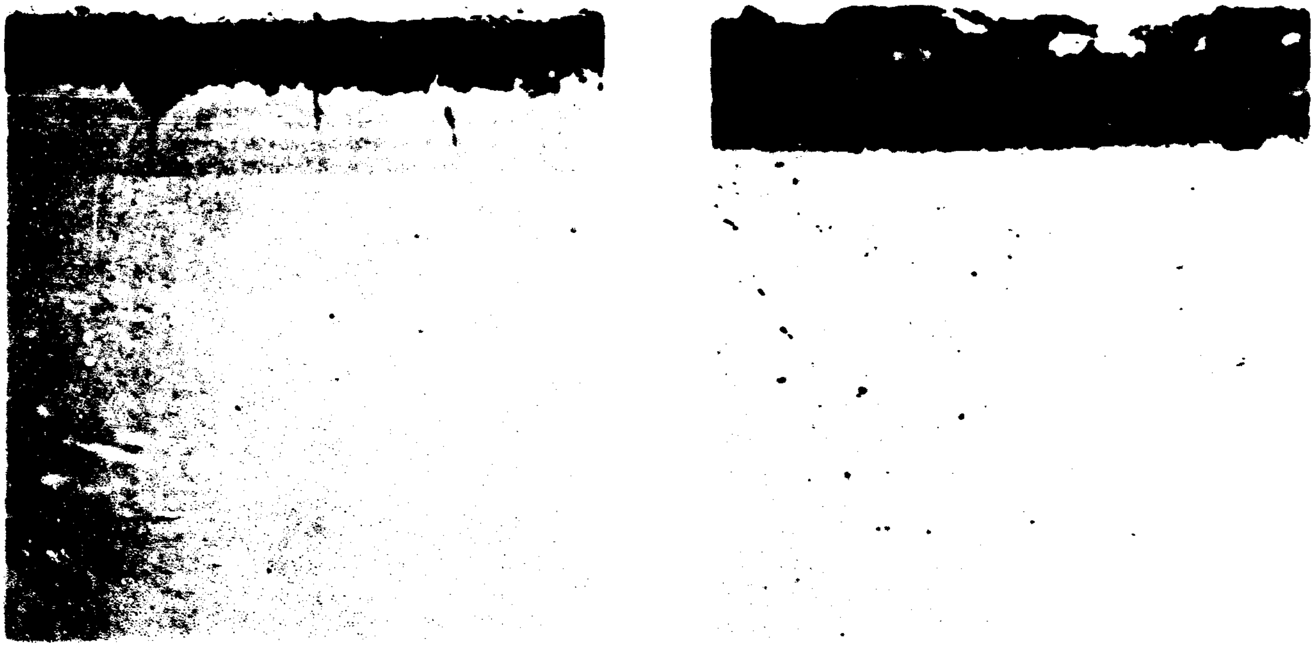
2 Hours - 3000°F
1 mm

Figure 39 Cr-Ti-Si Coated Cb-752 Alloy After 1 and 2 Hour Exposures at 3000°F at 1 Atmosphere and 1 mm Pressure 250X



1 Hour - 2800°F
1 Atm

2 Hours - 2800°F
1 Atm



1 Hour - 2800°F
1 mm

2 Hours - 2800°F
1 mm

Figure 90 Cr-Ti-Si Coated Cb-752 Alloy After 1 and 2 Hour Exposures at 2800°F at 1 Atmosphere and 1 mm Pressure 250X of necessity involve protection of joints from atmospheric contamination and oxidation. A limited investigation of the factors involved in the protection of simple sheet joint configurations was conducted as a part of this program. Three types of joints were considered: (a) spot welded, (b) fusion welded and (c) riveted. It should be noted that the object of this investigation was only to study protection of joints and did not include studying the fastening procedures themselves. Therefore, the quality of the joints was not always optimum, however, they were considered adequate to study the factors involved in joint protection. The investigative effort, therefore, was primarily concerned with determination of the effects of various combinations of processing steps in fabricating and coating of joints, i.e., fabricate and coat or coat and then fabricate, etc. The combinations investigated were:

a) butt weld + Cr-Ti-Si coat

b) spot weld + Cr-Ti-Si coat

c) Cr-Ti coat + spot weld + silicon coat

d) rivet + Cr-Ti-Si coat

e) Cr-Ti coat (both rivets and sheet) + rivet + silicon coat

f) Cr-Ti-Si coat (both rivets and sheet) + rivet

Since the object of the investigation was to determine the effect of fabrication procedures, only one sheet alloy, D-43, was utilized in the study. It was felt that the relationship of fabrication procedure to protective capability would not be significantly altered by differences in sheet materials. All rivet joints were made using Cb-752 alloy rivets supplied by Standard Pressed Steel.

