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FINAL REPORT ON REFRACTORY METAL COATINGS BY CHEMICAL VAPOR DEPOSITION, final report.

Gene F. Wakefield
Texas Instruments, Incorporated

TECHNICAL REPORT AFML-TR-66-397

December 1966

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Research and Technology Division
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FINAL REPORT ON REFRACTORY METAL COATINGS BY CHEMICAL VAPOR DEPOSITION

Gene F. Wakefield

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FOREWORD

This Final Technical Documentary Report was prepared by the Materials Research and Development Laboratory, Materials and Controls Division of Texas Instruments Incorporated. The work was initiated by the Chemical Processing Branch (MATC) of the Manufacturing Technology Division, Air Force Materials Laboratory, Research and Technology Division, under Contract AF 33 (615)-3046, Project 8-264. The program was accomplished under the technical direction of Mr. G. E. Eichelman and Mr. W. P. Johnson, Chemical Processing Branch, Manufacturing Technology Division, Wright-Patterson Air Force Base, Ohio. The manuscript was released by the authors on 28 November 1966, for publication as an RTD Technical Report.

The work described, to develop the chemical vapor deposition process for application of refractory metal coatings, was performed during the period from 15 May 1965 through 15 September 1966. The contract was managed by Dr. Gene F. Wakefield of Texas Instruments Materials and Controls Division, Dallas, Texas. Contributions to the effort were made by D. R. Williams, C. Cockrum, W. Parker and R. Bracken. Texas Instruments report number is 04-66-36.

Closely related efforts were covered under MMP Projects 8-346, "Refractory Metal Coatings by the Fused Salt Process", 8-184, "Fluidized Bed Techniques for Coating Refractory Metals", and 8-344, "Electrophoretic Deposition of Refractory Metal Coatings".

This project has been accomplished as a part of the Air Force Manufacturing Methods Program, the primary objective of which is to develop, on a timely basis, manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

Metallurgy - Rolling, Forging, Extruding, Casting, Fiber, Powder
Chemical - Propellant, Coating, Ceramic, Graphite, Nonmetallics
Electronic - Solid State, Materials & Special Techniques, Thermionics
Fabrication - Forming, Material Removal, Joining, Components

Suggestions concerning additional manufacturing methods development required on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.

Melvin E. Fields

MELVIN E. FIELDS, Colonel, USAF
Chief, Manufacturing Technology Division
Air Force Materials Laboratory

ABSTRACT

The basic processes necessary to manufacture refractory metal coatings using chemical vapor deposition technology were investigated. The processes developed were demonstrated on a typical oxidation resistant coating of titanium-chromium-silicon but would have general applicability to other similar coatings. The processes utilized both two-stage deposition (metal alloy coating followed by silicon deposition) and a new method developed for the rapid (10 minute) deposition of all three elements in a single step. The processes were used for deposition of metallic coatings and for controlled variation of the composition of titanium and chromium alloys. Substrate property degradation and interaction were minimal for all types of coatings.

Performance of the coatings was evaluated by oxidation testing in air and was found to be nominally comparable to coatings by other processes. Reliability and reproducibility, indicated by statistical analysis of results, were high for this initial effort program.

The processes have potentials for utilization in rapid and economical manufacturing of a variety of coatings on parts with complex shapes.

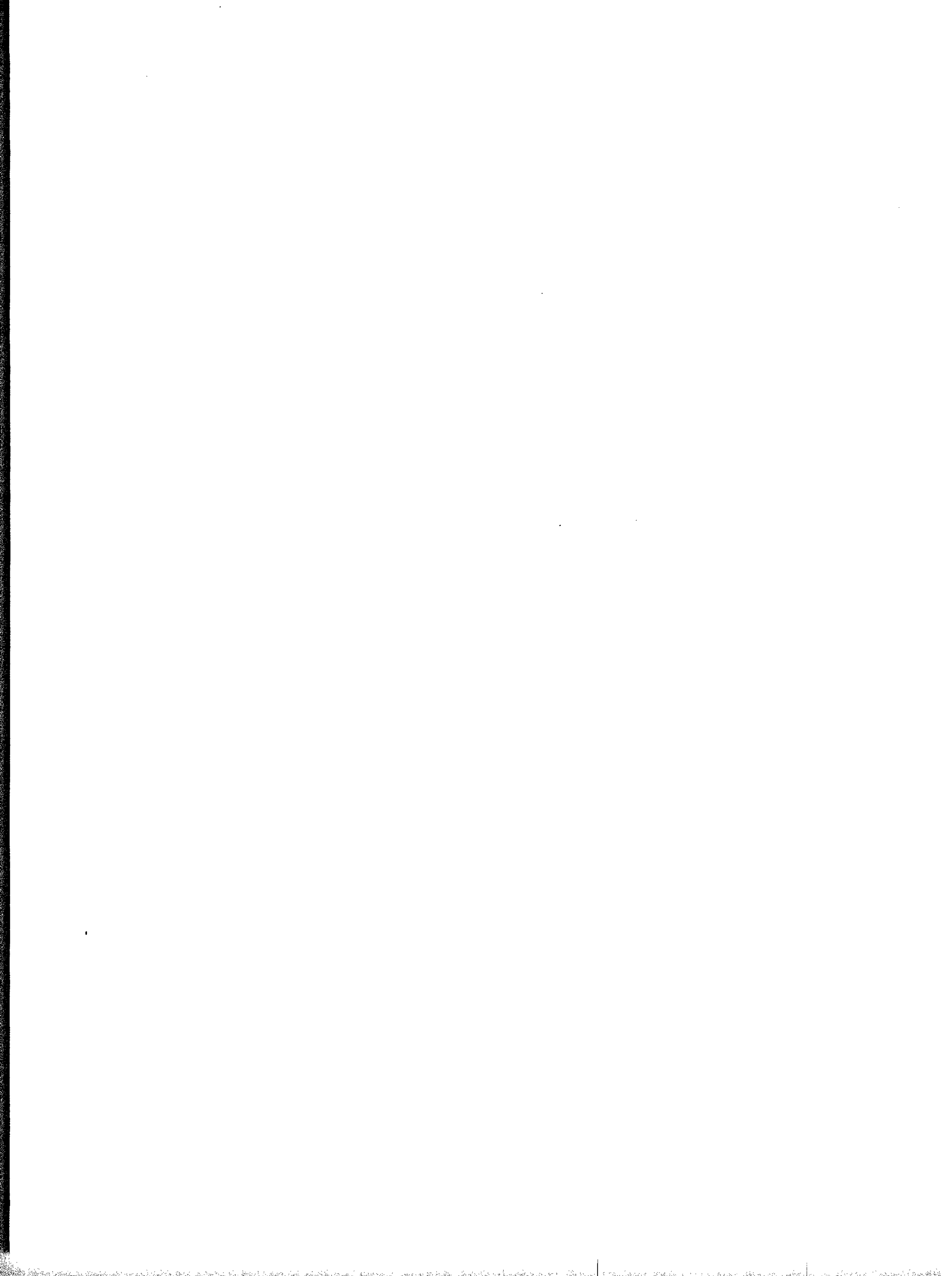

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION.	1
	A. Background	1
	B. Principles Influencing Solid Formation from the Gas Phase	5
	C. Method of Approach	9
II	EXPERIMENTAL DESCRIPTION.	11
	A. Materials.	11
	B. Equipment.	13
III	PROCESS DEVELOPMENT FOR METAL AND ALLOY DEPOSITION.	18
	A. Titanium Deposition.	18
	B. Deposition of Chromium Metal	36
	C. Comparison of Titanium and Chromium Deposits	47
	D. Alloy Codeposition Process Study	51
	E. Relationship of the Gas-Phase Concentration to Deposit Compositions	86
	F. Silicon Deposition Process	86
IV	COATING PROTECTIVENESS STUDIES.	90
V	IRREGULAR SHAPES.	152
	A. Welded Joint (Series D-0).	152
	B. Curved Samples (Series D-1).	152
VI	TRIDEPOSITION PROCESS	158
VII	PROTECTIVENESS EVALUATION	172
	A. Process Evaluation	172
	B. Program Assessment	176
VIII	CONCLUSIONS	179
IX	RECOMMENDATIONS FOR FUTURE DEVELOPMENT.	181

APPENDIX

PARAMETERS AND RESULTS OF ALL COATING DEPOSITION EXPERIMENTS

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Overlay Concept.	4
2	Illustration of a Specific Overlay Deposition which has been Made	4
3	Surface of B-66 Alloy, (a) as-received, (b) Etched for Deposition	12
4	Cross Section of B-66 Alloy as-received.	12
5	Coating System Control Unit.	14
6	Coating System Flow Diagram.	15
7	Photograph of Coating Reactor.	16
8	Schematic Diagram of Coating Reactor	17
9	Liquid $TiCl_4$ Metering Setup.	23
10	Sample Weight Change versus Percent $TiCl_4$.	24
11	Plots of Deposition Rate of Titanium from Statistical Plan . .	27
12	Three-Axis Plot of Titanium Deposition Data.	29
13	Coating of Titanium on B-66 Alloy Run 80, 17-Micron Titanium Thickness.	33
14	Surface of Titanium "as deposited" on B-66 Alloy	33
15	Titanium Deposited on B-66 Alloy Showing Coating Over Corner Section.	34
16	Arrhenius Plot of Titanium Deposition Data	35
17	Plots of Deposition Rate of Chromium from Statistical Plan . .	42
18	Planes of Constant Deposition Rate of Chromium	44
19	Arrhenius Plot of Chromium Deposition Data	48
20	Surface of Chromium Deposited on Columbium	49
21	Columbium Surface After a Brief Deposition of Chromium	50
22	Cross Section of Chromium Deposits	52
23	Codeposition of Titanium and Chromium Run 630.	54
24	Electron Microprobe Profile Scan of Coating 630 Showing Qualitative Concentration.	55
25	Codeposition of Titanium on Chromium, Run 643.	57
26	Electron Microprobe Profile Scan of Coating 643 Showing Qualitative Concentration.	57
27	Codeposition of Titanium and Chromium, Run 672	59
28	Codeposition of Titanium and Chromium, Run 686	59

LIST OF ILLUSTRATIONS
(continued)

FIGURE		PAGE
29	Electron Microprobe Scan of Coating 672 Showing Qualitative Concentration.	60
30	Microprobe Profile Scan of Coating 686 Showing Qualitative Concentration.	61
31	Ti-Cr Coating Prepared with 75% Ti - 25% Cr Alloy Chloride Source.	63
32	Ti-Cr Coating Prepared with 40% Ti - 60% Cr Alloy Chloride Source.	63
33	Electron Microprobe Profile Scan of Coating 788 Showing Qualitative Concentration	65
34	Electron Microprobe Profile Scan of Coating 780 Showing Qualitative Concentration	66
35	Sketch of Two-Compartment Chloride Generating Chamber	67
36	Deposition Rate versus Process Parameter.	70
37	Codepositions of Titanium and Chromium.	75
38	Surface Photograph of "as-deposited" Ti-Cr Alloy.	78
39	Profiles of Coating Composition Measured with an Electron Microprobe.	79
40	Ti-Cr Coatings on Two Sides of B-66 Substrates.	84
41	Composition of Coating Deposit versus Concentration of Gas Phase for Codeposition of Titanium-Chromium Alloys.	87
42	Silicon Coating on Tantalum	88
43	Silicon Coating on Molybdenum	88
44	Titanium-Chromium-Silicon Coating on B-66	89
45	Schematic Diagram of Coating Reactor used to Trideposit Ti-Cr-Si Coating.	159
46	Cross Sections of Ti-Cr-Si Coatings on Curved Sample No. 1635 Prepared in the Trideposition Process	161
47	Percent Cumulative Failures vs Cyclic Oxidation Life at 2300°F for all Samples of C- and D- Series	173
48	Percent Cumulative Failures vs Cyclic Oxidation Life at 2500°F for all Samples of C- and D- Series	174

LIST OF TABLES

TABLE		PAGE
I	Plan for Titanium Deposition.	26
II	Multiple Regression and Correlation Analysis of Titanium Depositions	31
III	Factorial Analysis of Variance for Titanium Depositions . . .	32
IV	Activation Energies of Reactions Occurring During Titanium Depositions	36
V	Statistical Plan and Results for Chromium Deposition Investigation	39
VI	Second Statistical Plan and Results for Chromium Deposition Investigation	41
VII	Multiple Regression and Correlation Analysis of Chromium Depositions	45
VIII	Factorial Analysis of Variance for Chromium Depositions . . .	46
IX	Plan and Results for Cr-Ti Alloy Depositions	69
X	Multiple Regression and Correlation Analysis of Ti-Cr Alloy Depositions	73
XI	Factorial Analysis of Variance for Alloy Depositions.	74
XII	Alloy Deposition Reproducibility Series	83
XIII	Results of Oxidation Testing at 2300°F.	168
XIV	Results of Oxidation Testing at 2500°F.	170
XV	Coating Life (Hours) at Specified Levels of Reliability . . .	175

SECTION I

INTRODUCTION

The general purpose of this program was to investigate a pure chemical vapor deposition process adaptable to any common refractory metal and designed for improved control of process variables, with the ultimate goal of providing uniform and impervious coatings with a high degree of reproducibility. A process was designed and developed to apply a coating of titanium, chromium, and silicon to the refractory alloy B-66. The effects of process variables on coating performance and coating-substrate system properties were related and the potential for coating more complex shapes evaluated. The potential of the process for scale-up to coating larger and more complex shapes was indicated.

A. Background

The aerospace and aircraft industry's need for materials having high strength at elevated temperatures has stimulated widespread interest in the application of the refractory metal alloys. This is because one of the biggest problems facing designers of aircraft and aircraft engine components is the selection of proper materials to withstand increasingly severe demands of temperature and oxidizing environment to which they will be subjected. Unfortunately, the number of materials from which to choose has been quite limited. Many times a compromise choice or modified performance must be accepted. The refractory metals tantalum, molybdenum, columbium, and tungsten are especially desirable for applications requiring high strength at elevated temperature, particularly where ease of fabrication and ductility are needed. However, before any of these materials can satisfy a wide range of requirements, it must receive an oxidation-resistant coating.

Considerable effort has been expended in developing such coatings. The relatively few coatings now available indicate that this development work has proceeded slowly and in several directions, with major success in a coating of titanium, chromium, and silicon.

Much work has been done in developing methods of applying coatings and in deposition process studies. In programs at the University of Dayton* and at Solar, a division of International Harvester Company,† coating performance was found to be less predictable than desired. In some cases, the nonreproducible results tended to obscure or to limit the observation of interaction of the variables under investigation. Though many techniques -- e.g., pack cementation, fluidized bed, plasma spray, and fused salt -- give coatings on large, complex shapes, a greater degree of control would aid in achieving higher reproducibility.

A key to satisfying this requirement is to develop a technique by which process variables can be rigidly and independently controlled. One technique that offers this advantage is pure "chemical vapor deposition" (CVD). This concept is certainly not new in the field of refractory metals coatings, since pack cementation, the vacuum pack method, and the fluidized bed process are all forms of CVD. However, in all these techniques the vapor phase is, by design, interrupted by a solid phase of material normally acting as the source of vapor contacting the surface of the substrate to be coated. Because the reaction zone is inhomogeneous, control of critical process parameters is often limited. In the pack cementation or vacuum pack method, system response to a controlled change of furnace temperature is very slow, which means that this parameter's effect on the reaction can be only coarsely controlled. Also, since the active material is contained within the pack, any controlled temperature change will necessarily influence the other process variables, especially the composition or concentration of the vapor phase. On the other hand, if the source of the chemical vapor contacting the substrate surface were retained outside the reaction zone, any temperature change in the system could be counterbalanced by adjusting or controlling the outside vapor source. On the same basis, vapor composition could be changed independently of any other variable, including temperature. The fused salt deposition method is, like CVD, a homogeneous reaction medium and might also result in improved coating uniformity and reliability in performance. To investigate the fused salt approach a program, also with the

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* Air Force Contract No. AF 33(615)-1312.

† Air Force Contract No. AF 33(657)-9443.

goal of improved reliability, is being conducted by MATC at Solar, a division of International Harvester*.

Inherent in the CVD process is the ability to form an overlay coating. This is done, as illustrated in Figure 1, by applying a coating to a substrate and achieving bonding with only minimum interaction or interdiffusion between coating and substrate. In many cases an interlayer might be necessary between coating and substrate to serve as a diffusion barrier or as a bonding layer compatible with both substances, or to aid in matching thermal expansion. However, use of such a layer does not alter the basic concept of an overlay coating with minimum interaction with the substrate. This overlay principle is followed routinely in the semiconductor industry, and an example of its possibilities is shown in Figure 2. In this case, multiple layers of silicon containing a selected dopant, namely boron or antimony, have been deposited on a silicon substrate.

Extending this overlay concept to protective coatings is considered especially significant for several reasons. First, it helps make choice of coating independent of choice of substrate and vice versa. This means that development of each new alloy may not require development of a new coating. Minimizing the interaction between coating and substrate increases the possibility that desirable substrate properties will be retained in the coated part. This is in contrast to diffusion coatings, which diminish a foil substrate thickness by a significant amount during coating. The composition of the coating does not depend on the composition of the substrate, as does the composition of a coating formed by diffusing chemical elements into a substrate. For diffused coatings which incorporate a portion of the substrate, the role of the minor alloy constituents which become involved in the coating may not be understood and may prove quite detrimental.

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* Air Force Contract AF 33(615)-3173

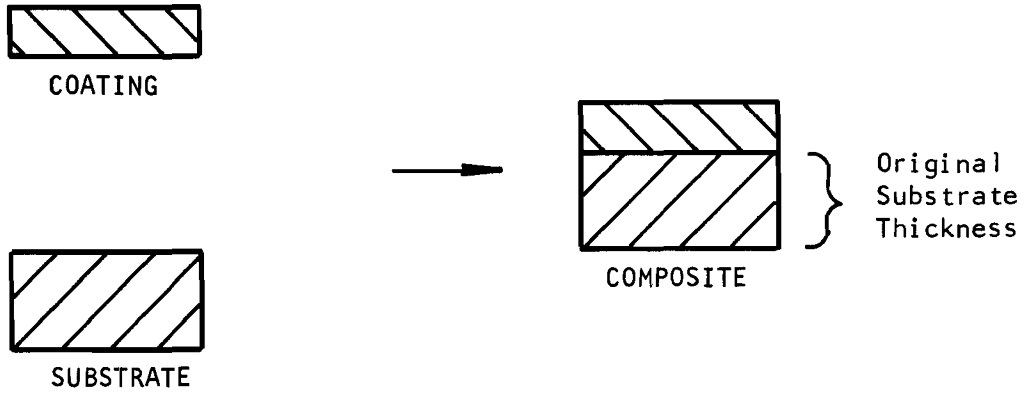

Figure 1 Overlay concept. A coating is bonded to a substrate with little interaction. The coating itself is independent of substrate composition.

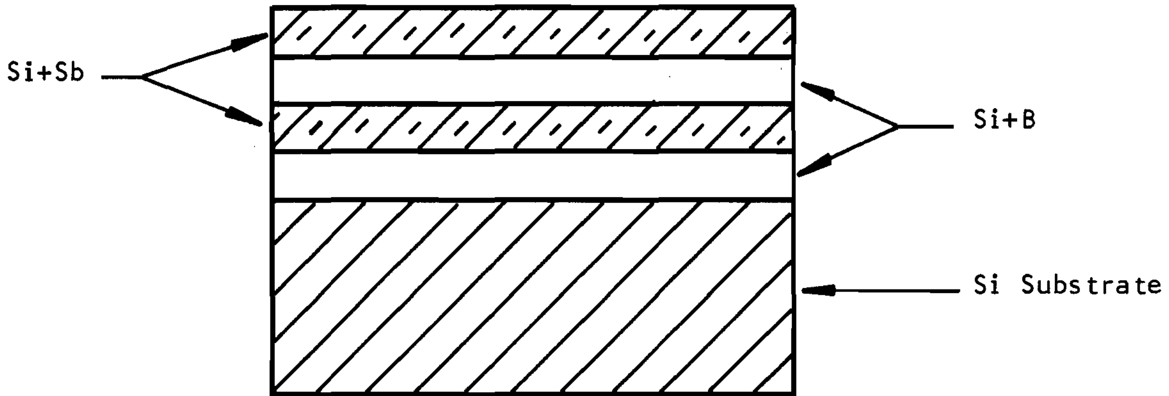

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Figure 2 Illustration of a specific overlay deposition which has been made. Multiple layers of silicon containing alternate additions were deposited on a silicon substrate.

A second advantage of the overlay concept is the versatility which can be gained, not only in applying layers of varying composition, but also with respect to the structure and morphology of any specific coating. In using fairly brittle coatings on substrates which are in general more ductile, grain size and orientation assume considerable importance in mechanical compatibility. As the overlay concept is put into more practical application, the ability to develop tailor-made coatings will permit better utilization of their inherent properties.

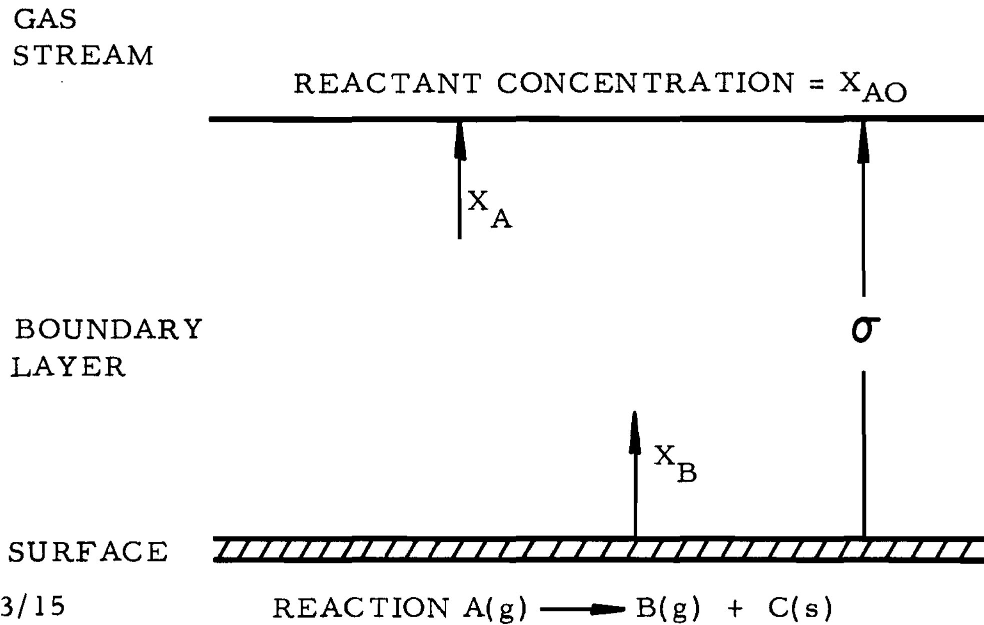
Another advantage inherent in this technique is in multicycle processes for depositing the coating, where the component need not be removed from the system between cycles. Coating refractory metal hardware by most other techniques requires a separate retort, vat, or container for each coating cycle, or the active coating materials must be removed from the equipment and replaced with different materials. However, by injecting the active materials into the reactor from an outside source, the only major operation required between cycles would be purging and cooling, if necessary, without removing the substrate. The savings in time and expense would be especially welcome in a manufacturing operation.

B. Principles Influencing Solid Formation from the Gas Phase

Deposition process mechanisms are investigated primarily to learn what parameters control coating characteristics and thus, coating performance. Such data determine how parameters in the coating process must be altered to obtain desired performance. It is this aspect of control that makes CVD an attractive and promising tool for coatings investigation and production.

In a gas-solid reaction several mechanisms may control the rate of reaction. These mechanisms affect deposit thickness and rate of formation. They also influence deposit morphology, which includes integrity, grain size, density, and whether the material deposits as dendrites or as an adherent layer.

Ideally, a gas-solid reaction can be divided into three steps, any one of which may be rate-limiting: (1) diffusion of the reactants to the surface and diffusion of products from the surface, (2) adsorption of reactants and desorption of products, and (3) reaction on the surface. The step which occurs at the slowest rate in a given series establishes the overall rate. A reaction is illustrated below.



In this instance gas phase concentration of A before reaction is given by X_{A0}. This material must diffuse toward the surface through a layer of counterdiffusing B. The thickness of this layer is δ. Once in the neighborhood of the surface the material is adsorbed. On the surface it reacts, and finally the product B is desorbed and diffuses back into the gas stream.

The most straightforward example of rate limitation is reaction rate limitation. In this case the surface is saturated with reactants. Changes in gas phase reactant concentrations and gas flow rates do not affect the reaction rate. Temperature alone can increase or retard the rate. However, in most cases of CVD, temperatures are high enough that chemical reaction rate is not the limiting step.

When adsorption is the rate-limiting step, the surface is not saturated with reactants. The adsorption equilibrium defines the rates of reaction, and the effects of reactant pressure changes are directly apparent in the rate of the reaction.

For a reaction

$$A(g) \rightarrow B(g) + C(s) \ ,$$

the rate of reaction, dX_A/dt, can be expressed as a function of surface coverage $[S_A]$ of A:

$$-\frac{dX_A}{dt} = k[S_A] \ .$$

Assuming a Langmuir isotherm, the surface coverage can be expressed as

$$[S_A] = k' \frac{b_A P_A}{1 + b_A P_A} \ ,$$

where b_A is related to adsorption energy

P_A is partial pressure of A.

The rate of reaction as a function of the gas pressure of the reactant is obtained thus:

$$-\frac{dX_A}{dt} = k'' \frac{b_A P_A}{1 + b_A P_A} \ .$$

For the special case of weakly adsorbed material (b_A small) or for low partial pressures of A (P_A small), the rate expression becomes

$$-\frac{dX_A}{dt} = k'' \, b_A P_A = k''' \, P_A \ .$$

That is, the reaction becomes first order in A for a sparsely covered surface.

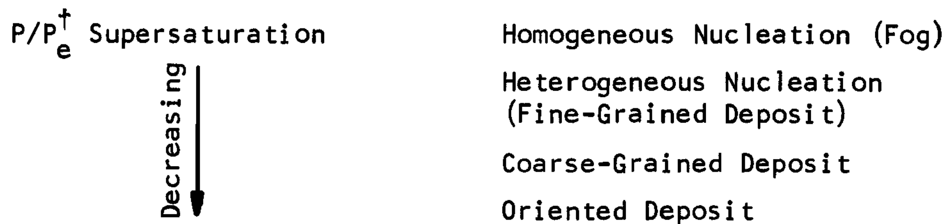
In many cases diffusion or gas phase transport is made the rate-controlling step by the character of the adsorption isotherm, the activation energy of the reaction, or simply the necessary geometry of the system.

Where forced convection has not been obtained, natural convection is the main vehicle for delivering reactant to and removing products from the surface. This usually produces nonuniform coatings with a small amount of material deposited on the work piece, collected mostly in the center. Forced convection of gases directly onto the work piece produces even deposits.

Besides the chemical reaction which yields the deposit, other factors influence the integrity of the deposit and its structural form. Obtaining integrity in deposited materials requires preventing gross flaws in the crystal structure and controlling deposit composition. Some defects can be prevented by using pure starting materials and avoiding gaseous and solid impurities. This is particularly noticeable in the deposition of titanium, where the least amount of oxygen or nitrogen in the atmosphere results in deposition of compounds rather than elemental metal.

The relative pressure (P/P_e) of the deposit also influences the rate of deposit formation and deposit morphology. This relative pressure, called the supersaturation ratio, gives a measure of the driving force that causes condensation or deposit growth on the substrate surface. As this ratio changes, the morphology changes as shown below.

Relation of Supersaturation to Deposit Morphology



†P is actual pressure over the deposit.

P_e is equilibrium vapor pressure of the deposit.

Such changes in morphology can greatly influence deposit strength and density. Low rates of deposition associated with low values of P/P_e may have to be accepted at times to obtain desired morphologies.

All these factors -- gas phase diffusion, forced convection, supersaturation, and surface saturation -- are important parameters in the gas-solid reaction. The understanding of their influence on the process and deposit and their control are essential to a reproducible, predictable coating process.

C. Method of Approach

The program to investigate and evaluate chemical vapor deposition for the general and specific goals has been carried out in three phases. Emphasis throughout the program was on developing process information useful in scale-up and in producing coatings of high reproducibility. To maximize the amount of information obtained, the series of experiments was designed, ordered, and results evaluated with the aid of statistical techniques.

1. Phase One: Coating Deposition Studies

Process parameters controlling formation of the individual alloy constituents chromium and titanium were studied. The elements were formed by the hydrogen reduction of their halides. Experiments determined the effect of processing variables on the rate and quality of the coating deposition. Information was generated on effects of the physical process variables, e.g., the relationship of substrate-jet geometry to coating uniformity, effect of flow rate on the uniformity of the deposit, and necessity of cooling samples in inert ambient. Physical, metallurgical, and chemical property analyses were used to evaluate coating composition and condition of the deposit.

Parameters controlling codeposition of the chromium and titanium alloys were investigated by determining the effects of process variables on the coating deposition rate and the quality of the deposit obtained. From evaluation of

these deposits, the most suitable process parameters were selected for codeposition of the chromium-titanium layers for subsequent use in the siliconizing studies.

The chromium-titanium layer was siliconized by hydrogen reduction of the silicon halide $SiCl_4$. These experiments used the most suitable chromium-titanium coated columbium alloy substrates developed in the earlier part of Phase One. Various chromium-to-titanium ratios and thicknesses were siliconized and the properties of the coating substrate system determined.

2. Phase Two: Coating Protectiveness Studies

Optimum process parameters were chosen on the basis of Phase One work, and small samples were coated and evaluated by oxidation testing. Multiple samples were tested to evaluate the reproducibility of the process and thus its value in achieving the objectives of this program. Thirty experiments, involving six samples each, were performed to determine what effects varying process parameters has on coating protectiveness and brittleness. The distribution of the samples among the specific tests is given in Section IV. After satisfactory process conditions were established for coating these specimens, test results were compared with results in the literature on previous tests of the Cr-Ti-Si coating system as produced by other techniques, especially the vacuum pack process.

3. Phase Three: Complex Shapes

After the potential of the CVD process for coating flat test specimens was established, the usefulness of the process for coating more complex shapes was investigated. A curved shape similar to a vane or leading edge segment, and lap-welded samples having hidden or faying surfaces were coated to demonstrate the "throwing power" of the process and its general utility for coating pieces of hardware of typical shapes. Coated parts were subjected to cyclic oxidation tests.

SECTION II

EXPERIMENTAL DESCRIPTION

A. Materials

Substrates: All coatings were deposited on columbium alloy B-66, obtained from the Westinghouse Astronuclear Laboratory. The nominal composition (vendor's analysis) is

Columbium	89%	Oxygen	0.015%
Molybdenum	5%	Nitrogen	0.012%
Vanadium	5%	Carbon	0.014%
Zirconium	1%	Hydrogen	$<$ 0.0005%

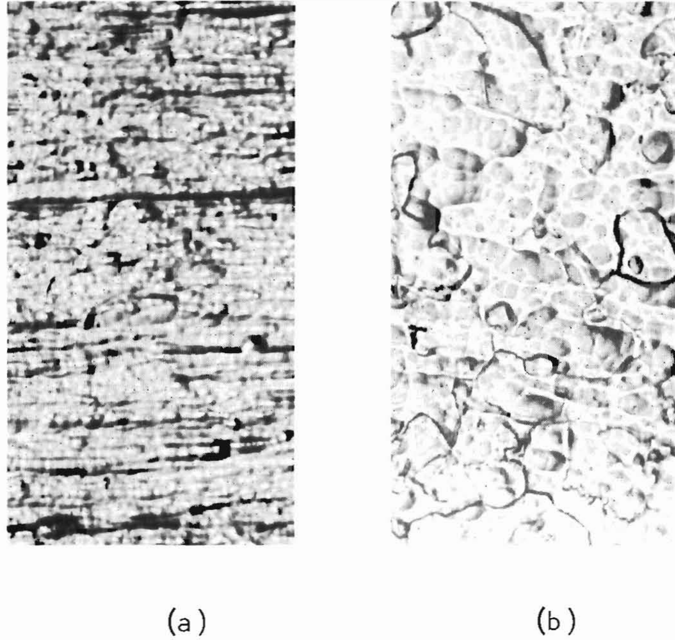
The material was received in the annealed condition, had a hardness of 249 Knoop, a surface as shown in Figure 3, and a cross section as shown in Figure 4. The samples were sheared to size, corners and edges rounded, etched in $HF:H_2SO_4:HNO_3$, rinsed, and stored under clean conditions until use.

Chemicals: $TiCl_4$ - Purified Grade $TiCl_4$ obtained from the J. T. Baker Chemical Company was used. Gas chromatographic analysis showed only trace quantities ($<$ 0.1%) HCl as impurity. All transfers of the chlorides were carried out so that the chemicals were contained in an inert atmosphere.

$CrCl_3$ - Anhydrous $CrCl_3$ was not readily available, and initial attempts to dehydrate the hexahydrate were only moderately successful. The $CrCl_3$ was finally prepared by passing chlorine over the carbon-free chromium metal at 800°C. A mixture of the di- and trichlorides was formed. The trichloride subsequently distilled to the cooler region of the reactor. Once obtained as anhydrous crystals, this material is not difficult to handle, as it does not absorb water.

$SiCl_4$ - Purified Grade $SiCl_4$ obtained from the J. T. Baker Chemical Company was used. The material was not exposed to the atmosphere.

Hydrogen - The hydrogen was purified just before use by palladium diffuser (Englehard Industries, Model 20-120-C, or Serfass Model 100-D).



(a) (b)

Figure 3 Surface of B-66 Alloy, (a) as-received, (b) etched for deposition (x 500)

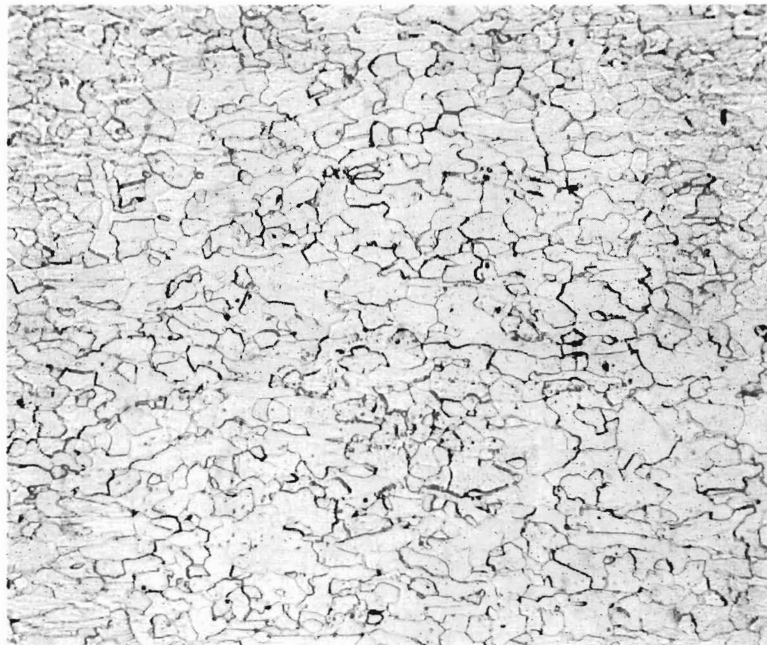


Figure 4 Cross section of B-66 Alloy as-received (x 500, etched)

Helium and Argon - These gases were purified by passing over titanium chips at 750°C. Purity of the gases (estimated < 2 ppm impurity) was checked periodically by heating a blank sample of the substrate in the gases and examining the surface for oxides or nitrides.

B. Equipment

The control unit for the coating system contained in one convenient location temperature and pressure regulators and devices for controlling and measuring all the gases except chromium chlorides. Except for system sample-jet geometry, all the main process variables were controlled from this unit. Figure 5 is a photograph of the control unit and Figure 6 the flow diagram of the coating system.

Temperature controllers for the system included Honeywell Versatronik temperature controllers (accuracy ± 5°C) on the $CrCl_3$ and helium cleaning furnaces; a Honeywell Pyro-Volt proportional controller (accuracy ± 2°C) for reactor temperature; and a mercurial thermoregulator (accuracy 0.01°C) on the water bath surrounding the $TiCl_4$ and $SiCl_4$ sources.

The gas flows were measured with Brooks Sho-Rate flow meters having a claimed accuracy of 5%, with the actual flow calibrated with a Precision Scientific Company wet test meter having a claimed accuracy of 0.5%. The results of the calibrations showed a deviation of less than 5% from the smoothed curve values, which was within the desired limits.

A photograph of the coating reactor is shown in Figure 7. Figure 8 is a schematic diagram of the reactor. The reactive gases were impinged directly on the sample so that gas velocity was high at the deposition surface. The temperature was controlled by a saturable-core reactor through the sensing thermocouple. Samples were inserted and removed through the gas lock chamber without introducing impurity gases into the system. This was a major aid in obtaining uniformity among samples and permitted a much faster operation; in addition, the reactor did not have to be cleaned frequently. The exact design of the delivery jet depended on the shape and size of the sample and the information desired from the experiment.

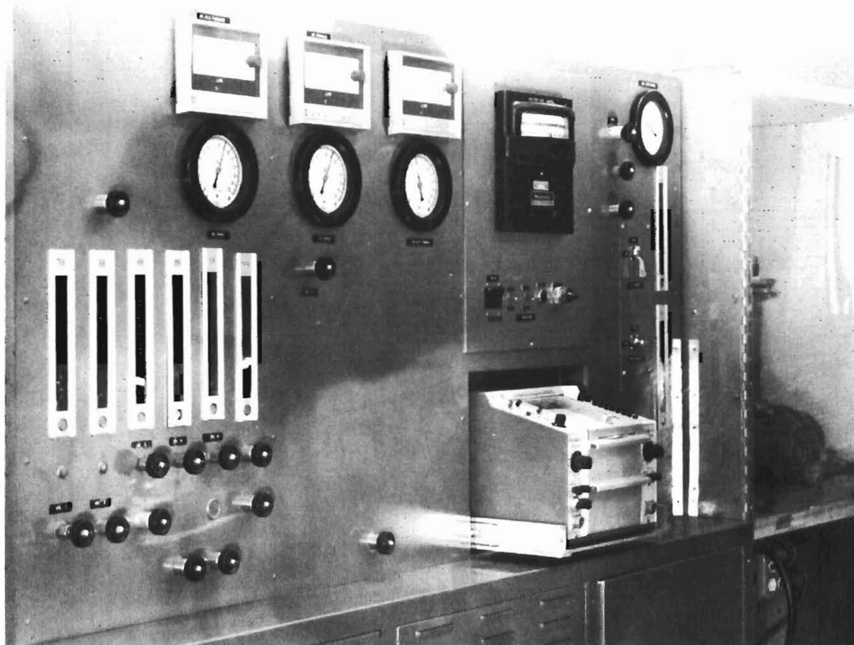


Figure 5   Coating System Control Unit

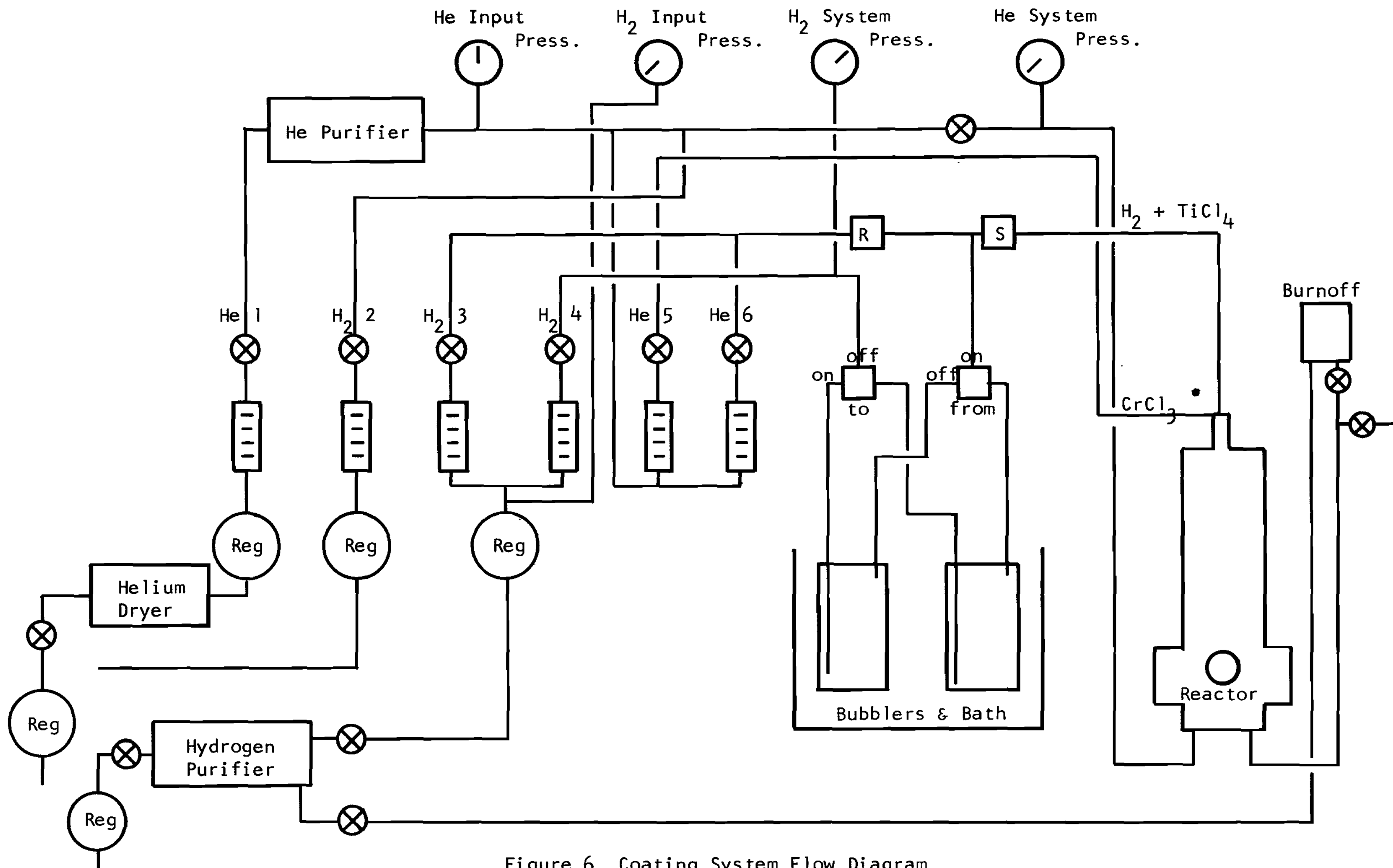


Figure 6 Coating System Flow Diagram

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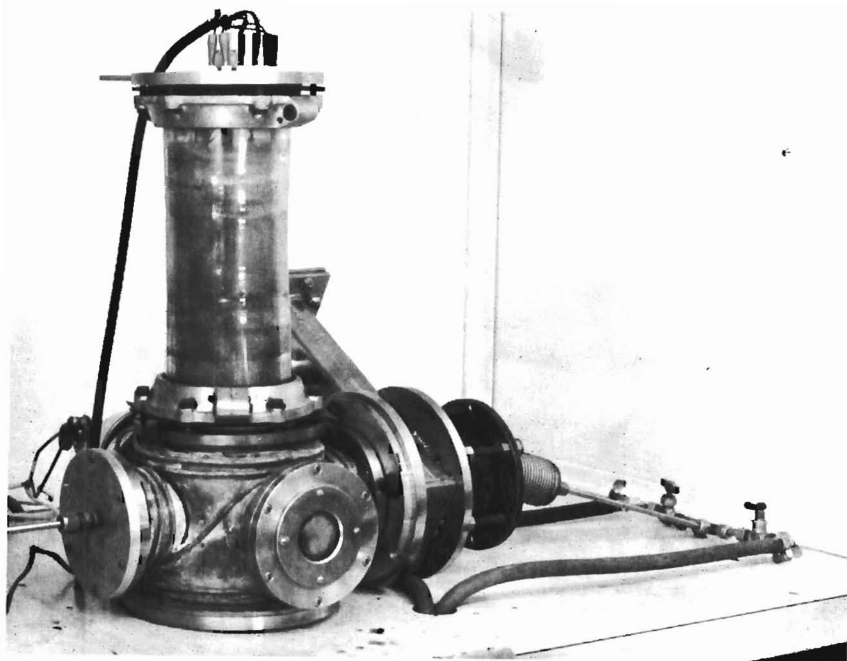