The evaluation techniques employed for this investigation included metallographic examination and cyclic oxidation tests at 2000°F and 2500°F.

The butt welds were made by the electron beam process and were felt to be typical of current state of the art quality welds. The spot welds on uncoated sheet were also felt to be typical quality. The spot welds made on Cr-Ti coated sheet were of sufficient quality to demonstrate the effect of this method of joint fabrication on protective characteristics, as were the rivet joints of uncoated sheet.

The rivet joints produced with Cr-Ti coated sheet and rivets may not be typical of commercial joints in view of the method employed in their fabrication. It was necessary to heat the rivets to approximately 1000°F in order to effect an upset and some surface contamination was observed after riveting. (Heating was done in an inert atmosphere, but riveting was done in air). The surface contamination was removed by etching, and obviously some of the Cr-Ti coating was removed during etching. Thus, the protective capability of these joints may be somewhat less than could be expected from commercial quality joints. The joints produced from rivets and sheet Cr-Ti-Si coated before riveting are also considered to be representative of what could be expected from this procedure. Some coating damage was caused on the rivets by upsetting. However, it should be noted that no attempt to repair this damage, such as by re-coating with silicon, was investigated.

A schematic representation of the appearance of the various joints is shown in Figure 91. Photomicrographs of coatings formed over the butt weld zone are seen to be identical to those formed on base metal sheet (see Figure 92). Photomicrographs are also shown of coatings formed on spot welded specimens.

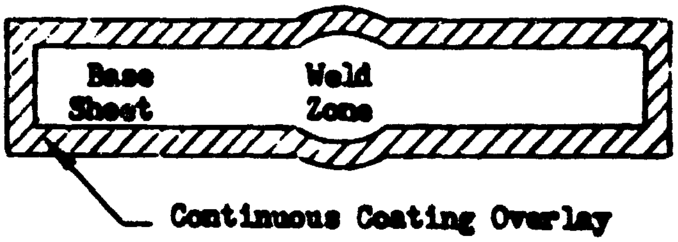
A schematic representation of the appearance of the various joints is shown in Figure 91. Photomicrographs of coatings formed over the butt weld zone are seen to be identical to those formed on base metal sheet (see Figure 92).

As seen in the schematic drawings no coatings were formed between the two layers of sheet (either riveted or spot welded) if the coating was applied after joint fabrication. Joints fabricated after Cr-Ti coating had only a continuous Cr-Ti coating layer after silicon coating, the silicon layer forming only on exposed surfaces. The Cr-Ti-Si coating was seriously damaged on the rivet surfaces by upsetting after coating.

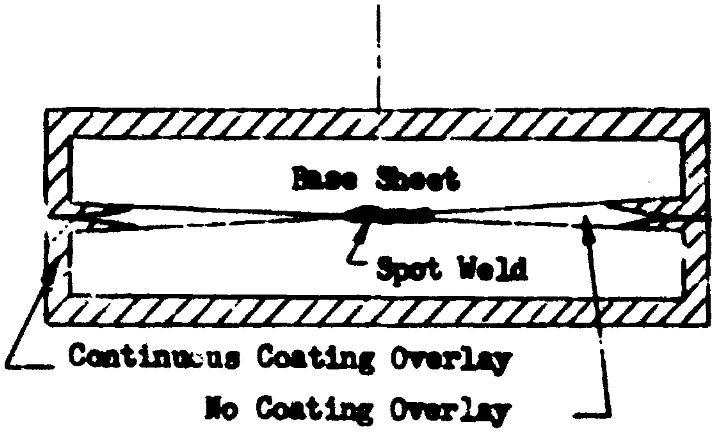
The results of the cyclic oxidation tests are given in Table 34. The protective capability of the joints is presented as a percentage of the protective capability of coatings formed on uncoated sheet. Coating protective efficiency was 100 percent for the butt welded joints at both test temperatures. Specimens spot welded prior to coating failed after only a few hours of testing due to the lack of a protective layer in the unfused area between the sheets. Cr-Ti coating prior to spot welding improved the performance of the joint measurably. Joint specimens riveted prior to coating exhibited the same characteristics as spot welded joints fabricated and coated in the same sequence. Cr-Ti coating prior to riveting did not improve the protective life of the joint as in the case of spot welded joints. However, it is felt that the Cr-Ti alloy may have been damaged as a result of the riveting operation, as previously explained. Damage to the coating on the rivets during upsetting is reflected in the poor life of riveted joints Cr-Ti-Si coated prior to riveting. The rivets were destroyed by oxidation but the sheet itself was protected for the duration of the test.

9.2 Application of the Cr-Ti-Si Coating to Columbium Hardware

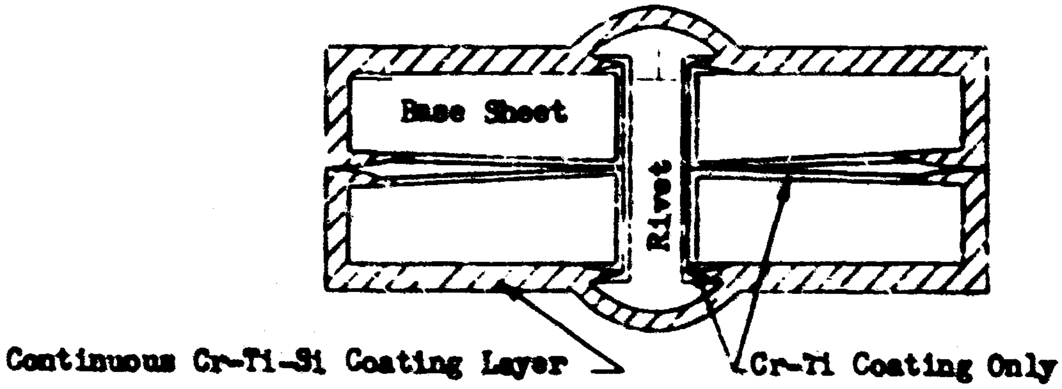
Much of the information gained from the Air Force sponsored Cr-Ti-Si coating development programs has been utilized in the application of the Cr-Ti-Si coating to columbium alloy hardware. Initially, the scale up of the vacuum pack process from a purely laboratory bench scale to a pilot scale operation was undertaken to prove feasibility. However, this scale up soon became a matter of meeting the requirements of the Air Force contractors needing columbium coatings for structure development programs. The first requirement came with the Air Force-McDonnell Aircraft columbium alloy fin and rudder structures program (AF 33(616)-6578) which required coatings on several thousand threaded fasteners and components too large for the small laboratory size coating furnace. On the basis of solely development information, the vacuum pack process was scaled up from a 3" diameter x 8" high pack retort to a 7-1/2" diameter x 18" high pack retort. The vacuum pack process for this size retort and furnace was further improved and optimized for the Air Force-McDonnell Aircraft ASSET program (AF 33(616)-8106). As the requirements for larger parts on the ASSET program and on the Air Force-Martin brazed honeycomb panel program (AF 33(657)-7276) became apparent the vacuum pack process was again scaled up to a pack retort size of 24 x 24 x 8 inches and the transition made from



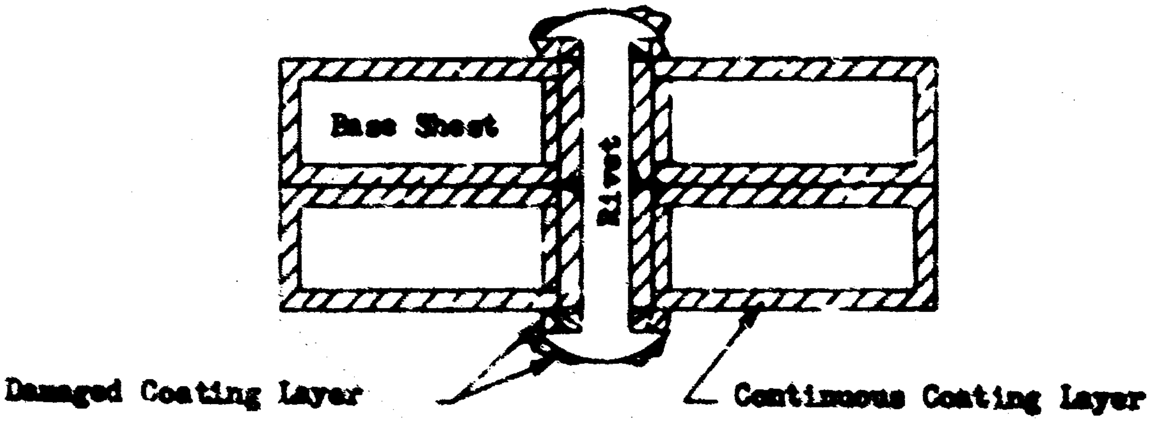
A. Butt Welded Plus Cr-Ti-Si Coated Joint