Figure 7. Photograph of Coating Reactor

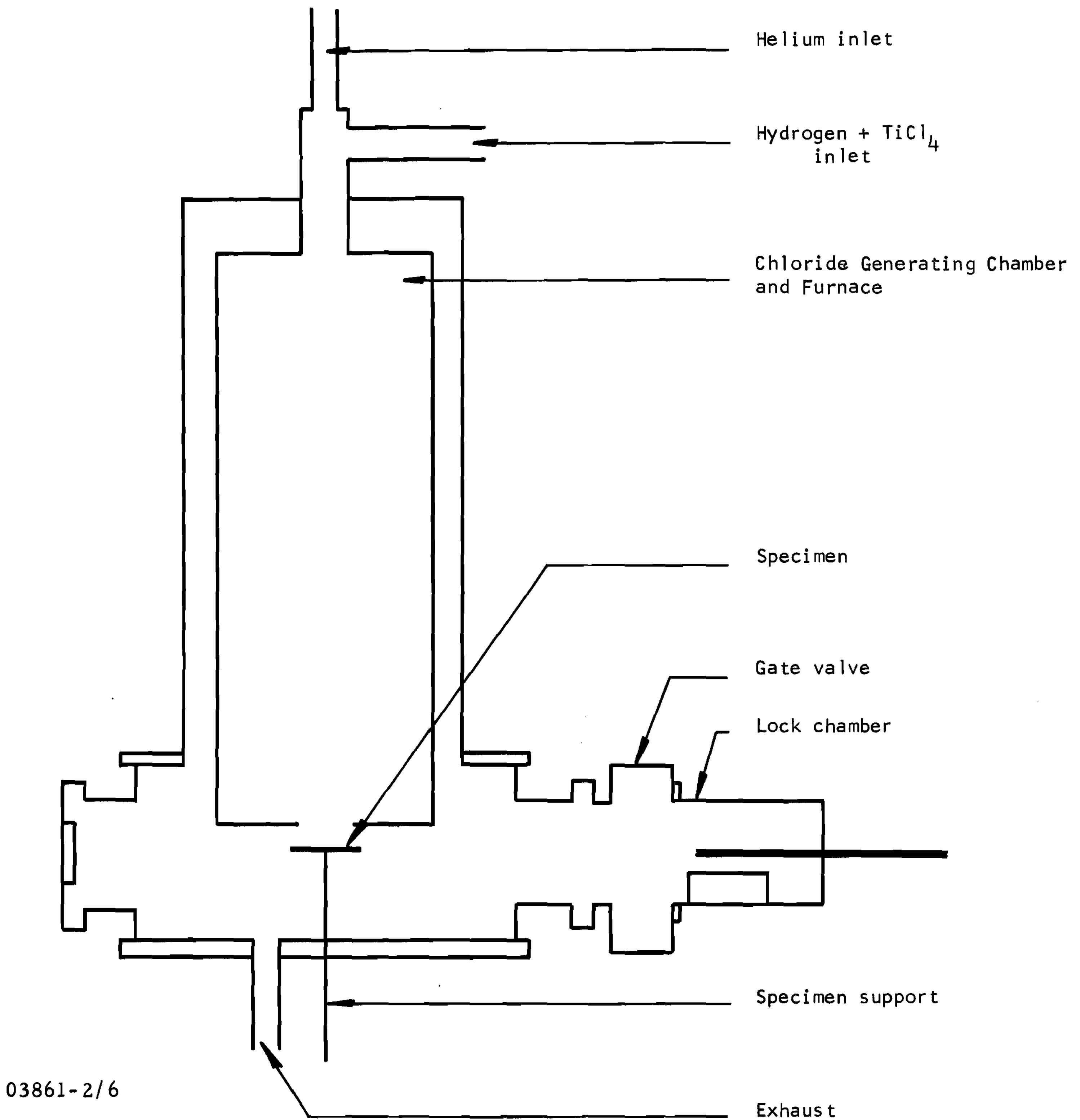


Figure 8 Schematic diagram of coating reactor

SECTION III

PROCESS DEVELOPMENT FOR METAL AND ALLOY DEPOSITION

A. Titanium Deposition

In work carried out at Texas Instruments prior to this study, hydrogen reduction of $TiCl_4$ at 1350°C under various reactant flow rates and concentrations had been found to deposit approximately 0.2 $mg/min/cm^2$ of titanium. At this rate, preparation of samples would not be rapid, and the rate would be less at lower temperature. Consideration of the total number of samples to be prepared suggested that a depsotion rate of 0.05 to 0.1 mil/min (1 to 2 $mg/min/cm^2$) at 1100 to 1350°C was desired; therefore, a way of obtaining more rapid deposition of titanium was sought.

Thermodynamic factors of the reaction are such that deposition rates might be increased (at least for reactions proceeding under equilibrium conditions) by altering reaction parameters in various ways. Calculations indicated that this would only slightly increase the deposition rate, however. The most promising changes indicated were to alter flow rate, gas concentration, and geometry, and to add an inert carrier gas, preheat the reactive gases, and partially prereduce the $TiCl_4$.

1. Pressure of Products

The free energy of the reduction reaction is increased by increasing the pressure of the HCl produced by the reaction. The calculations of the assumed set of conditions in Example 1 below show the effect of HCl pressure and demonstrate the desirability of keeping it low. One way this may be done is to use high flow rates so that product gases are rapidly removed from the reaction zone. Experiments 46 through 50 (in the Appendix) were run at various flow rates to test this approach. Although HCl pressure was reduced, deposition rates increased only slightly.

Example 1 - Hydrogen reduction of $TiCl_4$

$$TiCl_4 + 2H_2 \longrightarrow Ti + 4HCl$$

$$\Delta F^\circ = 87{,}700 - 35.8T \ *$$

$$\text{at } 1500^\circ K \ \Delta F^\circ = +\ 34{,}000 \text{ cal/mole}$$

$$\Delta F_{1500} = \Delta F^\circ_{1500} + RT \ln K$$

$$= 34{,}000 + 1.98 \times 2.303 \times 1500 \log K$$

$$= 34{,}000 + 6.86 \times 10^3 \log \frac{(P_{HCl})^4 a_{Ti}}{(P_{H_2})^2 P_{TiCl_4}}$$

$$a_{Ti} = 1,\ P_{H_2} \cong 1,\ \Delta F_{1500} = 34{,}000 + 6.86 \times 10^3 [\log (P_{HCl})^4 - \log (P_{TiCl_4})]$$

where ΔF° is standard free energy change
R is gas constant
T is temperature in °K
a is activity
P is pressure in atmospheres.

Assume sets of conditions:

(1) $P_{HCl} = 0.01$, $P_{TiCl_4} = 0.01$

$$\Delta F_{1500} = 34{,}000 + 6.86 \times 10^3 [\log 10^{-8} - \log 10^{-2}] = -7{,}100 \text{ cal/mole}$$

Reaction is slightly favorable.

*McQuillan and McQuillan, Titanium (London, Butterworth's Scientific Publications, 1956), p. 11.

(2) $P_{HCl} = 0.1$, $P_{TiCl_4} = 0.01$

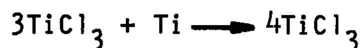
$$\Delta F_{1500} = 34{,}000 + 6.86 \times 10^3 \, [\log 10^{-4} - \log 10^{-2}] = +21{,}000 \text{ cal/mo}$$

Reaction is unfavorable.

Therefore, the reduction of $TiCl_4$ requires that the pressure of HCl be limited to low values (less than 10^{-2} atmosphere).

HCl pressure can also be lowered by diluting the gas stream with an inert gas. This lowers reactant concentrations, but these concentrations have less effect on reaction thermodynamics than does HCl concentration. (P_{TiCl_4} to the first power and P_{H_2} squared, but P_{HCl} to the <u>fourth</u> power.) Experiments 43 and 45, listed in Appendix A, were performed to test this, using argon as the diluent. Deposition rates were not significantly increased.

Still a third way to reduce HCl pressure is to prereduce $TiCl_4$ to the trivalent state before the deposition reaction. This can be accomplished with the reaction:



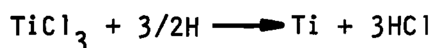
$$3TiCl_3 + Ti \longrightarrow 4TiCl_3$$

for which

$$\Delta F^\circ_{1200} = -16.55 \text{ cal/mole.}$$

Placing titanium chips in a tube heated by the $CrCl_3$ furnace results in the above reaction to yield $TiCl_3$ vapor, which is carried in the gas stream to the sample.

For the reduction of $TiCl_3$



$$TiCl_3 + 3/2H \longrightarrow Ti + 3HCl$$

$$\Delta F^\circ_{1500} = +23{,}000 \text{ cal/mole}$$

$$\Delta F_{1500} = \Delta F^\circ + RT \ln \frac{P_{HCl}^{\;3}}{(P_{H_2})\,(P_{TiCl_3})}$$

$P_{H_2} \cong 1$

$$= 23{,}000 + 6.86 \times 10^3 [\log (P_{HCl})^3 - \log P_{TiCl_3}]$$

Assume conditions

(3) $P_{TiCl_3} = 0.01,\ P_{HCl} = 0.002$

$$\Delta F_{1500} = 23{,}000 + 6.86 \times 10^3[2 \log 2 \times 10^{-3} - \log 10^{-2}]$$

$$= -\ 300 \text{ cal/mole}$$

Reaction slightly favorable.

(4) $P_{TiCl_3} = 0.1;\ P_{HCl} = 0.002$

$$\Delta F_{1500} = 23{,}000 + 6.86 \times 10^3[2 \log 2 \times 10^{-3} - \log 10^{-1}]$$

$$= -\ 5{,}300 \text{ cal/mole}$$

Reaction favorable.

Experiments 67 through 98 (Appendix A) were carried out in this fashion and yielded deposition rates in the desired range (1 to 2 mg/minute).

2. Concentration of Reactants

Increasing $TiCl_4$ pressure provides a more favorable energy for the reduction reaction (assumed sets of conditions, Example 2). In the original experimental setup, the partial pressure or concentration of $TiCl_4$ obtainable was limited to saturation of the carrier gas stream with liquid $TiCl_4$ at 20°C; i.e., since the vapor pressure of $TiCl_4$ at 20°C is 10 mm of mercury, the maximum concentration possible is 10/760, or 1.35% $TiCl_4$. The concentration could be increased by heating the liquid $TiCl_4$ above 20°C, but this would require all transfer lines to be kept at least this warm. A more practical technique is to meter the liquid $TiCl_4$ directly into the heated furnace. This permits $TiCl_4$ concentrations up to 100%.

Example 2 - Increase $TiCl_4$ pressure

Assume conditions

(5) $P_{TiCl_4} = 0.1,\ P_{HCl} = 0.01$

$$\Delta F_{1500} = 34,000 + 6.86 \times 10^3[\log 10^{-8} - \log 10^{-1}]$$

$$= -14,000 \text{ cal/mole}$$

Reaction is favorable.

(6) $P_{TiCl_4} = 0.5,\ P_{HCl} = 0.01$

$$\Delta F_{1500} = 34,000 + 6.86 \times 10^3[\log 10^{-8} - \log 0.5]$$

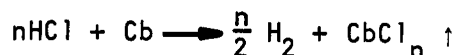
$$= -18,500 \text{ cal/mole}$$

Reaction is more favorable.

A method for controlling high concentrations of $TiCl_4$ was set up (Figure 9) and the role of $TiCl_4$ investigated in experiments 53 through 66 (Appendix A). These showed that in some instances the deposition rate can be increased. When $TiCl_4$ concentration was greater than 30%, the substrate lost weight (see Figure 10), probably through one of the reactions:

$$nTiCl_4 + Cb \longrightarrow nTiCl_4 + CbCl_n \uparrow$$

or



$$nHCl + Cb \longrightarrow \frac{n}{2} H_2 + CbCl_n \uparrow$$

(A similar effect has been widely noted in the production of silicon by hydrogen reduction of the chlorides.) In the case of either reaction, attack on the substrate can be eliminated by using a lower $TiCl_4$ and/or a higher hydrogen pressure.

3. Change in Geometry

Though not apparent from the thermodynamic analysis, the geometry relating the gas delivery jet and the sample is quite important in forming $TiCl_3$ and in gas-sample contact time. The jet arrangement was modified to control gas

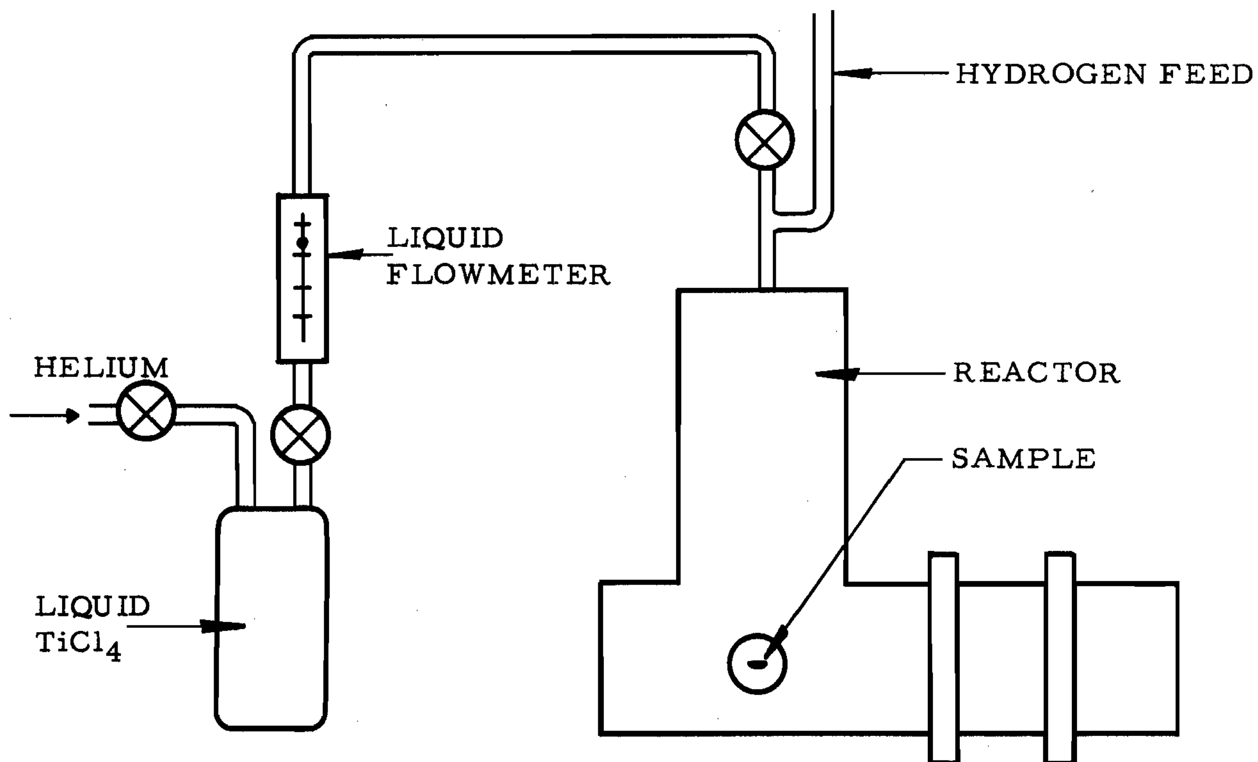


Figure 9 Liquid $TiCl_4$ Metering Setup

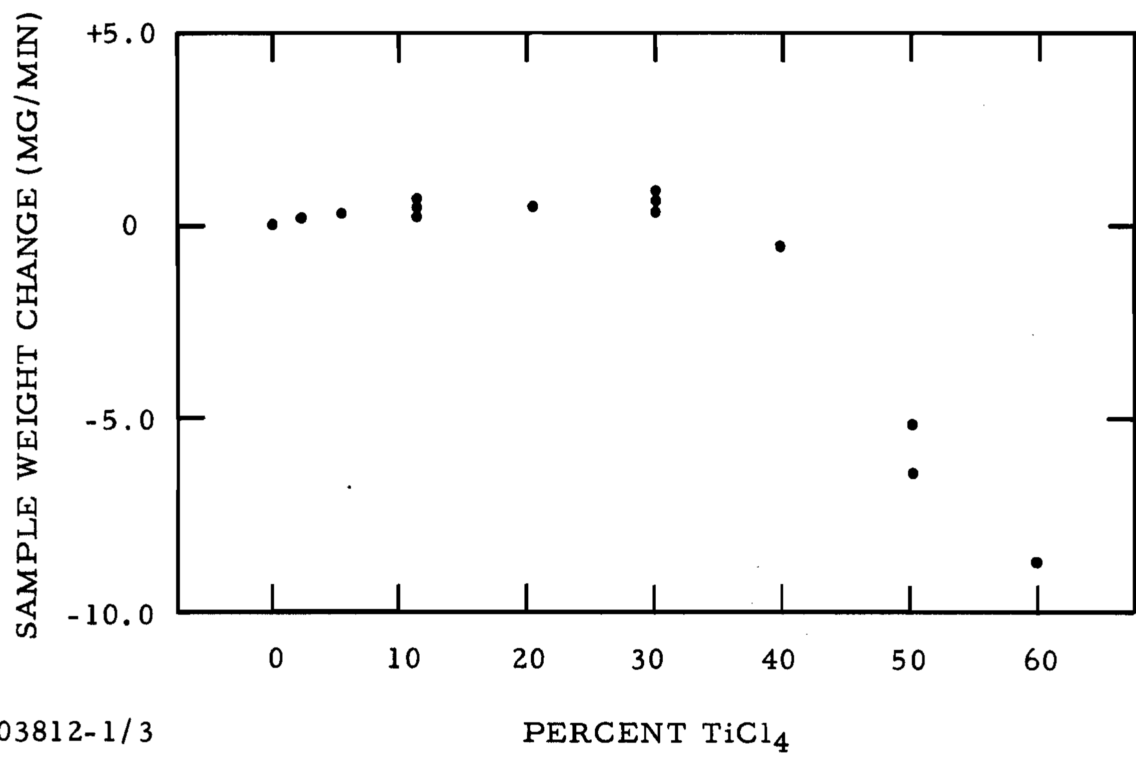


Figure 10 Sample Weight Change versus Percent $TiCl_4$

velocity over the sample and to increase contact time. Deposit uniformity also benefited by this change.