B. Spot Welded Plus Cr-Ti Coated Joint
C. (Same Coating Pattern for Riveted Plus Cr-Ti-Si Coated)



D. Cr-Ti Coated Plus Riveted Plus Si Coated Joint



E. Cr-Ti-Si Coated Plus Riveted Joint

Figure 91 Schematic Drawing of Coated Joints

Butt Welded

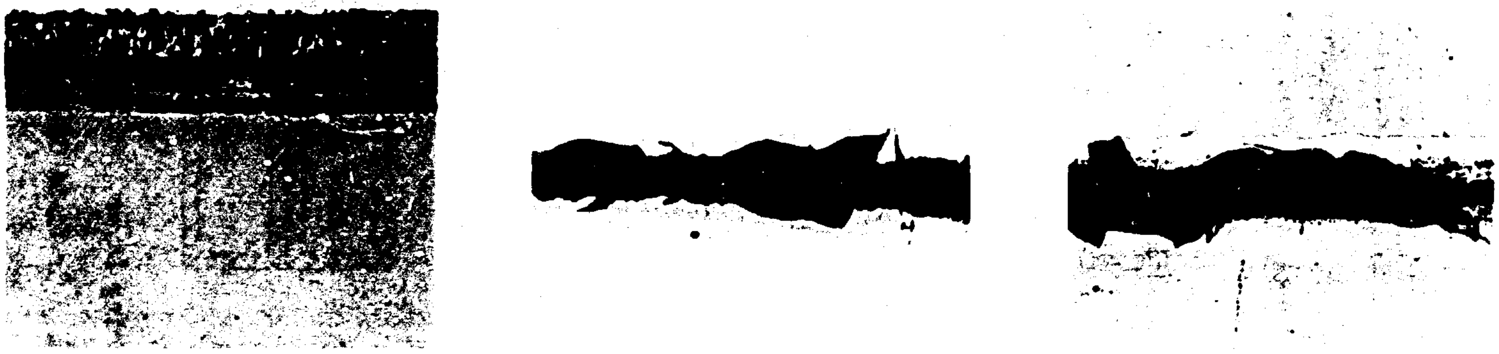
Spot Welded and Cr-Ti-Si
Coated

Cr-Ti Coated, Spot Welded
and Si Coated

Coating on Weld Metal

Coating at Edge of Welded Coupons

Coating at Edge of Welded Coupons



Coating on Base Alloy Sheet

Coating in Gap Between Welded
Coupons 0.015 Mils From Edge

Coating in Gap Between Welded
Coupons 0.025 Mils From Edge

Figure 92 Cr-Ti-Si Coatings Formed on Welded D-43 Alloy Sheet 250X

TABLE 34

Cyclic Oxidation Protective Characteristics of Various D-43 Alloy Joint Configurations at 2000 and 2500° F

Joint Configuration	Process Sequence	Cyclic Oxidation Protective Life: % of Life of Coated Base Alloy Sheet		Average Life Hours	
		2000° F	2500° F	2000° F(1)	2500° F
Butt Weld	Weld+Cr-Ti-Si Coat	100	100	150	60
Spot Weld	Weld+Cr-Ti-Si Coat	38	8	57	5
Spot Weld	Cr-Ti Coat+Weld+ Si Coat	64	28	96	17
Rivet	Rivet+Cr-Ti-Si Coat	17	8	26	5
Rivet	Cr-Ti Coat+Rivet+ Si Coat	25	17(3)	37	7
Rivet	Cr-Ti-Si Coat+ Rivet	10(2)	23(2)	14	14

(1) Oxidation tests of coated base alloy sheet discontinued at 150 hours - no visible coating failure

(2) Tests of rivet joints discontinued at 14 hours - rivet destroyed by oxidation, but no visible coating failure on sheet

(3) Tests of rivet joints discontinued at 7 hours - rivet destroyed by oxidation, but no visible coating failure on sheet

induction to resistance element heating.

The following figures illustrate typical columbium alloy hardware components Cr-Ti-Si coated by TRW:

Figure 93 Leading edges - ASSET Program
Figure 94 Nose cone bulkhead assembly - ASSET Program
Figure 95 Threaded fasteners - ASSET Program
Figure 96 Brazed honeycomb structural panels
Figure 97 Brazed honeycomb curved heat shield panels
Figure 98 Folded and welded sheet vanes (turbine prototype)

Table 35 lists typical experimental parts Cr-Ti-Si coated by TRW.

The successful application of the Cr-Ti-Si coating to these various columbium alloy components demonstrates the value of all background information gained from previous and current development programs. The investigations carried out in this program have further advanced and aided in scale up of the Cr-Ti-Si coating process. Process conditions which must be closely controlled to achieve reliability have been determined, at least within the range of variables investigated in this program.

10. CONCLUSIONS

Based upon the data and work described in the preceding sections the following conclusions can be made:

1) The Cr-Ti alloy layer comprising the first step in formation of the Cr-Ti-Si coating can best be formed from either a 50Cr-50Ti or a 60Cr-40Ti alloy metallic pack. A system pressure of 1.5 mm for the 3" diameter x 8" high retort and 10^{-2} mm for the 7-1/2" diameter x 18" high retort provides a Cr-Ti coating which when alloyed with silicon provides useful protective life over the temperature range 1800 to 2500°F.

2) Silicon coating from a silicon pack at 2100°F for 6 hours at 10^{-2} mm system pressure provides a Cr-Ti-Si coating with useful protective life over the temperature range 1800-2500°F.