4. Preheating Reactive Gases

Calculations of the residence time of the gases in the sample region show that for average flows, contact time is extremely short. Assuming a reactive volume of gas around the sample to be about 2 cm^3, a flow rate of 2000 cm^3/min would yield a residence time of 0.06 second. (Such a condition may be demanded by the requirement of maintaining a low HCl pressure.) It is not likely that all the gas would approach thermal equilibrium in this time. By running the $CrCl_3$ furnace at various temperatures, the gas stream was preheated to the levels indicated in experiments 50 through 52 in Appendix A. However, this preheating had little effect.

After having outlined the general range of interest of the variables, a statistical cube design series of experiments was set up and carried out. Preliminary experiments had indicated that the major variables would be the temperature of the reactor, flow rate of gases, and temperature of the titanium chips used in prereducing the $TiCl_4$. The series listed in Table I consists in running the corners of a cube with a central point replication four times. The results of this type of experiment were analyzed by a multiple regression and correlation analysis and a factorial analysis of variance. For the statistical analysis, the rate of weight gain was used as the dependent variable. The results of this series are shown in the plots of Figure 11, where the dependent variable is plotted versus each independent variable.

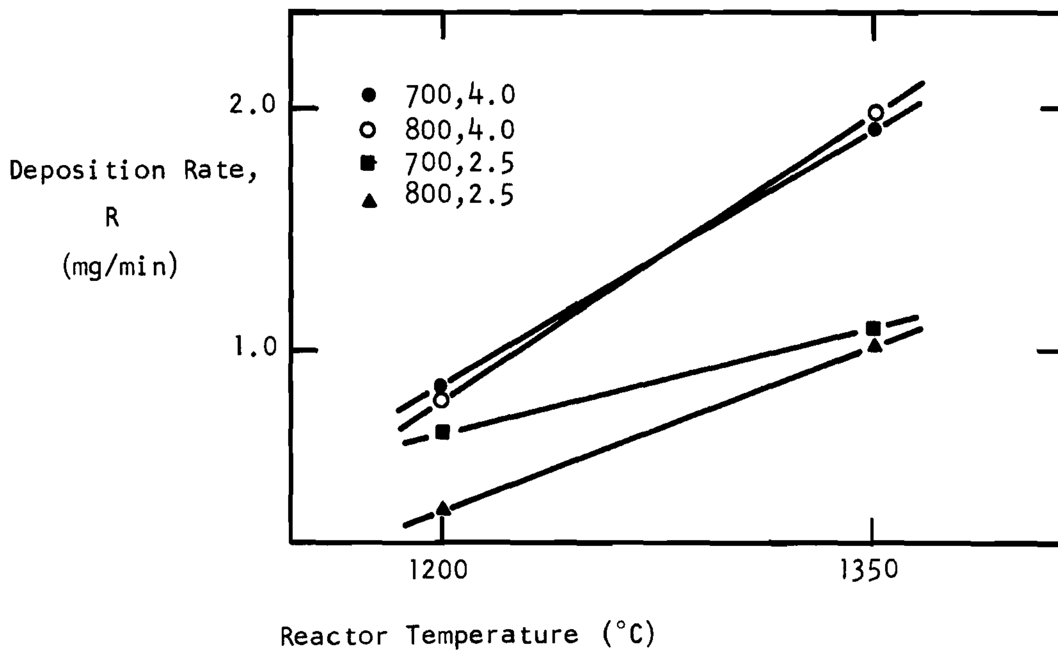
The titanium deposition results can be portrayed on a three-dimensional scale as shown in Figure 12 in addition to the two-dimensional plots of Figure 11. Since there are two independent variables and one dependent variable, the deposition rate is uniquely defined for specific temperatures and flow rates. Thus, the deposition rate can be represented as a plane in the temperature, flow rate, deposition rate, three-dimensional plot. That is, the deposition rate that will occur for any particular value of flow and reactor temperature

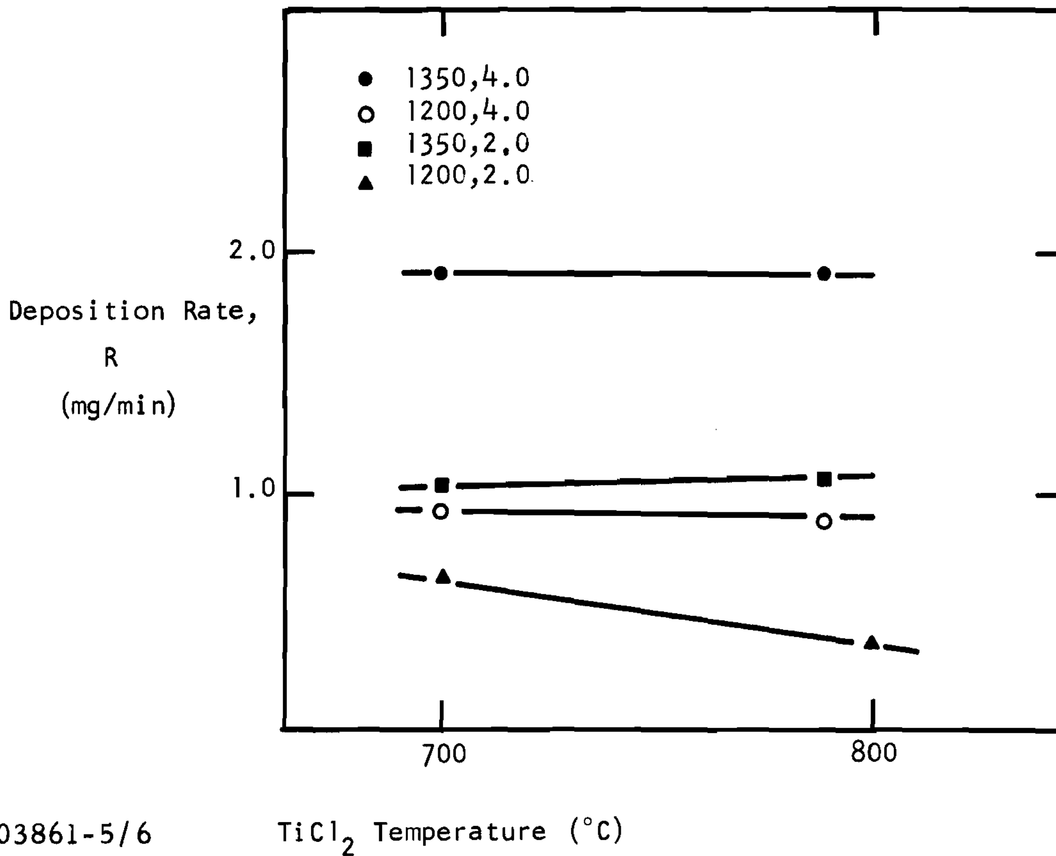
TABLE I

Plan for Titanium Deposition

Run No.	x_1	x_2	x_3	y
86	-1	1	1	1.91
87	-1	-1	-1	0.70
88	0	0	0	1.05
89	1	-1	-1	0.30
90	0	0	0	0.77
92	-1	-1	1	1.04
93	0	0	0	0.88
94	1	1	1	1.92
95	1	1	-1	0.78
96	1	-1	1	1.16
97	-1	1	-1	0.83
98	0	0	0	1.28

Variable	Level	-1	0	1
x_1	Prereduction furnace temperature (°C)	700	750	800
x_2	Flow rate (liters/min)	2.5	3.3	4.0
x_3	Reactor temperature (°C)	1200	1275	1350
y	Weight gain (mg/min)			





03861-5/6 $TiCl_2$ Temperature (°C)

Figure 11 Plots of Deposition Rate of Titanium from Statistical Plan

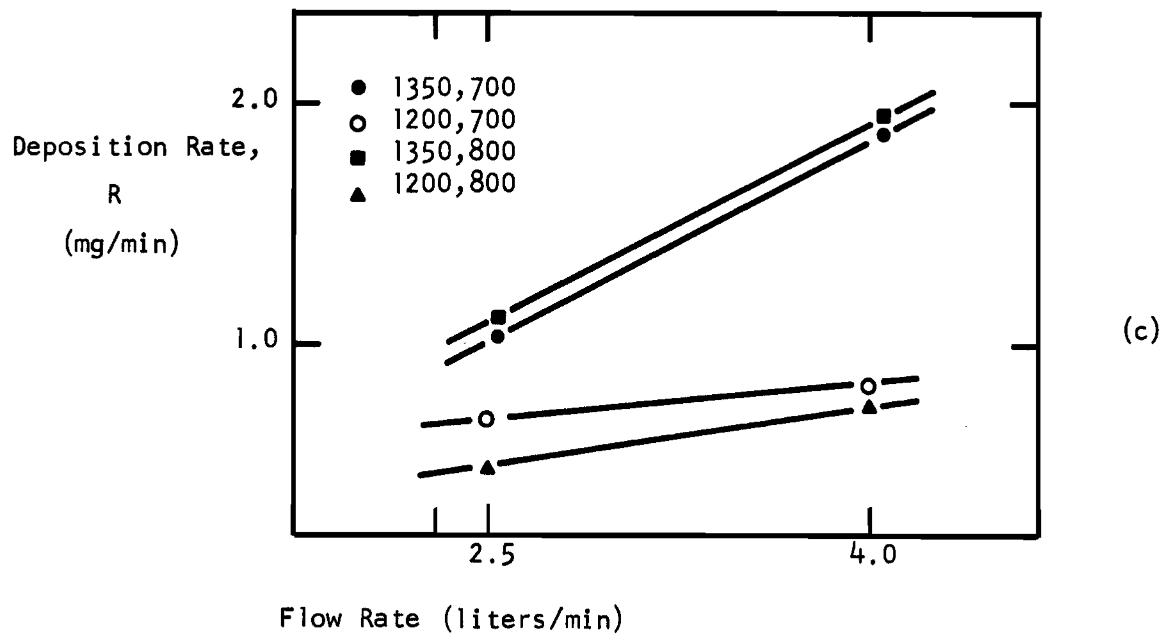


Figure 11 (Continued) Plots of Deposition Rate of Titanium from Statistical Plan

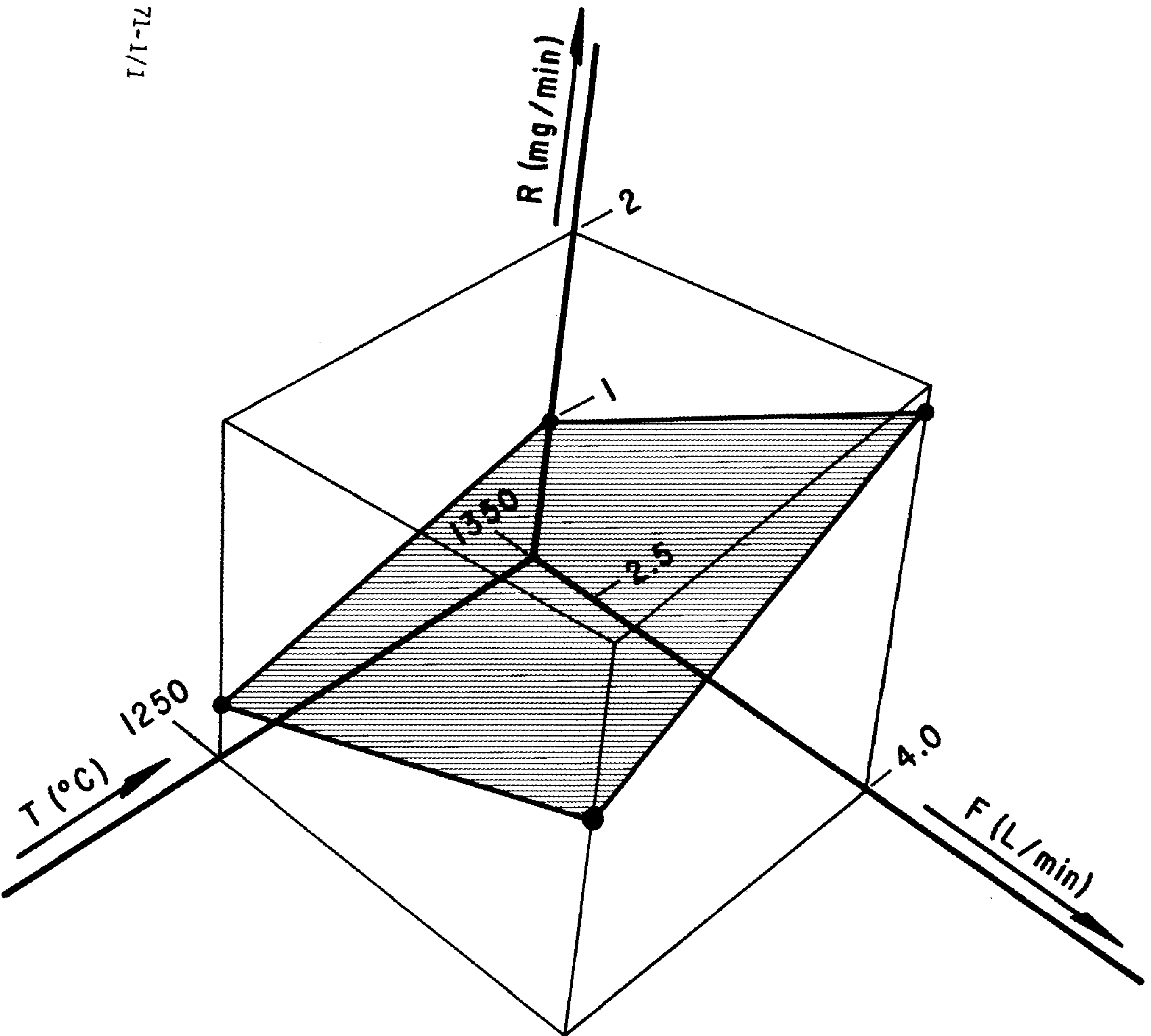


Figure 12 Three-Axis Plot of Titanium Deposition Data

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is the point intersecting the deposition plane. This then represents the response surface of the deposition rate as influenced by the flow and the reactor temperature.

Results of the multiple regression analysis are shown in Table II. The last column lists the value of F required to establish a level of confidence for the parameters. The 95% level was selected as the goal for this study. The variable x_1, which is the titanium tetrachloride prereduction temperature, is not a significant factor. The variable x_2, the total flow-rate of gases, is significant a levels greater than 95% for this study. The variable x_3, the reactor temperature, is likewise significant considerably beyond the 95% confidence level.

Table III shows the factorial anaysis of variance of the data for titanium depositions. Column 5 shows the F values required for the 95% confidence level. These figures agree with the multiple regression analysis. In addition, this table shows that these are the only variables significant in this model at this level and that no first-order interaction between the variables approaches the 95% level of confidence.

A photomicrograph of a typical titanium coating is shown in Figure 13. The grain structure of the coating is a continuation of the original substrate. This same structure is evident in the photograph of the titanium surface shown in Figure 14. Figure 15 illustrates the degree of edge coverage normally obtained in these depositions.

A possible aid in interpreting and understanding titanium deposition rate data is to plot the logarithm of the deposition rate versus 1/T in a typical Arrhenius plot, as shown in Figure 16. The data appear to group on two general lines, the upper one including the deposition at high flow rate, the lower one including the depositions at the lower flow rate. The slopes of these curves, which are related to the overall ΔH, heats of reaction of the deposition, differ only slightly. While the deviation is not large enough to be interpreted

TABLE II

Multiple Regression and Correlation Analysis of Titanium Depositions

Variable	Regression Coefficient	Observed T Value	T Value* for 95% Level
x_1	-8.00×10^{-4}	-0.48	2.36
x_2	0.37	3.36	2.36
x_3	5.70×10^{-3}	5.17	2.36

Intercept: -6.82

Standard Error of Estimate: 0.23

Multiple Correlation Coefficient: 0.9195

* Reference: "Introduction to Statistical Method", Ehrenfeld, S., and Littauer, S., (McGraw-Hill Book Co., New York, 1965).

TABLE III

Factorial Analysis of Variance for Titanium Depositions

NUMBER OF VARIABLES 3

NUMBER OF REPLICATES 1

VARIABLE	NO. OF LEVELS
1	2
2	2
3	2

GRAND MEAN 1.08000

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUMS OF SQUARES	F * VALUE	F ** REQUIRED
1	1	0.01280	<1	10.1
2	1	0.62720	8.65	
3	1	1.46205	20.2	
12	1	0.00720	<1	
13	1	0.04205	<1	
23	1	0.13005	1.79	
RESIDUAL	1	0.02645	<1	10.1
TOTAL	7	2.30780		

* $\hat{\sigma}^2 = 0.0725$

** For 95% confidence level

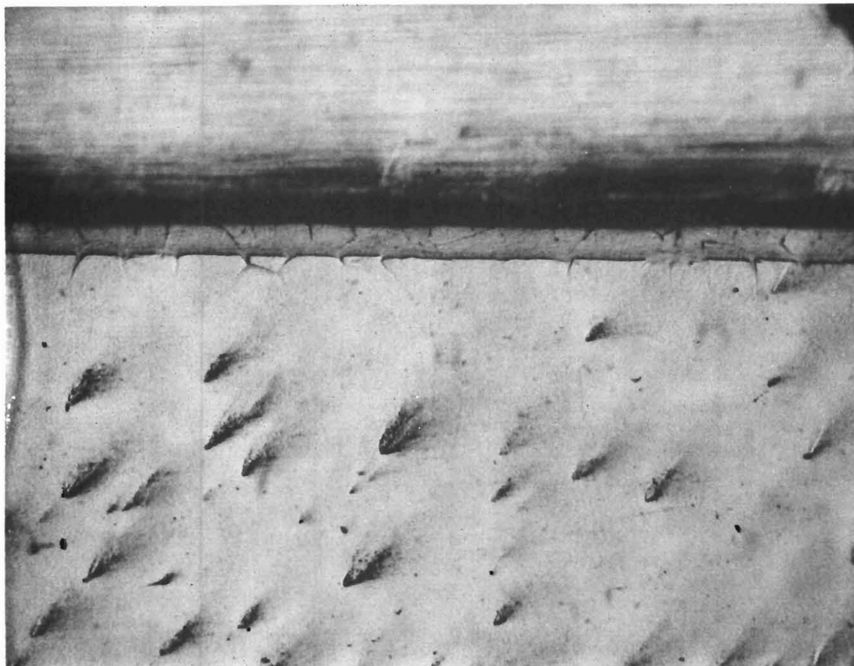


Figure 13 Coating of titanium on B-66 Alloy (x 265, unetched) Run 80, 17-micron titanium thickness

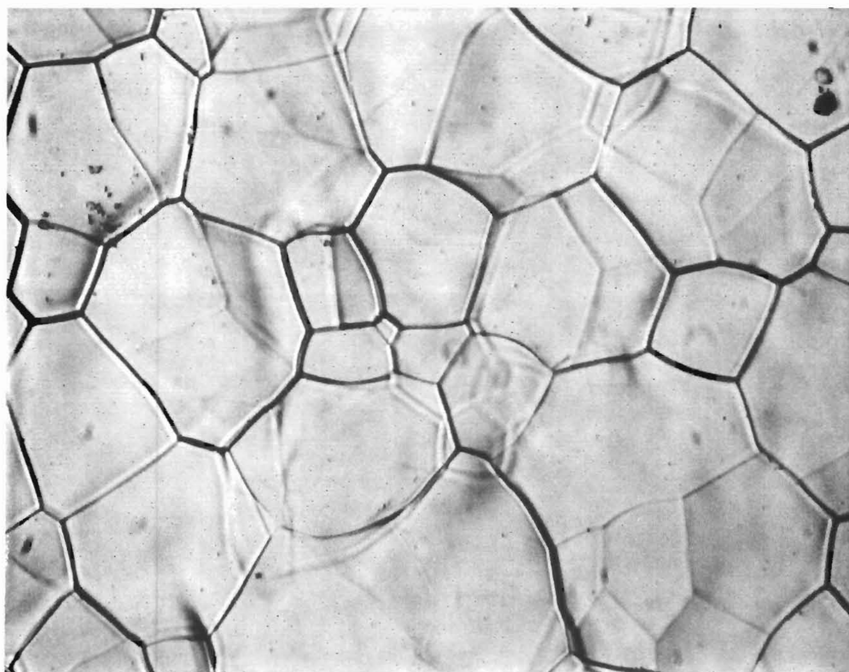


Figure 14 Surface of titanium "as deposited" on B-66 Alloy (x 500)

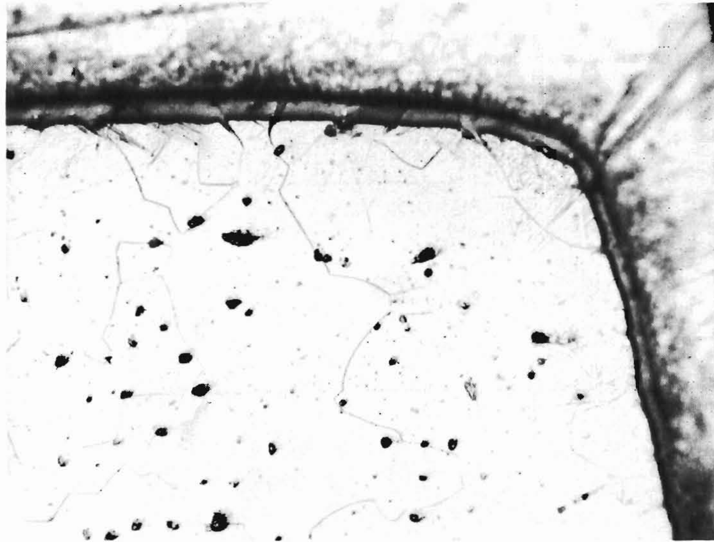


Figure 15 Titanium Deposited on B-66 Alloy Showing Coating Over Corner Section (X 135)

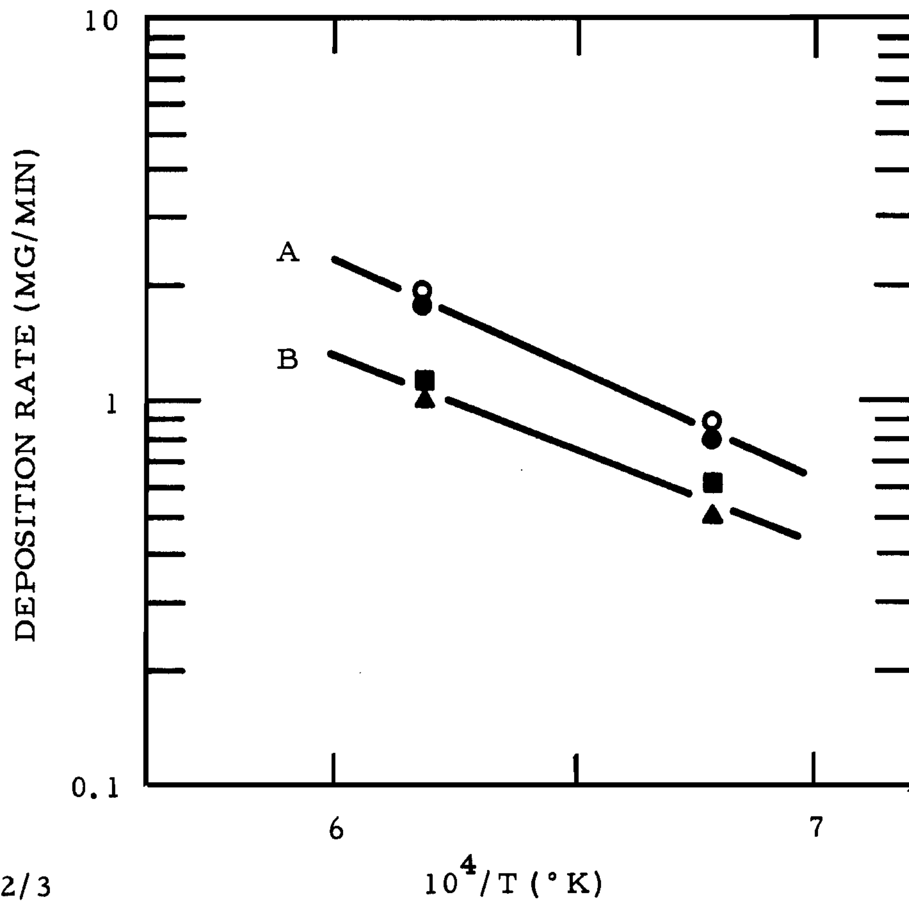


Figure 16 Arrhenius Plot of Titanium Deposition Data. Curve A includes data points for flow = 5.5, Curve B Flow = 2.5.

unequivocally, the lower energy of reaction at the lower flow rate is characteristic of other chemical vapor deposition experiments and is sometimes interpreted as indicating a high degree of diffusion control. The values of the energies obtained are approximately 24 and 22 kcal/mole for the upper and lower curve. In Table IV these two values are compared with known values for possible reactions which may occur during deposition. These data are consistent with previous work at Texas Instruments which included the total reduction at the sample. Present process studies include only the second reaction.

TABLE IV.

Activation Energies of Reactions Occurring During Titanium Depositions

Reaction	ΔH (kcal/mole)	Reference
$TiCl_4 + 2H_2 \rightarrow Ti + 4HCl$	(41)*	R. B. Byer and D. M. Mason, *Ind. Eng. Chem. Process Design and Dev.*, 2, 78 (1963)
	37	R. Bracken, "Chemical Vapor Deposition of Titanium," Texas Instruments Report
$TiCl_3 + 3/2H_2 \rightarrow Ti + 3HCl$	22-24	This work

* assuming $TiCl_3$ intermediate is limiting factor

B. Deposition of Chromium Metal

The attempt to obtain chromium chloride in the vapor state in reproducible and controllable fashion was initially based on the saturation of an argon gas stream passing through a bed of solid chromium trichloride ($CrCl_3$) at an elevated temperature. However, this process has several deficiencies. One is the difficulty in obtaining pure $CrCl_3$. The reaction of most chlorine-containing chemicals produces only chromium dichloride ($CrCl_2$) rather than the trichloride.

Only in the reaction of elemental chromium and chlorine is $CrCl_3$ produced. $CrCl_3$ is listed in literature as being relatively stable and so should sublime without decomposition. However, when the trichloride was held at elevated temperatures, it seemed to change to the dichloride. This indicates that the trichloride sublimes by decomposing to the tetrachloride (which is known to exist and has a relatively high vapor pressure at these temperatures), leaving a solid residue of the dichloride. Such an occurrence would gradually lower the effective pressure of chromium in the vapor state and make the source difficult to control over long periods of time.

The dichloride was considered as a source of chromium chloride vapor to be reduced at the sample. Problems inherent in using the dichloride are that it tends to absorb water and that it is a liquid at the temperature required for vaporization. A slight equipment modification was therefore necessary so that the dichloride could be used in the liquid form. The $CrCl_2$ was prepared by reaction of HCl gas and chromium metal. Following preparation, the chloride was purified by sublimation and loaded into the reservoir of the reactor system. This procedure apparently did not successfully eliminate all impurities because deposits obtained with this material were discolored, indicating the presence of oxides and/or nitrides. This process was very difficult to use, and results did not justify continuing with it.

An alternate way to form $CrCl_2$ is the in-situ reaction of HCl with chromium metal in the furnace used to heat the chloride reservoir in previous experiments. This procedure eliminates the need for handling hygroscopic chlorides. A gas supply was attached to introduce a small, controllable flow of HCl gas into the argon stream which flowed over the chromium metal, where the HCl reacted to generate $CrCl_2$ and hydrogen. This vapor flowed to the reaction zone, mixed with hydrogen, and impinged on the sample. The concentration of chromium was conveniently controlled by regulating the flow of the HCl gas. An added advantage was that the materials maintained in the furnace area were metallic and thus did not adsorb water. Purity of the gas stream should equal that of the reacting gases and in fact some impurities (such as nitrogen) may be gettered

out by the chromium metal. Deposits made using this source of $CrCl_2$ were shiny, and metallic in appearance, with no discoloration. A convenient, reliable control of the concentration of chromium in the gas phase was thus obtained.

As is often the case, obtaining uniform deposits was as difficult as controlling the reacting gases. When $CrCl_2$ is carried in an argon gas stream and mixed with hydrogen immediately above the sample, uniform mixing of the gases is essential for uniform deposits. For this reason, it was necessary to investigate the relation of jet design and behavior of reaction gas to the formation of uniform deposits. A device similar to an oil-burner nozzle, consisting of two concentric rings of nozzles, was settled on. Under the proper flow conditions and deposition rates this device produced a uniform deposit.

An initial series of the planned experiments was carried out as shown in Table V. When plotted, some of the values appeared anomalous in that the observed rates did not correlate with the expected values. Comparison of the rate data with the order in which the points were run revealed that deposition rates exceeded the expected values in runs immediately following the highest HCl gas flow. This was consistent throughout the plan. In addition, following the high HCl flow a small amount of smoke or vapor could be seen coming from the chromium reservoir, even when only argon was passing through the reservoir. It was obvious that in these cases more chromium chloride was formed in the reservoir than was carried out in the argon stream. Such a situation nullified most of the values taken at the high chloride points as well as values following these points or where chlorides were retained from previous experiments. In a re-run of the statistical plan this effect was eliminated by: (1) allowing additional time between runs, several minutes at least, during which argon was passed through the chromium reservoir; (2) increasing furnace temperature to increase vapor pressure and the amount of $CrCl_2$ vaporized; (3) decreasing maximum HCl flow passed over the chromium to less than the maximum amount that could be utilized.

The statistical plan for the chromium was re-run and the data analyzed by multiple regression and correlation analysis, and analysis of variance. The

TABLE V

Statistical Plan and Results for Chromium Deposition Investigation

Run No.	x_1	x_2	x_3	y
191	0	0	0	24.4
192	1	1	-1	7.0
193	-1	-1	-1	18.0
194	-1	-1	1	10.2
195	0	0	0	25.5
196	-1	1	-1	13.9
197	1	1	1	7.2
198	1	-1	1	53.7
199	0	0	0	16.1
200	-1	1	1	13.0
201	1	-1	-1	13.2
202	0	0	0	14.5
203	1	1	1	9.3

Variable	Level	-1	0	1
x_1	Reactor Temperature (°C)	1200	1265	1325
x_2	$CrCl_2$ Concentration (%)	0.3	0.6	0.9
x_3	Flow Rate (ℓ/min)	2.5	4	5.5
y	Weight Gain (mg)			

plan and results are given in Table VI. Results are displayed graphically in Figure 17. Figure 17(a) is a plot of the deposition rate as a function of the reactor temperature, Figure 17(b) shows the deposition rate versus the $CrCl_2$ concentration in the gase phase, and Figure 17(c) is deposition rate as a function of the total gas flow rate. In all cases, the higher levels for these variables yielded increased deposition rate. Figure 17(c), deposition rate as a function of chloride concentration, shows that the process was diffusion- or transport-limited, since deposition rate increased with increased flow. From an operational standpoint, this means that when processes work in these regions, flow must be carefully controlled to maintain control of deposition rate. The same comment obviously applies to temperature and concentration.

In titanium depositions flow rate was not as critical as temperature. This was particularly true of depositions at lower temperatures.

Chromium deposition data can also be represented in a three-dimensional plot, as in Figure 18. In this case, three of the variables are independent (temperature, flow, and concentration) so that the dependent variable (deposition rate) is not uniquely defined for any particular two values. However, deposition rate can be depicted as response surfaces, as shown in Figure 18, where the planes correspond to constant deposition rates. From this plot and the corresponding three-dimensional plot for titanium, experimental parameters were selected for the co-deposition of titanium and chromium which would yield alloys of various compositions. This, of course, is based on the assumption that the depositions will proceed independently, a factor shown later to be invalid in the range of experimental variables studied.

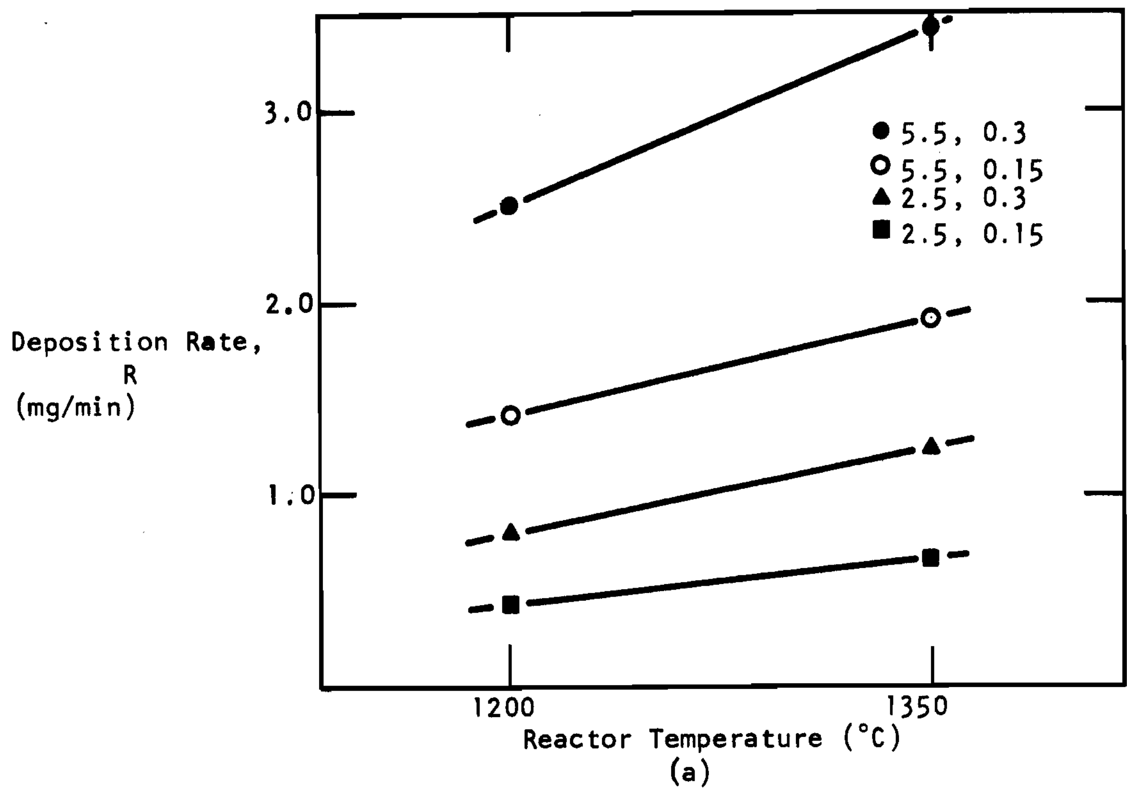
The chromium deposition plan was analyzed by multiple regression, as shown in Table VII, and also by an analysis of variance, as shown in Table VIII. Comparing the F values to that required for a 95% confidence level shows that all three independent variables are significant at this level. The correlation coefficient indicates a relatively good fit of the data by the equation.

TABLE VI

Second Statistical Plan and Results for Chromium Deposition Investigation

Run No.	x_1	x_2	x_3	y
358	0	0	0	0.98
359	-1	1	-1	0.81
360	-1	1	1	2.50
361	0	0	0	1.82
362	1	-1	-1	0.68
363	-1	-1	1	1.43
364	1	1	1	3.43
365	0	0	0	1.87
366	1	1	-1	1.23
367	1	-1	1	1.91
370	-1	-1	-1	0.42
372	0	0	0	1.54

Variable	Level	-1	0	1
x_1	Reactor Temperature (°C)	1200	1275	1350
x_2	$CrCl_2$ Concentration (Percent)	0.15	0.225	0.3
x_3	Flow Rate (ℓ/min)	2.5	4.0	5.5
y	Weight Gain (mg/min)			



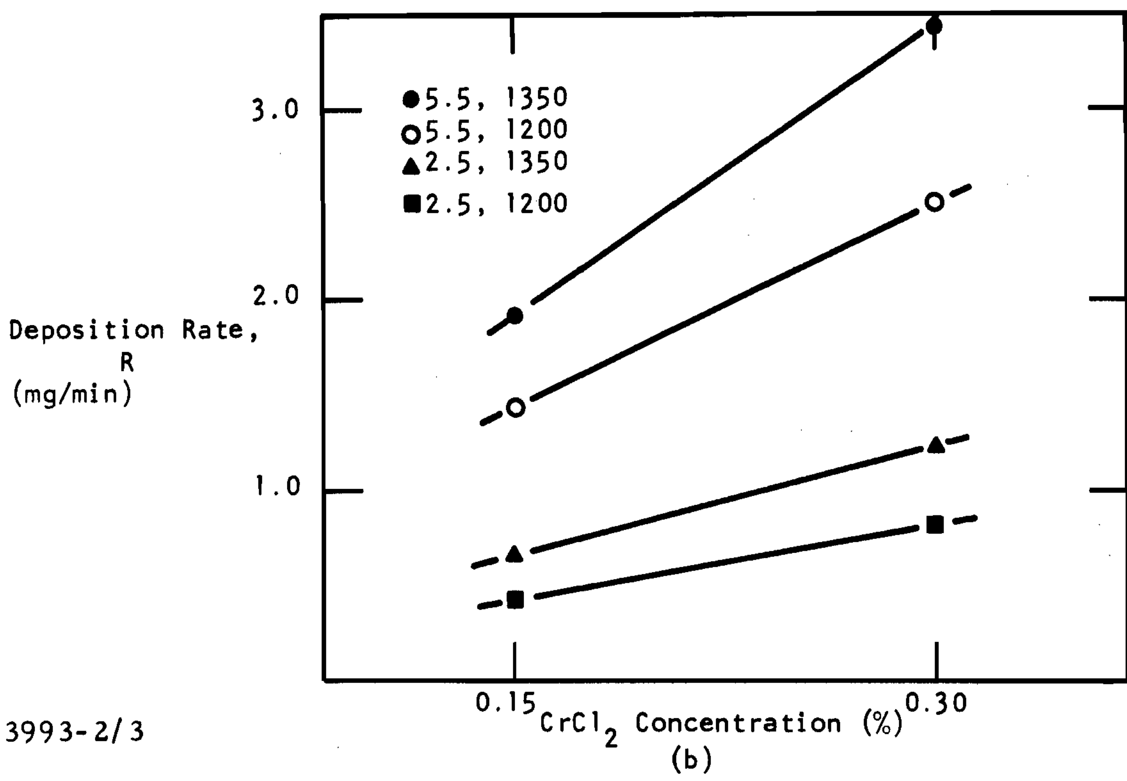


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Figure 17 Plots of Deposition Rate of Chromium from Statistical Plan