3) System pressure, temperature and Cr-Ti alloy pack composition are the major factors influencing the performance of Cr-Ti-Si coatings formed by the vacuum pack process.

4) Temperature gradients within scaled up furnaces and retorts for coating large parts must be minimized to maintain coating thickness and compositional uniformity.

5) Three basic characteristics of all reliably protective Cr-Ti-Si coatings are: (1) a distince titanium enriched diffusion zone of 0.5-1.0 mils in thickness, (2) sufficient chromium diffusion into this titanium enriched

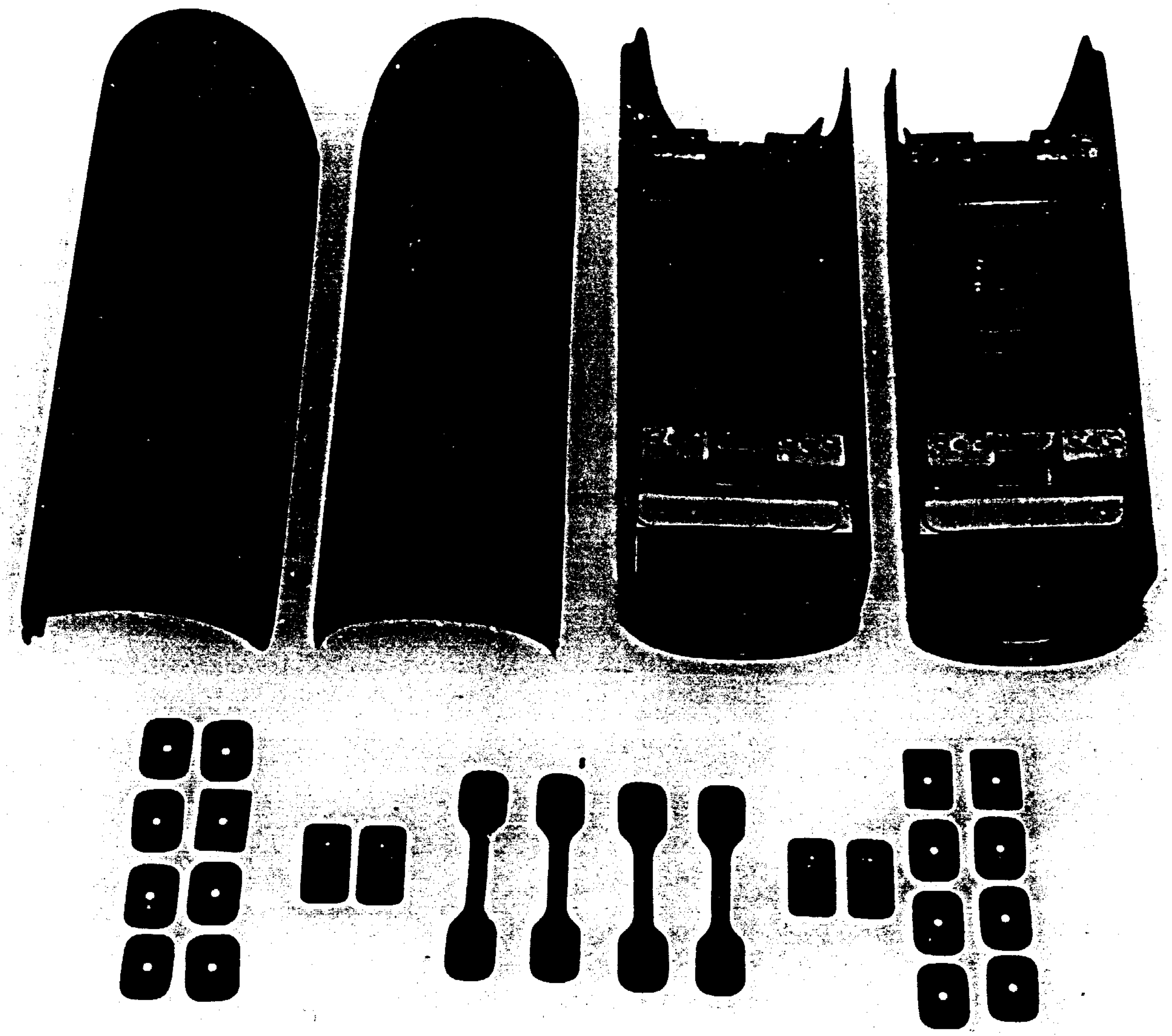


Figure 93 USAF-MAC ASSET Cr-Ti-Si Coated Leading Edge Assemblies (D-14 Alloy)

Figure 94 USAF-MAC ASSET Cr-Ti-Si Coated Nose Cone Bulkhead Assembly (D-14 Alloy)

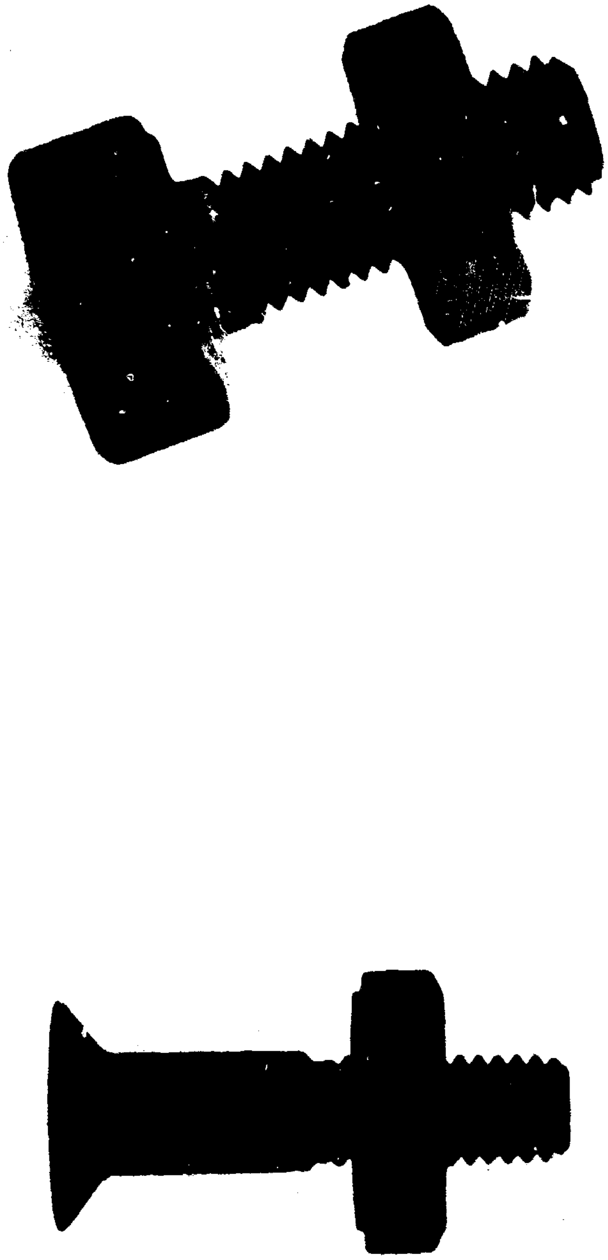


Figure 95 USAF-MAC ASSET Cr-Ti-Si Coated Bolts and Nuts (D-14 Alloy) (Top) As Coated and (Bottom) Exposed 24 Hours at 2500°F in Air

Figure 96 USAF-Martin Cr-Ti-Si Coated Brazed Honeycomb Structural Panels (D-36 Alloy)