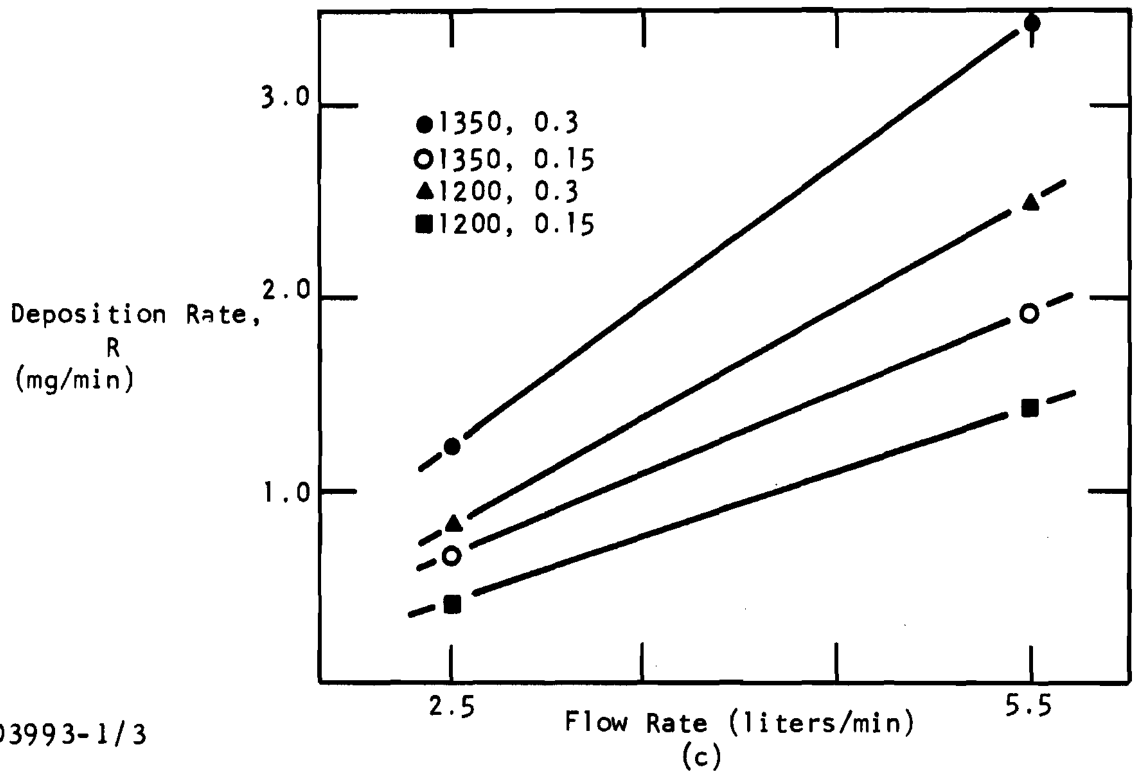
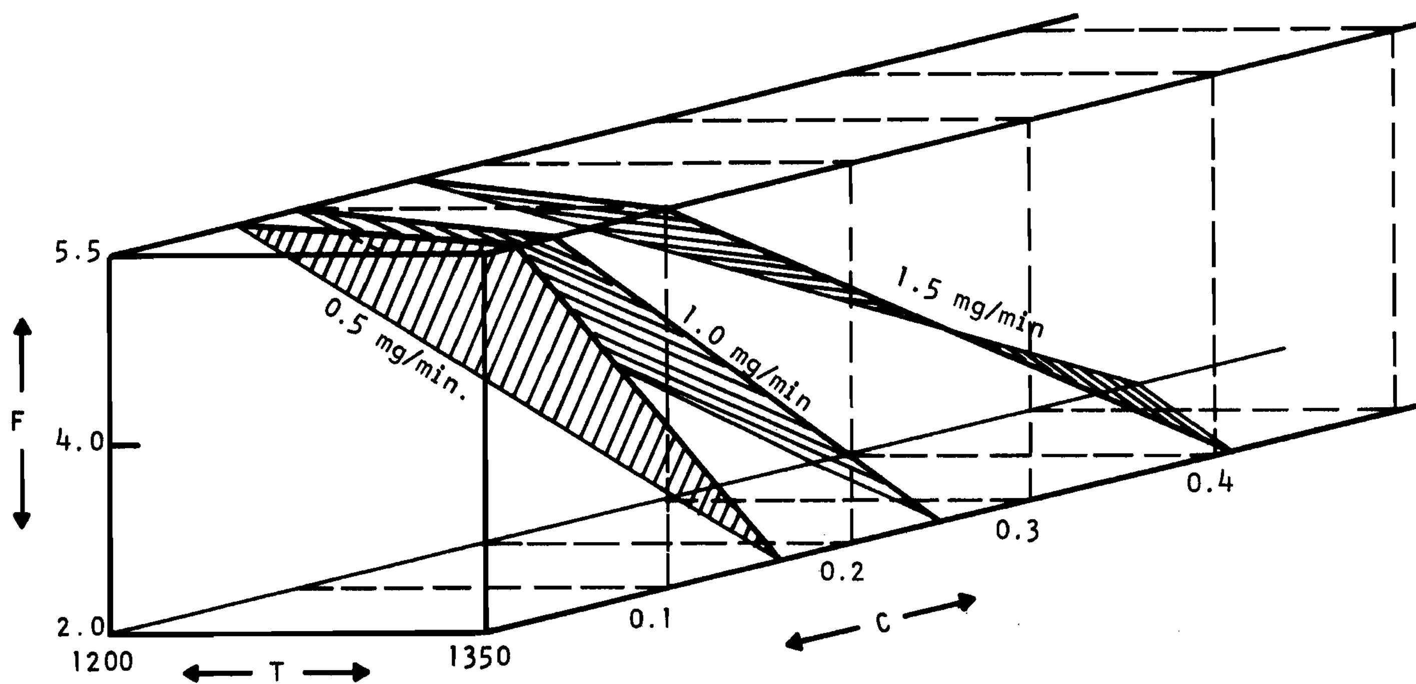


Figure 17 Plots of Deposition Rate of Chromium from Statistical Plan (continued)



03993-3/3

Figure 18 Planes of Constant Deposition Rate of Chromium

[F = Flow, liters/min; T = Reactor Temperature, °C; C = Concentration of $CrCl_2$, %.]

TABLE VII

Multiple Regression and Correlation Analysis of Chromium Depositions

Variable	Regression Coefficient	Observed T Value	T for 95% Level
x_1	3.483×10^{-3}	1.99	2.36
x_2	5.883	3.36	2.36
x_3	5.108×10^{-1}	5.84	2.36

Intercept: -6.255

Standard Error of Estimate: 0.371

Multiple Correlation Coefficient: 0.9359

TABLE VIII

Factorial Analysis of Variance for Chromium Depositions

NUMBER OF VARIABLES 3

NUMBER OF REPLICATES 1

VARIABLE	NO. OF LEVELS
1	2
2	2
3	2

GRAND MEAN 1.55125

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUMS OF SQUARES	F VALUE *	F REQUIRED **
1	1	0.54601	3.187	10.1
2	1	1.55761	9.093	
3	1	4.69711	27.278	
12	1	0.04651	0.271	
13	1	0.06661	0.388	
23	1	0.34031	1.987	
RESIDUAL	1	0.01051	0.061	10.1
TOTAL	7	7.26469		

* $\hat{\sigma}^2 = 0.1713$

** For 95% confidence level

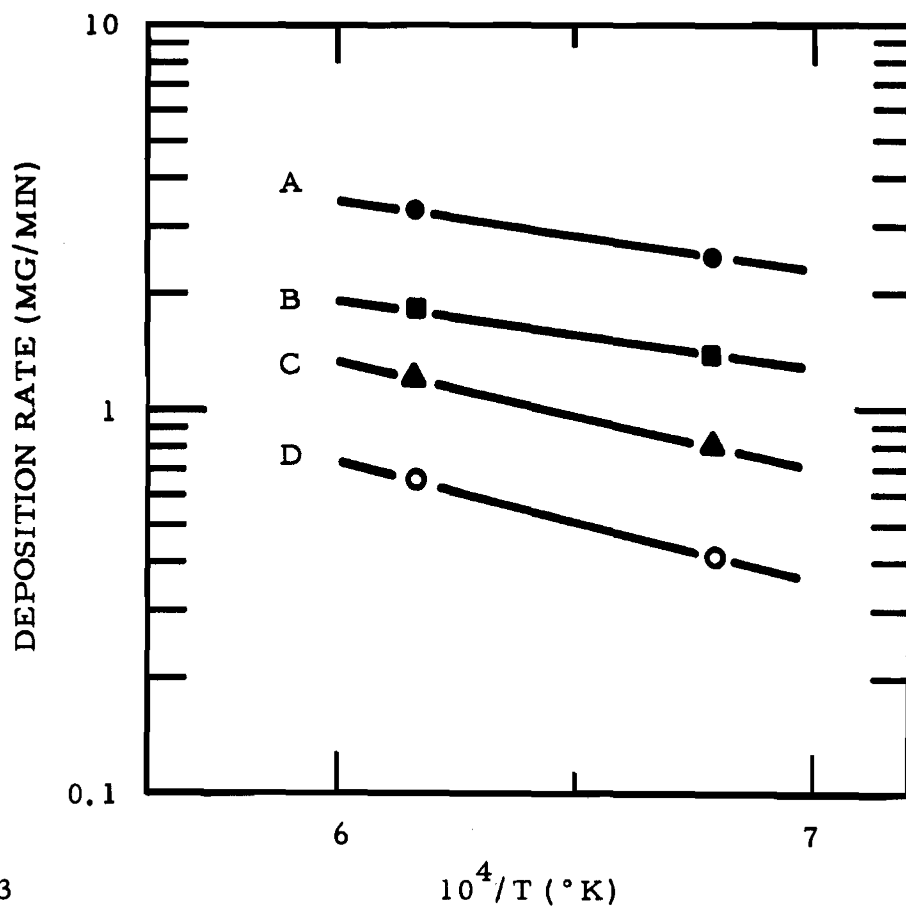
This series of the statistical plan produced chromium layers uniform over the sample, except for the one deposited at the highest rate. The high rate produced some nodular or needle growth, which is characteristic of a high supersaturation ratio.

Analysis of the deposition rate on an Arrhenius type plot is shown in Figure 19, where the logarithmic deposition rate is plotted versus the inverse of absolute temperature. The data fall on four lines, each correpsonding to a particular combination of concentration and flow rate. Such a division emphasizes the independence of the deposition parameters. As was the case for the titanium depositions, the slope of the lines for the two higher temperatures yields a highest heat of reaction value, 12 kcal/mole, while the slope for the lower flow rate curves corresponds to about 9 kcal/mole. The small values of ΔH from this data indicate that the deposition is primarily diffusion-controlled, since reaction-controlled processes usually have heats of reaction larger than these values.

C. Comparison of Titanium and Chromium Deposits

The major differences between the deposition data for chromium and titanium were accompanied by the significant difference in appearance of the two deposits. The surface of the as-deposited titanium material was shown in Figure 14. The grain structure of the substrate material could be seen clearly. The chromium deposits, as shown in Figure 20, however, did not show this grain structure, but appeared microcrystalline, with the many growth steps more typical of vapor-deposited material. These differences were significant, since further examination showed them to result from different reaction mechanisms. This difference has important implications for the deposition of chromium.

Examination of the chromium-columbium interface reveals narrow-intermetallic compound interlayer, which might have tended to prevent continued propagation of the substrate grains into the coating. An additional, or perhaps alternative, explanation was suggested by a series of photographs of the surface after only a very short deposition, as shown in Figure 21. This picture shows isolated nodules



04052-1/3

Figure 19 Arrhenius Plot of Chromium Deposition Data

Line	Flow	$CrCl_2$ Conc.
A	5.5	0.3
B	5.5	0.15
C	2.5	0.3
D	2.5	0.15

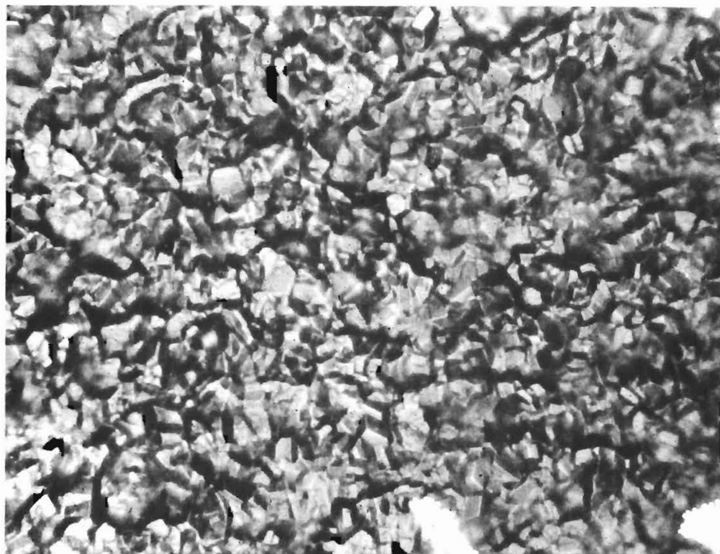


Figure 20 Surface of Chromium Deposited on Columbium (500X)

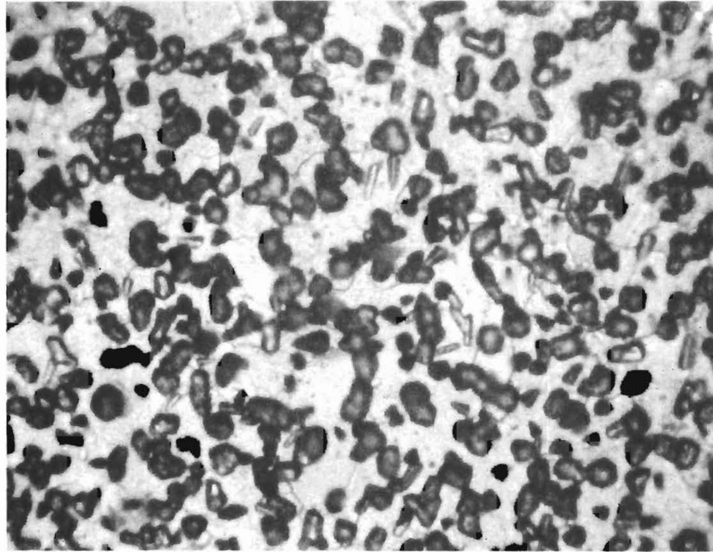


Figure 21 Columbium Surface After a Brief Deposition of Chromium (500X)

or particles which are crystallites growing on the surface of the columbium and yet leaving portions of the substrate bare. (It appears in this case that the crystallites are more concentrated in the grain boundary areas.) This may have occurred because the chromium chloride was very strongly adsorbed on chromium but only weakly adsorbed on columbium. Only when the crystals reach some critical size or population density do they contact and form a continuous coating.

However, many times when chromium coatings were grown relatively rapidly, voids occurred in the coating, as shown in Figure 22(a). Those grown at a somewhat slower rate, such as those shown in Figure 22(b), have fewer voids, though the possibility for voids still exists. The type of mechanism observed for titanium deposition is obviously to be preferred.

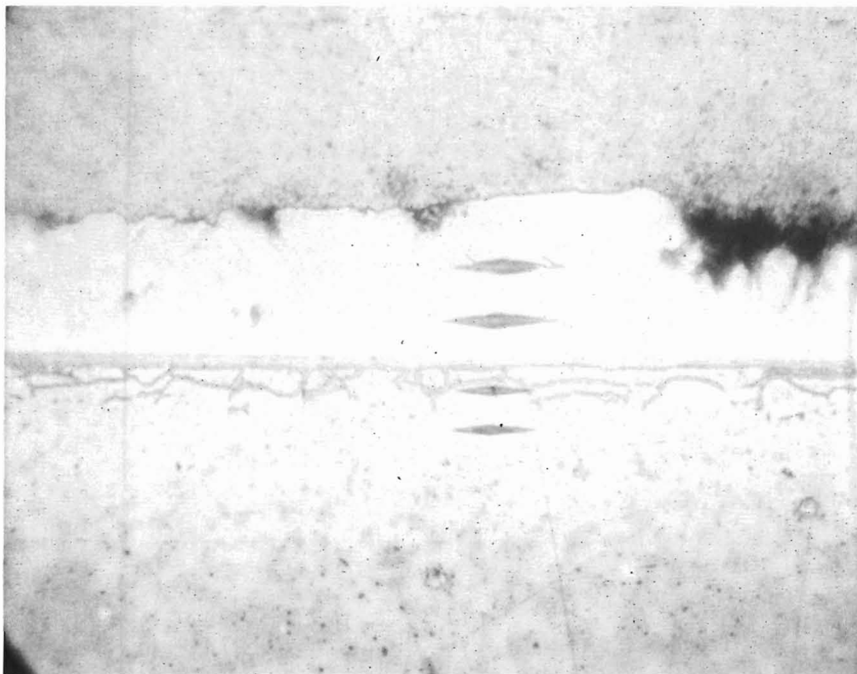
It should be noted, however, that the chromium depositions reported here were made at temperatures higher than necessary for deposition of chromium alone. These temperatures were used so the data obtained could be compared directly with titanium deposition data and could be used to estimate co-deposition rates. For deposition of chromium alone, temperatures 500 to 700° lower would be used, and the interaction between columbium and chromium would be lessened. It is probable that a different mechanism would control low-temperature depositions.

D. Alloy Codeposition Process Study

Several different processes were developed for codeposition of titanium and chromium in various alloy ratios. Since the various processes differed mainly in the manner by which the reducible metal chlorides were produced and transported to the reduction site, the major equipment modification on the coating reactor involved the chloride chamber.

Each process and the resulting deposits are discussed separately.

(a)



(b)

Figure 22 Cross Section of Chromium Deposits

1. Separate Production of Titanium and Chromium Chlorides

The processes which had been developed for depositing individual components were operated simultaneously. Reducible titanium chloride ($TiCl_3$) was formed from titanium metal immediately before the $TiCl_3$ was impinged on the substrate. Chromium chloride was produced by reacting HCl gas with chromium metal. Although these processes were adequate for depositing individual components, the coreduction process yielded deposits having several faults. Even though deposition concentrations, flows, and temperatures were varied over wide ranges, deposits generally lacked chemical and physical uniformity. This was probably because the two metal chlorides were fed through different nozzles and apparently were not uniformly mixed.

The deposits were characterized by a center portion of primarily titanium and an exterior portion consisting mainly of chromium. Deposition rates were approximately one-fourth those expected. This process failed to yield satisfactory coatings for the experimental conditions investigated. The chloride nozzles were clogged by metal deposits during deposition runs. The attempted use of this process is listed in Appendix A, runs 485 to 632.

Figure 23 shows a photomicrograph of the cross section of a coating prepared by this method. The coating is typical except that it is somewhat thicker than ordinary because of the higher hydrogen and HCl flows during this run. When etched, as shown in Figure 23, some grain structure could be observed in the coating, and interlayers were evident. An electron microprobe scan as shown in Figure 24 gave a qualitative concentration profile of the coating and indicated that the coating was mainly titanium and that some interdiffusion had occurred. The concentration of chromium was extremely low. The microhardness indicated two zones within the coating, which was in general relatively soft.

2. Production of Mixed Chlorides

a. From Chromium Metal and $TiCl_4$

Nonuniform mixing of the metal chlorides could be eliminated by producing them at the same place. One method was to prereduce the $TiCl_4$ with chromium metal (rather than titanium) in the chamber above the sample.

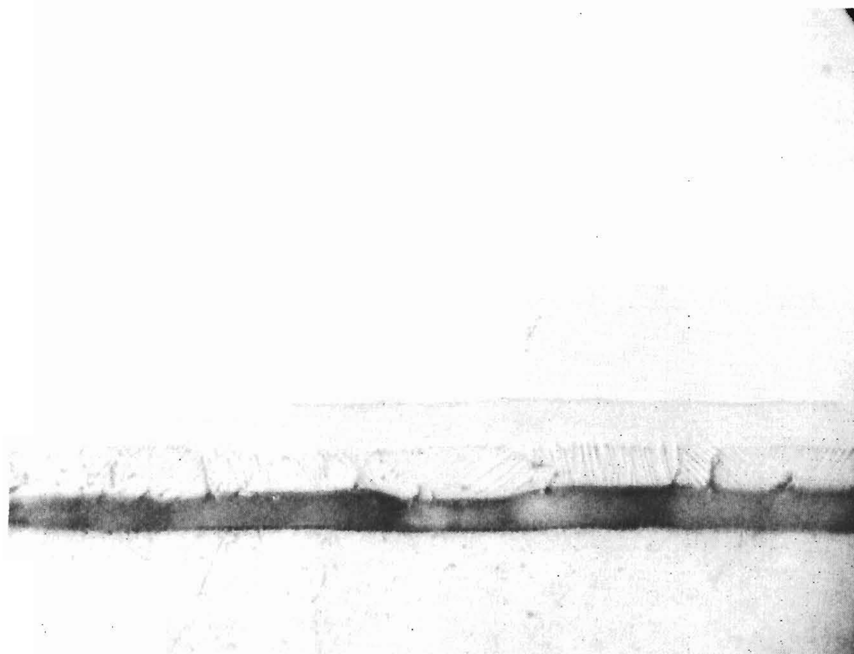


Figure 23 Codeposition of Titanium and Chromium
Run 630 (X500)

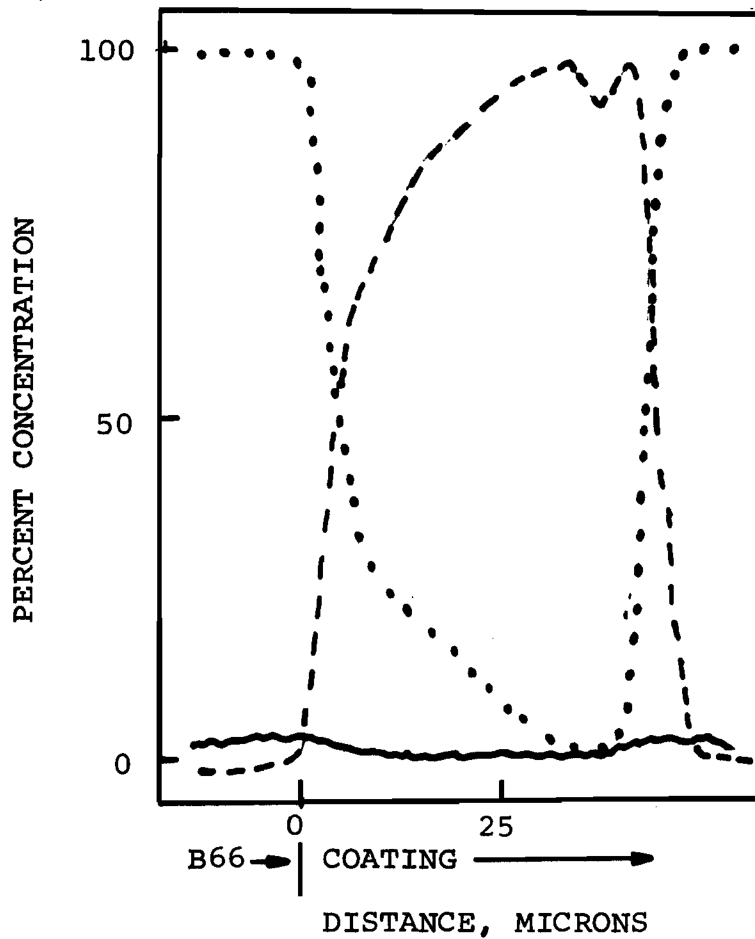


Figure 24 Electron Microprobe Profile Scan of Coating 630 Showing Qualitative Concentration

(...Cb, ---Cr, —Ti)

Temperature and concentrations were maintained at levels to keep the chlorides in the vapor state.