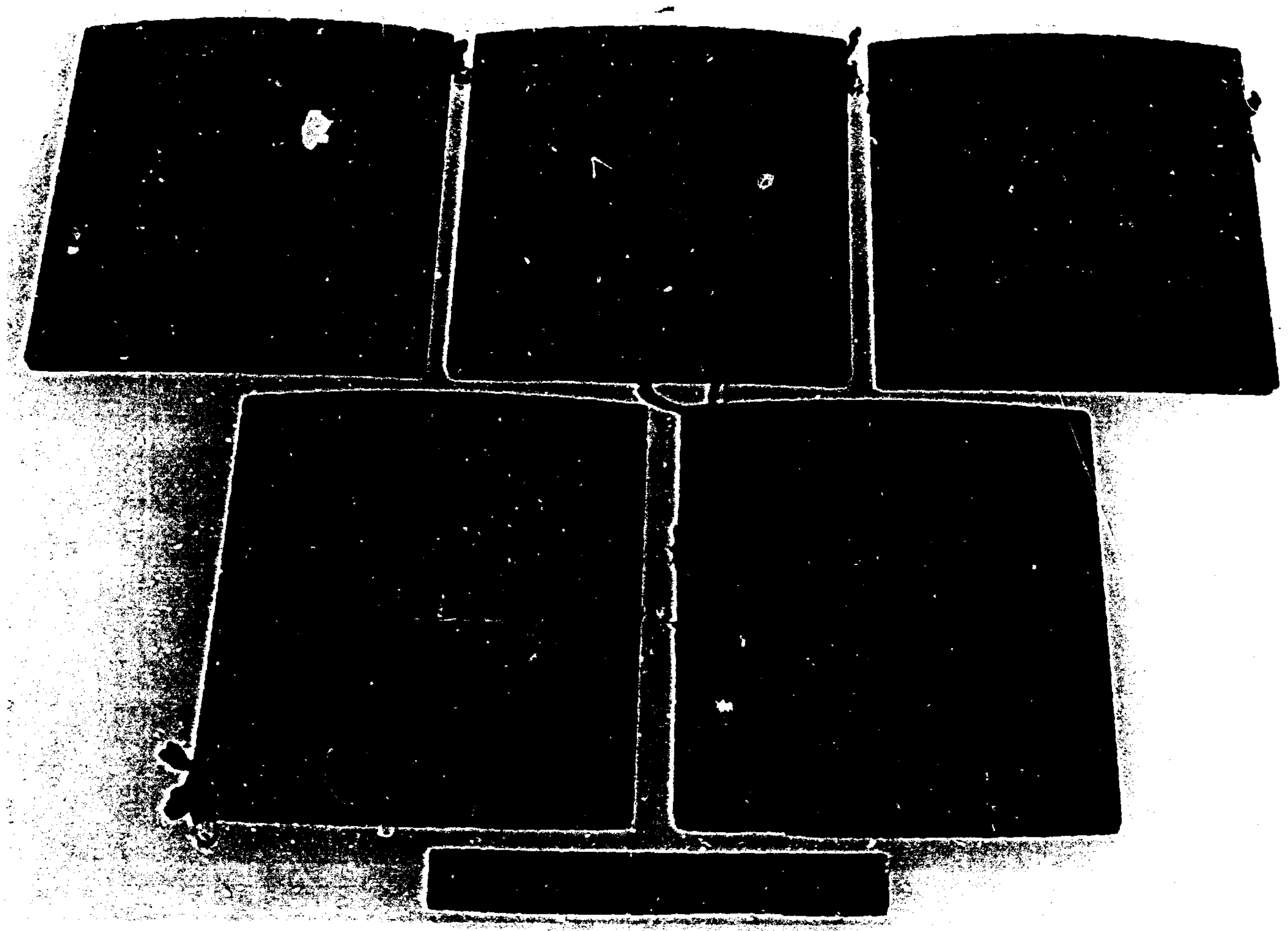


Figure 97 USAF-Martin Cr-Ti-Si Coated Brazed Honeycomb Curved Heat Shield Panels (D-36 Alloy)