This process was more convenient operationally because only the $TiCl_4$ flow had to be controlled, instead of both HCl and $TiCl_4$. The possibility that unreacted HCl gas was available to inhibit subsequent reduction was also eliminated and resulted in higher deposition rates.

The reaction for the production of the chloride is

$$2TiCl_4(g) + Cr \longrightarrow 2TiCl_3(g) + CrCl_2(g),$$

which is thermodynamically favorable in the temperature range 750°C to 850°C. In the presence of excess chromium, as was the case where the $TiCl_4$ was passed through a bed of chromium, the Ti:Cr ratio in the gas phase was 2:1. Deposit composition could be varied by controlled alteration of this ratio. The temperature of deposition altered slightly the ratio of metals in the deposit, high temperatures favoring titanium reduction, low temperatures favoring more chromium.

Experiments utilizing this source of reducible chlorides were carried out in runs 633 to 667 in Appendix A. The deposition rate was reasonable (about 0.1 mil/min), and the coatings were uniform across the samples. The photomicrograph of a cross section, Figure 25, shows two zones in the coating and an even top surface. This particular coating was harder than normal, which indicated the presence of impurities. A microprobe scan of the cross section, Figure 26, indicated a variation in the titanium and chromium distribution in the coating and little interdiffusion with the substrate. The concentration of chromium was higher than the desired equimolar mixture, but the process worked well for high chromium alloys.

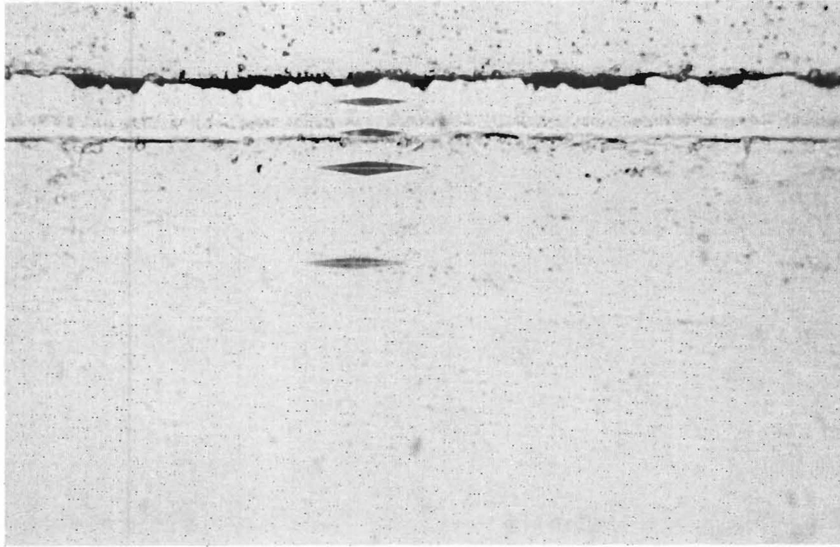


Figure 25 Codeposition of Titanium on Chromium, Run 643 (X500)

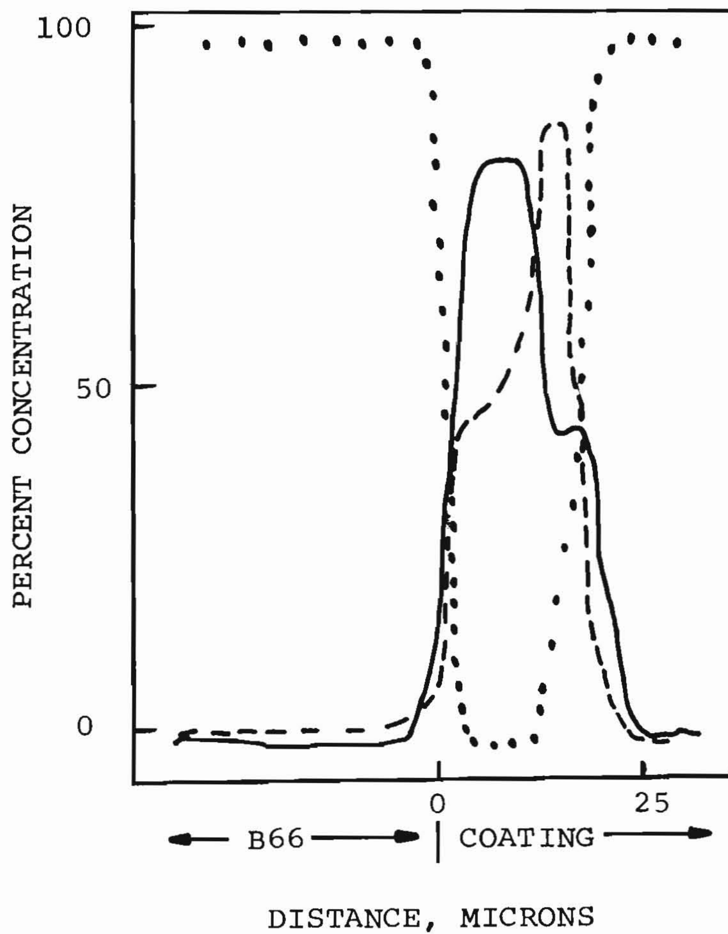


Figure 26 Electron Microprobe Profile Scan of Coating 643 Showing Qualitative Concentration

[...Cb, ---Cr(X1.5), —Ti(X1.5)]

b. From a Mixture of Titanium and Chromium Metal

The possibility of increasing the Ti:Cr ratio in the gaseous chloride stream above the 2:1 value of the previous process was investigated by use of a prereduction mixture of titanium and chromium chunks. More titanium should appear in the vapor because formation of titanium chlorides is thermodynamically favored over formation of chromium chloride. However, in long-term use of this method it might be difficult to maintain a constant-composition gas phase because of the preferential consumption of titanium.

Experiments utilizing this source of reducible chlorides were carried out as listed in runs 668 to 686, in Appendix A. Many of the deposition rates were rapid (about 0.2 mil/min). Coatings typical of this process are shown in Figures 27 and 28. The coating in Figure 27 was prepared from a chloride source in which the $TiCl_4$ was contacted first with titanium, then with chromium, in the chloride generation chamber. The alloys thus deposited contained a high proportion of titanium, as indicated by their appearance and structure and as substantiated by the qualitative electron microprobe scan of Figure 29. From this scan, chromium concentration was estimated at about 5%. Interaction with the substrate is minimal, and the coating is uniform and soft.

The coating in Figure 28 was prepared with a chloride source which contacted the $TiCl_4$ with chromium metal first and then with titanium metal. The coating formed rapidly and exhibited an unusually uniform surface for the high chromium concentration (about 95%) indicated by the microprobe scan of Figure 30. The absence of voids in the chromium and the absence of interaction with the substrate are notable features.

This coating process and its two variations yielded interesting results but were apparently not satisfactory for depositing alloys of nearly equal concentrations of titanium and chromium.

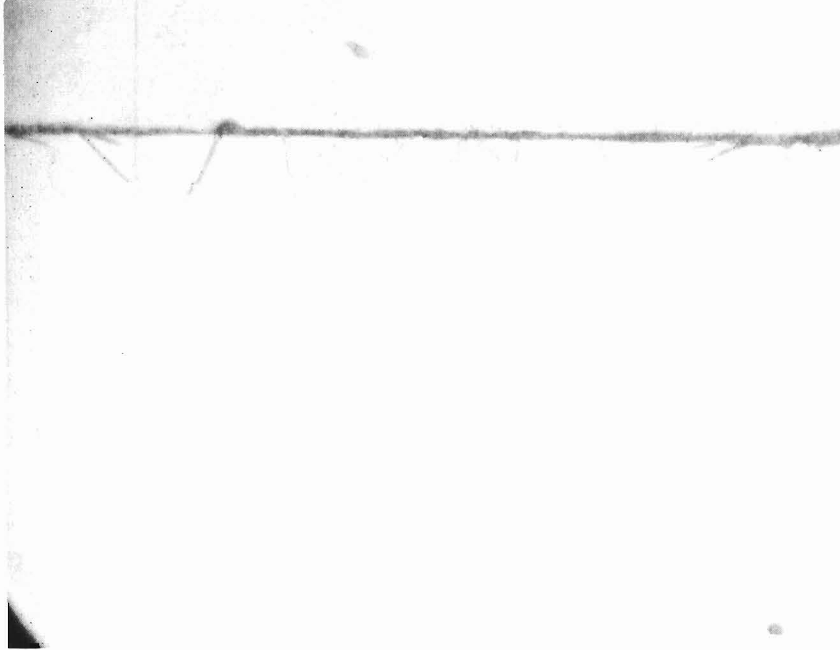


Figure 27 Codeposition of Titanium and Chromium, Run 672 (X500)

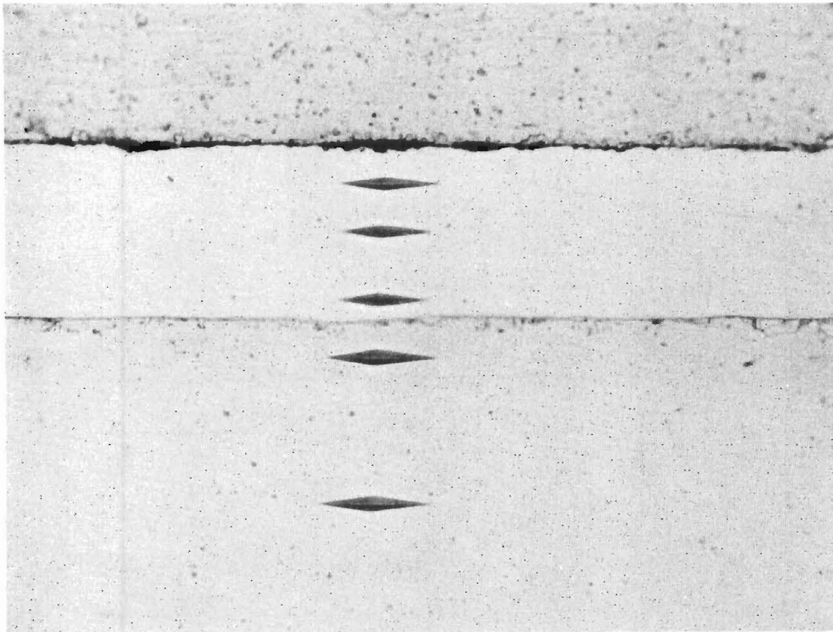


Figure 28 Codeposition of Titanium and Chromium, Run 686 (X500)

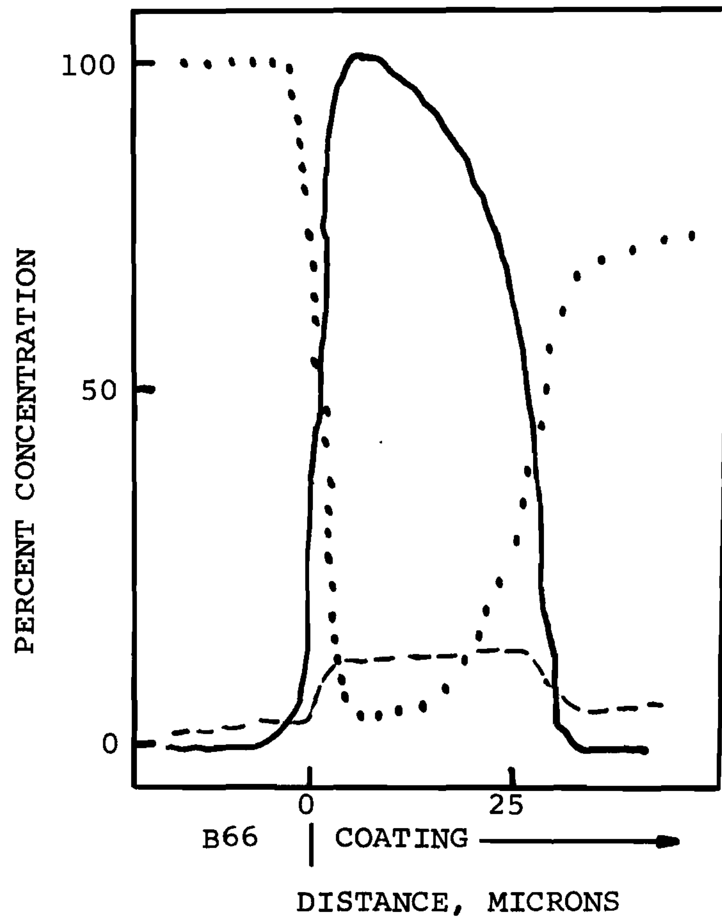


Figure 29 Electron Microprobe Scan of Coating 672 Showing Qualitative Concentration

(...Cb, ---Cr, —Ti)

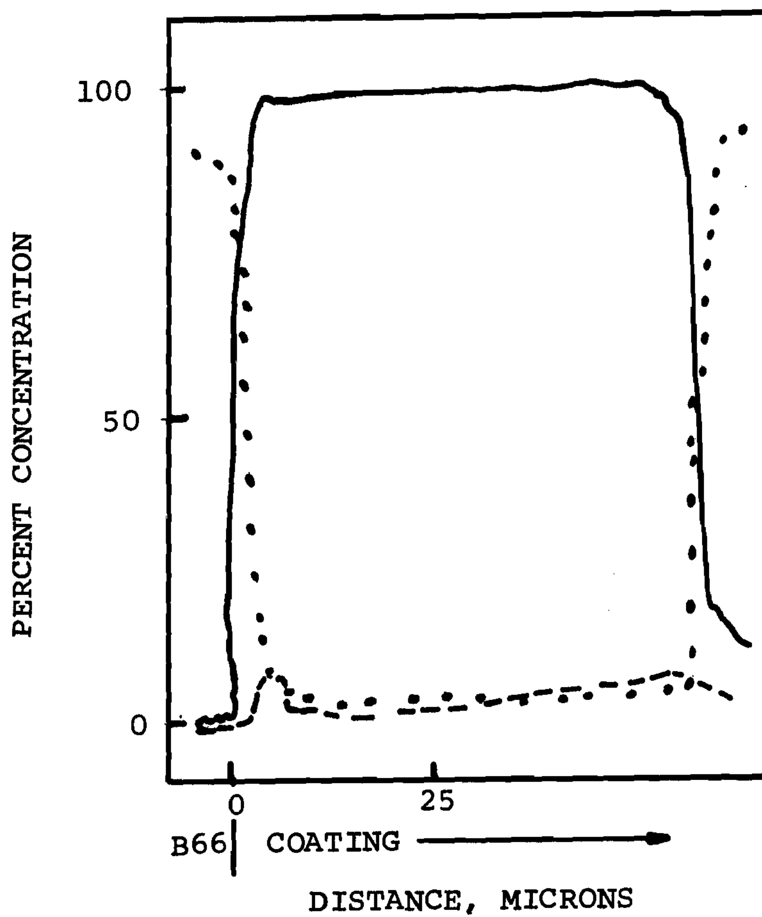


Figure 30 Microprobe Profile Scan of Coating 686 Showing Qualitative Concentration

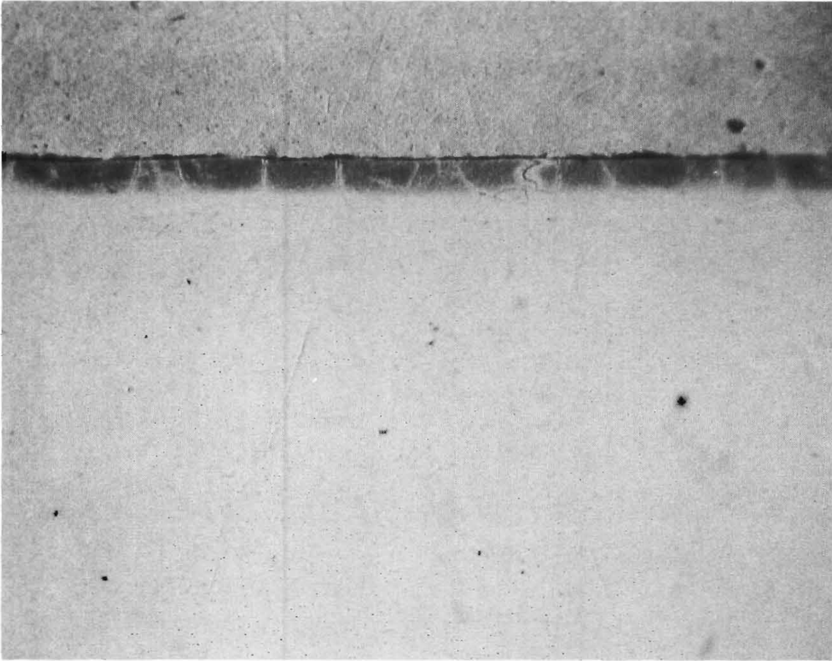
(...Cb, ---Cr, —Ti)

c. From Titanium-Chromium Alloys

The previous methods for producing mixed titanium and chromium chlorides yielded deposits containing a high concentration of one of the elements. Obtaining deposits having ratios closer to the midrange of the binary system requires a different ratio of titanium and chromium chlorides in the gas phase. Reaction of $TiCl_4$ with alloyed titanium-chromium might serve to control this ratio. This method, if workable, could be conveniently used to include additional elements, such as vanadium, to form alloys of three or more components. Alloys of 60% Cr-40% Ti and 25% Cr-75% Ti obtained from Oregon Metallurgical Corporation were installed in the chloride generation chamber and depositions made.

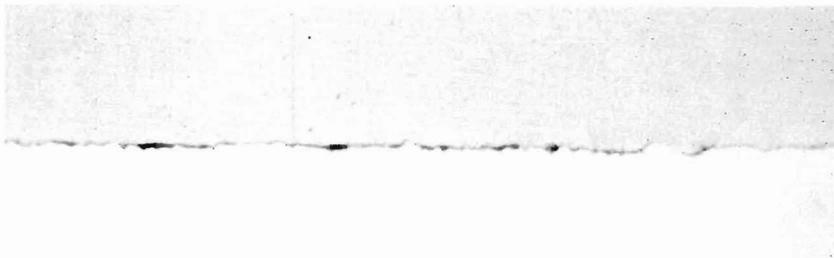
Runs 778 to 781 of Appendix A utilized the 25% Cr-75% Ti alloy. Coating appearance and uniformity were good, and the surface appeared similar to titanium surfaces. Figure 31 is a photomicrograph of a cross section of a coating made in this manner. The deposition rate was slower than from pure metal chloride sources. Electron microprobe analysis (discussed later in this section) showed that these deposits were nominally in the range desired. This method thus demonstrated the capability of yielding mid-range composition alloys of Ti-Cr. The lowered deposition rate and slight variation in the composition occurring in the coating cross section may not be typical of this method in general and could be eliminated or overcome with additional experimentation.

Runs 782 to 788 in Appendix A utilized the 60% Cr - 40% Ti alloy as a chloride source, and again the deposition rate was slower than it was with the elemental (dual chamber) source. The coating surface had the "alloy" appearance, and uniformity was fair. Figure 32 is a photomicrograph of the coating cross section. Electron microprobe analysis showed the deposits were primarily chromium. This method of generating chloride would therefore be satisfactory for forming alloys of high chromium content rather than alloys in the mid-range of composition.



780
500 X

Figure 31 Ti-Cr Coating Prepared with 75% Ti - 25% Cr Alloy Chloride Source



788
500 X

Figure 32 Ti-Cr Coating Prepared with 40% Ti - 60% Cr Alloy Chloride Source

Samples from the alloy chloride source depositions were also analyzed. The 60% Cr-40% Ti alloy gave a coating of the composition shown in Figure 33. Since the chromium content is above the desired value for this study, this particular method is not preferred. Utilizing the 25% Cr-75% Ti alloy in the chloride generation chamber yielded deposits of the composition sketched. in Figure 34. These deposits are in the desired range for this study. A gradation in composition is noted for this sample, though this trend is not necessarily typical of the method. Since this process yielded coatings of the desired composition, it could be used for formation of the Ti-Cr-Si coating.

d. From Separated Titanium and Chromium

Mixed titanium and chromium chlorides were also generated over a wide range of Ti:Cr ratios by isolating the two metals in separate compartments in the chloride generation chamber (See Figure 35). The incoming $TiCl_4$, carried in an argon stream, was divided in the desired ratio by varying the size of the openings into the compartments. Gases exiting from the compartments were fed into a common line and impinged on the sample through a single jet. As with other methods of chloride generation, the hydrogen for reduction is mixed with the chlorides in the space between the jet and the sample surface.

Experiments using this dual-compartment chloride-generation process were carried out as listed in runs 698 to 759, Appendix A. After some preliminary depositions, results were consistent and in the general range desired, so it was feasible to carry out a statistical plan series. The plan used was similar to the individual component deposition plans, and the independent variables were also similar to the previous plans, i.e., reactor temperature, flow of gases, and flow of titanium chloride (which was also proportional to the concentration of total chlorides in the gas phase). An additional process variable which could be studied is the proportion of $TiCl_4$ passed over the metals in the chloride generation chamber. This would require only a change in the design of the chloride chamber. The ranges of the variables were approximately the same as in previous plans.