One page

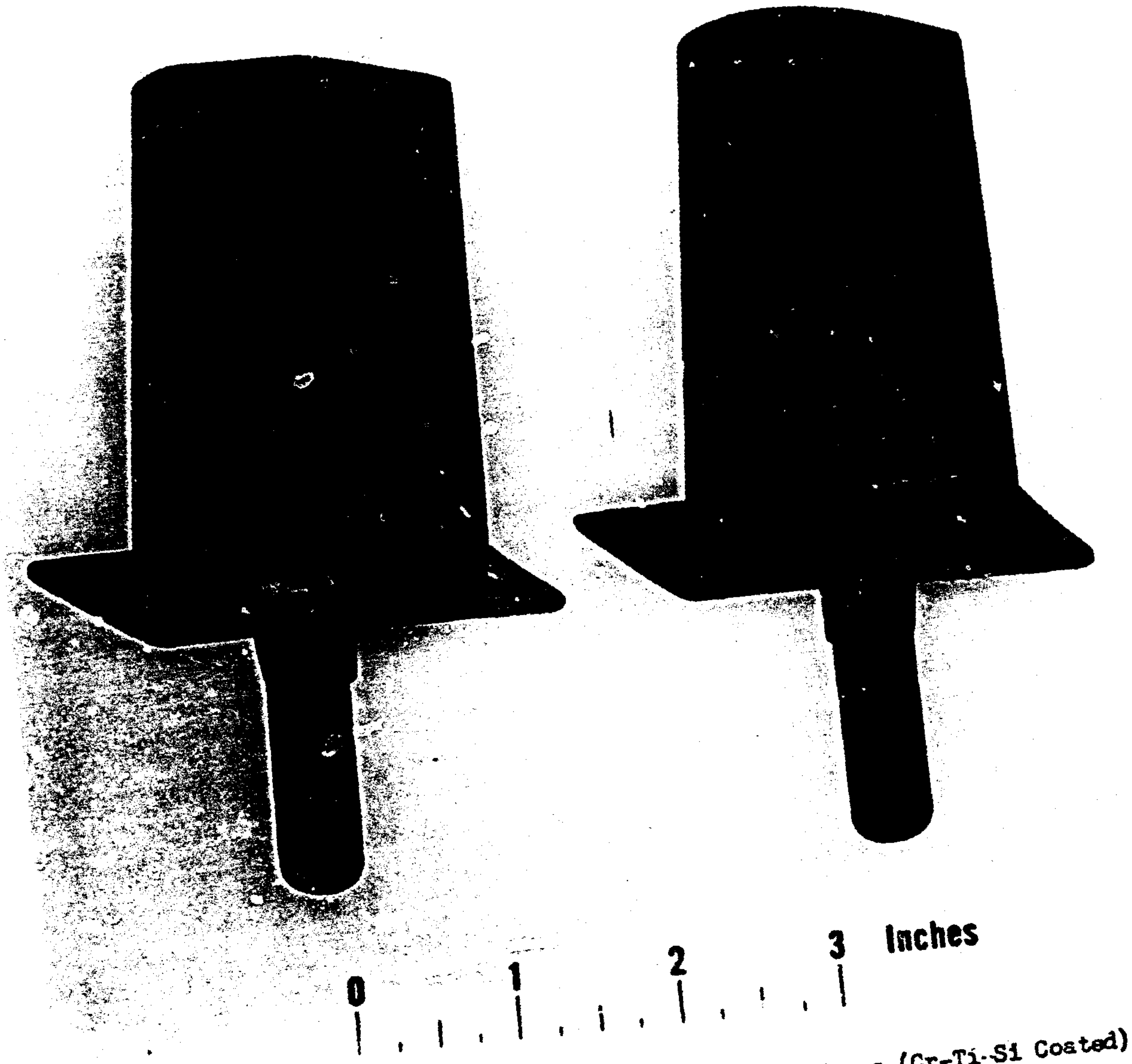


Figure 98 Folded and Welded Columbium Alloy Sheet Vanes (Cr-Ti-Si Coated)

TABLE 35

Columbium Alloy Experimental Parts and Components
Cr-Ti-Si Diffusion Alloy Coated
by the Vacuum Pack Process

Parts and Components	Organizations
1. Leading Edge Sections, Back-up Structures and Nose Cone Bulkheads - (flight hardware for 4 vehicles)	McDonnell (ASSET-AF)
2. Fasteners (bolts, nuts, washers, rivets and pins) - To Date in Excess of 8,000 Parts	McDonnell (ASSET-AF)
3. Pressure Sensing and Thermocouple Protection Tubes - (for 4 vehicles)	McDonnell (ASSET-AF)
4. Prototype Fasteners (bolts, nuts, splines and rivets) - To Date in Excess of 2,000 Parts)	Republic (AF Fastener Program)
5. Small Structural Panel (4" x 6")	Bell Aerosystems
6. Prototype Leading Edge Section (6" x 6" x 18")	Martin-Denver
7. Brazed Honeycomb Heat Shield and Structural Panels (18" x 18")	Martin-Baltimore (AF)
8. Test Turbine Blades and Nozzle Vanes (forged blades and forged and welded sheet vanes)	Pratt & Whitney Aircraft

region to form the chromium rich intermetallic phase as a continuous interface layer between the overlay and the substrate, (3) a continuous 0.3-0.5 mil Cr-Ti overlay coating, diffusion alloyed with the columbium substrate and (4) a continuous 1.0-1.5 mil Cr-Ti-Si overlay coating, diffusion alloyed with the Cr-Ti layer.

6) The reliability analysis conducted on Cr-Ti-Si coated D-43 and B-66 alloy specimens cyclic oxidation tested at 2000°F indicated a 98.5 ± 0.5% probability at a 99% confidence level of a 150 hour protective life.

7) The reliability analysis conducted on 345 Cr-Ti-Si coated D-43 alloy specimens indicated for a mean life value of 67 hours a 95 ± 1% probability at a 99% confidence level of a 28 hour protective life in the 2500°F cyclic oxidation test. For a mean life value of 83 hours a 95 ± 1% probability at a 99% confidence level was attained for a 32 hour protective life for 326 B-66 alloy specimens in the same test.

8) The reliability analysis conducted on 120 Cr-Ti-Si coated D-43 alloy specimens indicated for a mean life value of 7 hours a 95 ± 2% probability at a 99% confidence level of a 2 hour protective life in the 2700°F cyclic oxidation test. For a mean life value of 4 hours a 95 ± 3.5% probability at a 99% confidence level was attained for a 1 hour protective life for 120 B-66 alloy specimens in the same test.

9) Protective reliability at 2500 and 2700°F is influenced by specimen position in the retort and therefore by coating composition. Coating uniformity and protective reliability were enhanced in this study by not utilizing the coating space in the top few inches of the retort.

10) The Cr-Ti-Si coating is capable of providing oxidation protection for up to 4 hours for a variety of reduced pressure-elevated temperature environments.

11) Coating degradation and loss of post-oxidation protective life are greatest for reduced pressure exposure at 10^{-1} mm. Both coating element vaporization (chromium) and decomposition of SiO_2 to form SiO and atomic oxygen contribute to coating degradation.

12) With the exception of fusion welds, poorer Cr-Ti-Si coating protective performance was obtained on joints (spot welded and riveted) than was obtained on the base alloy sheet.

13) The potential utility of the Cr-Ti-Si coating has been demonstrated on experimental aerospace and aircraft gas turbine parts.

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