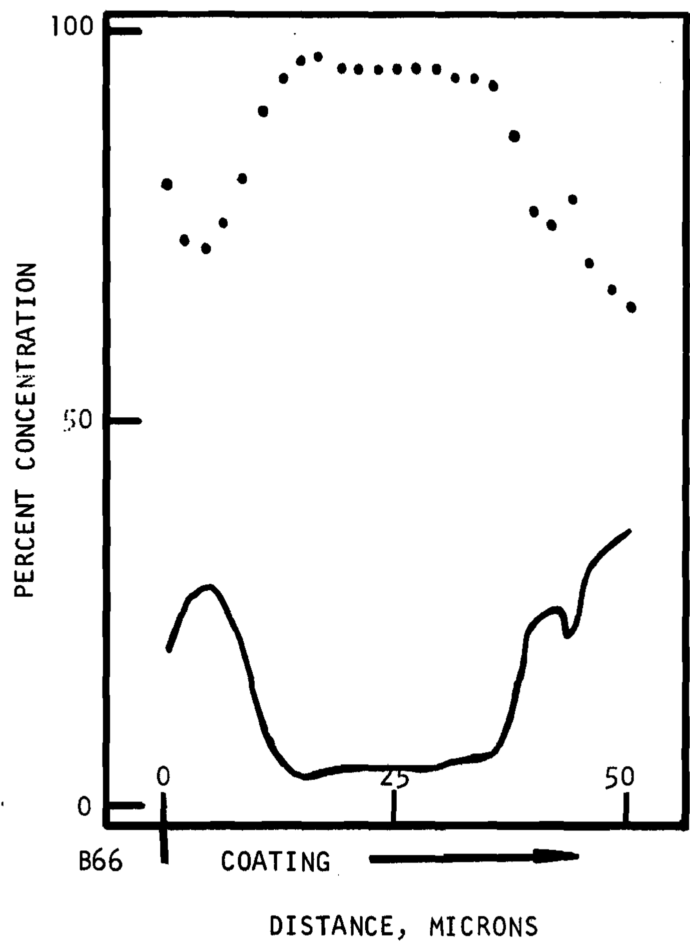


Figure 33 Electron Microprobe Profile Scan of Coating 788
Showing Qualitative Concentration (—— Ti, ... Cr)

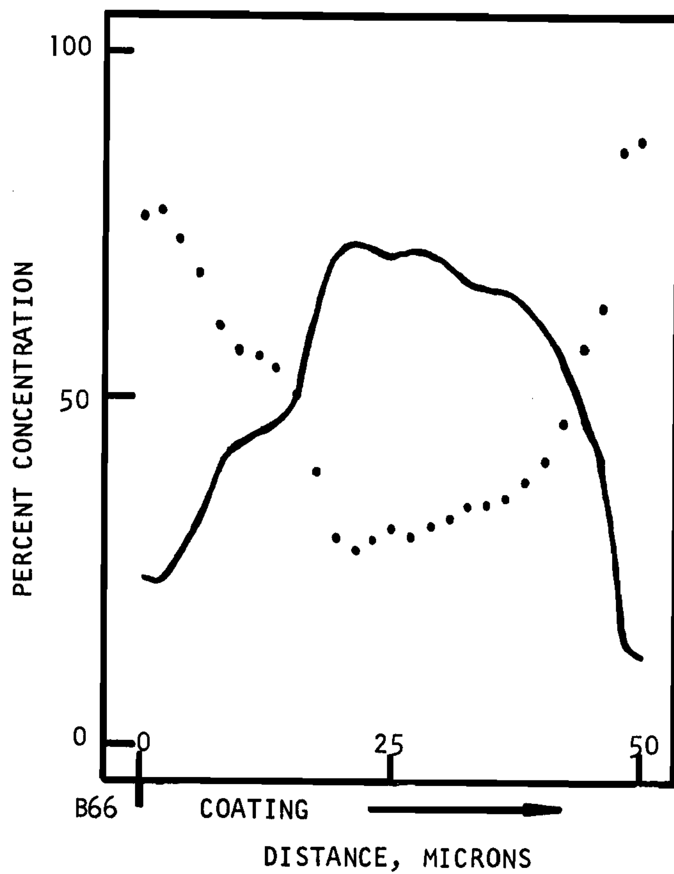


Figure 34 Electron Microprobe Profile Scan of Coating 780 Showing Qualitative Concentration (—— Ti, ... Cr)

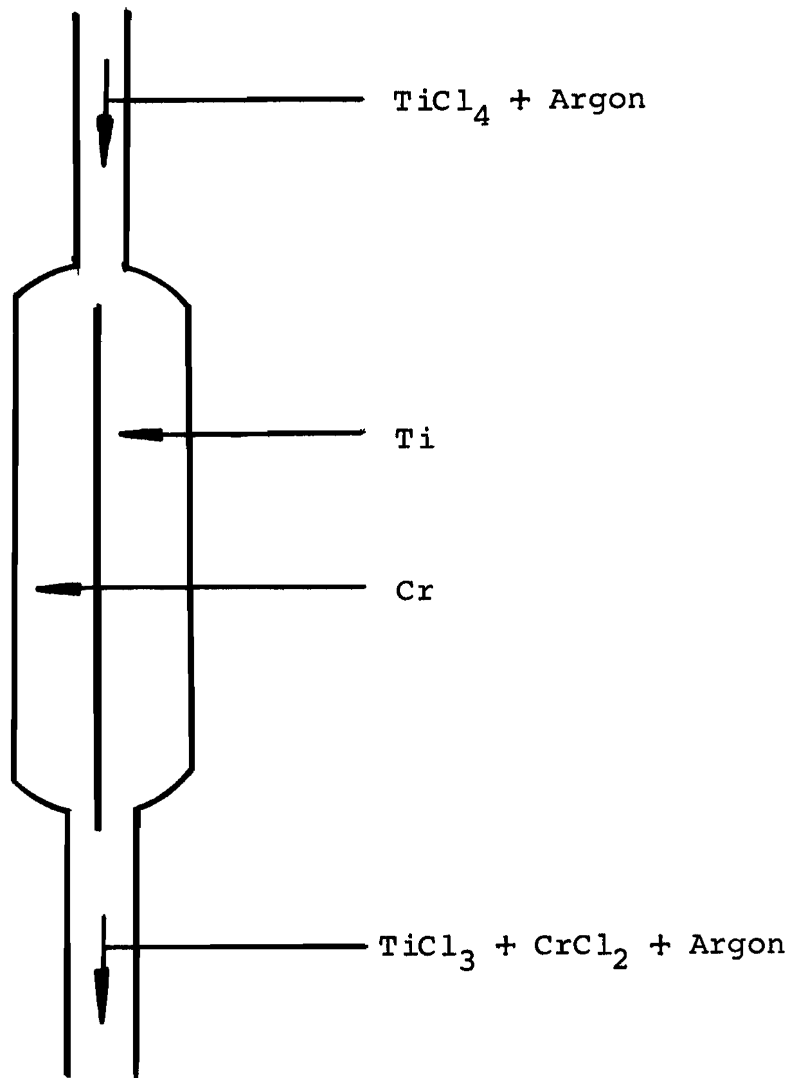


Figure 35 Sketch of Two-Compartment Chloride Generating Chamber

The runs in this plan and the resulting deposition rates are listed in Table IX.

Deposition rates from this plan are plotted as a function of the independent variables in Figure 36(a), (b), (c), and (d). All independent variables contributed positively and about equally to the deposition rate for the higher levels of the variables.

A multiple regression and correlation analysis of the data was run, and the results are given in Table X. The correlation coefficient showed a relatively good fit by this equation, though it was lower than might be expected from the apparent consistency of the plotted data. This could indicate that the linear model is not the best choice and that others could be found to give fit. The indicated F values in the table for a 95% confidence level show these variables are significant at this level.

The analysis of variance results are given in Table XI. They also indicate that the variables selected are significant at the 95% level and that the amount of interaction between variables is not significant at this level.

Figure 37 shows photomicrographs of cross sections of a portion of the plan. In general, coatings are of good quality and differ primarily in hardness and evenness of the top surface. Figure 38 is a photograph of a surface typical of the deposits of this series. It was quite different from the analogous photographs of titanium and chromium shown in previous reports. Codeposition was apparently controlled by a reaction mechanism different from that controlling single-element deposition, but the data are insufficient to precisely define this mechanism.

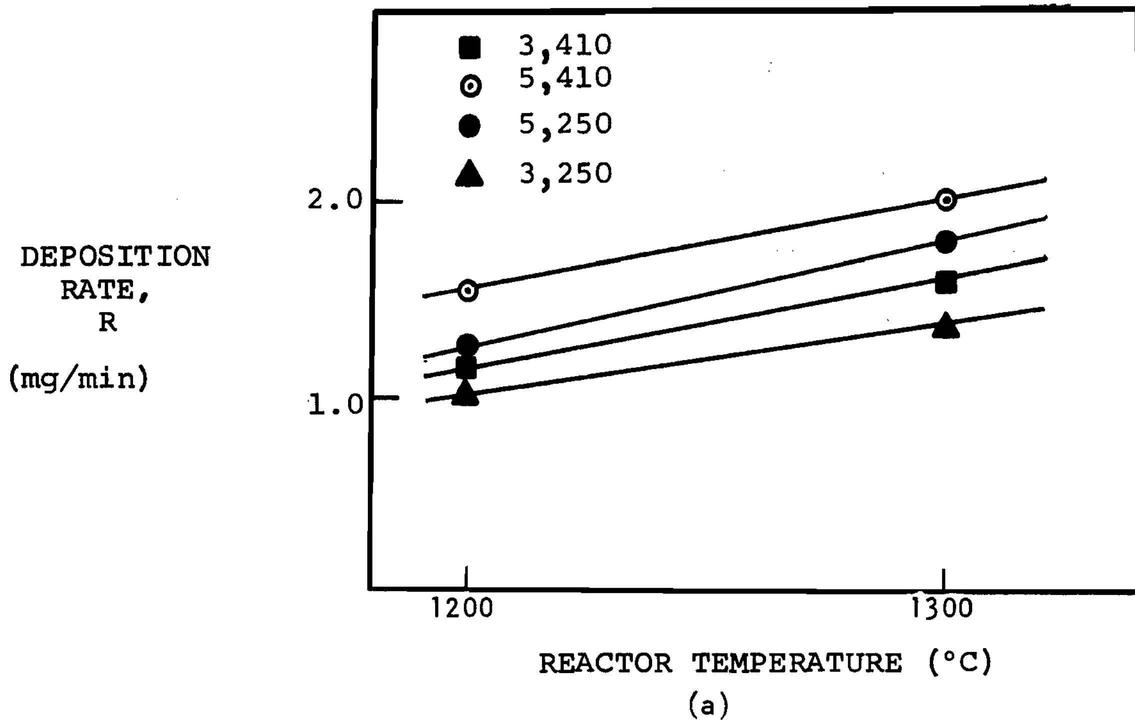
The electron beam microprobe was used to semiquantitatively analyze cross-sectioned samples from the statistical plan utilizing the dual chamber chloride source. Concentration counts for the individual elements were taken at 1-micron intervals. The profiles are plotted in Figure 39.

TABLE IX

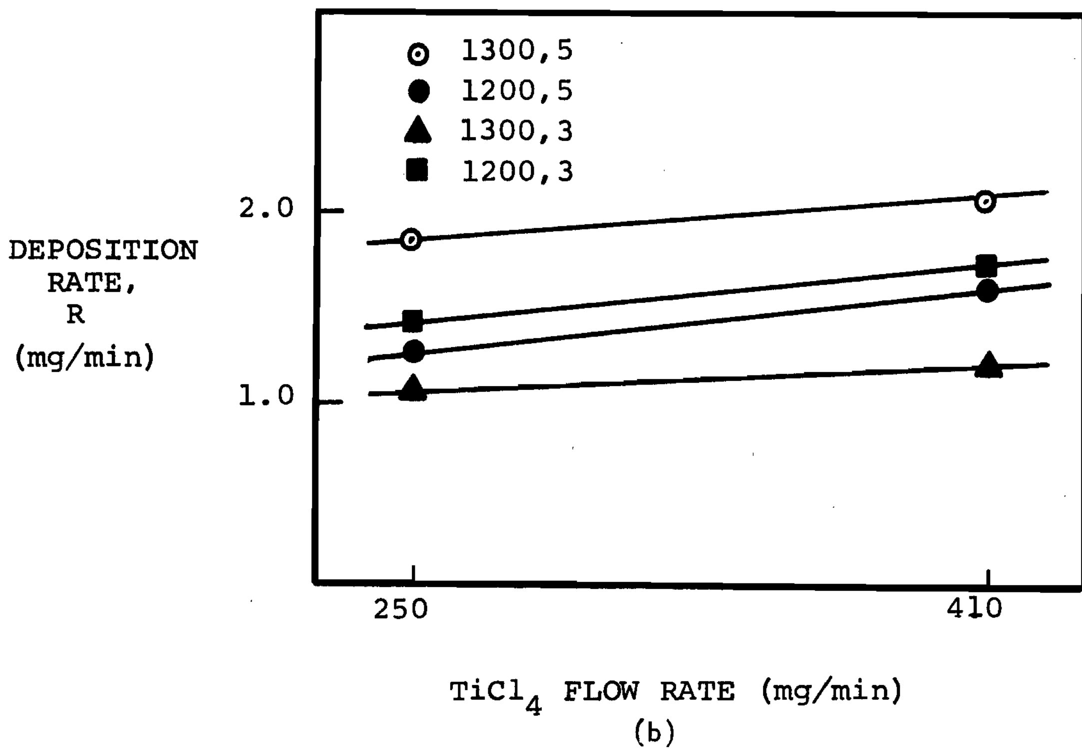
Plan and Results for Cr-Ti Alloy Depositions

Run No.	x_1	x_2	x_3	y
756	0	0	0	1.73
734	-1	1	1	1.63
735	-1	-1	-1	1.03
736	1	-1	-1	1.27
740	0	0	0	1.40
741	-1	1	-1	1.40
742	1	1	1	2.04
743	0	0	0	1.58
744	1	-1	1	1.57
759	1	1	-1	1.84
750	-1	-1	1	1.19
748	0	0	0	1.70

Variable	Level	-1	0	1
x_1	H_2 Flow Rate (ℓ/min)	3	4	5
x_2	Reactor Temperature (°C)	1200	1250	1300
x_3	$TiCl_4$ Flow Rate (mg/min)	250	330	410
y	Weight Gain (mg/min)			



(a)



(b)

Figure 36 Deposition Rate versus Process Parameter

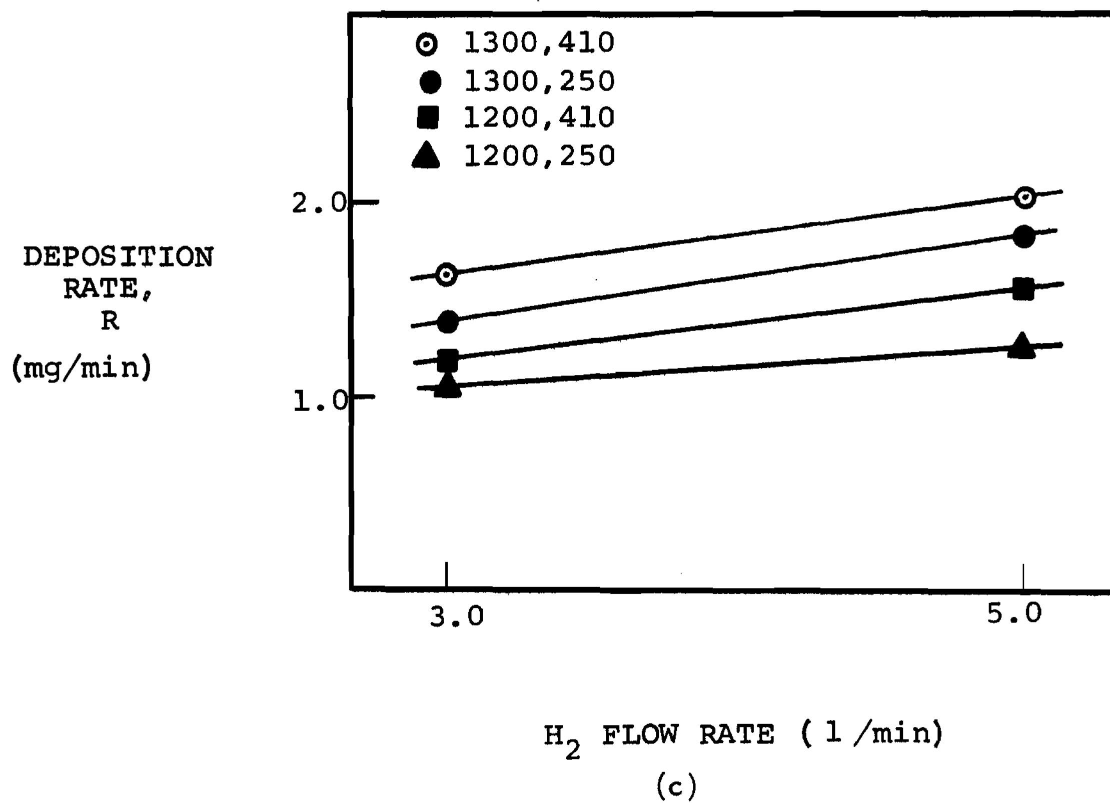
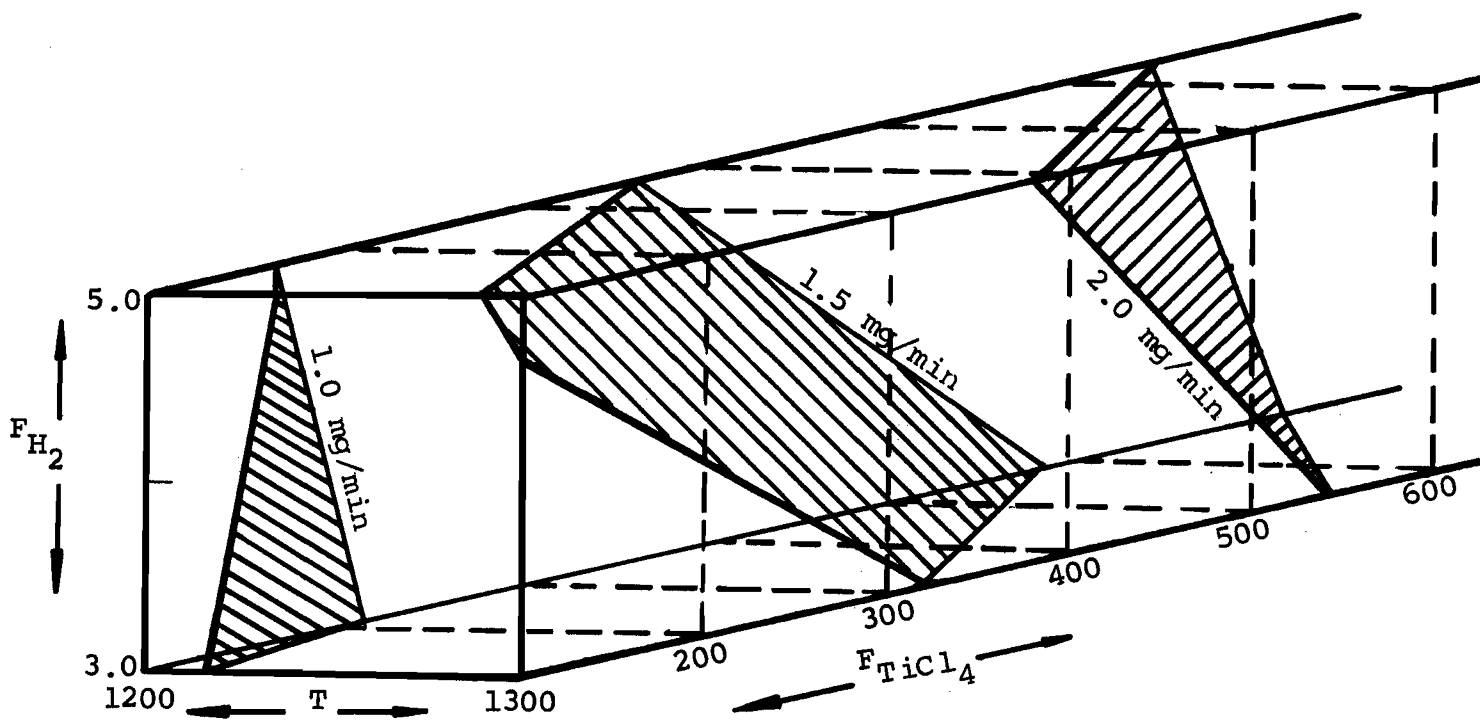


Figure 36 (continued)



(d)

Figure 36 (continued) Planes of Constant Deposition Rate of Chromium-Titanium Alloy

(T = Reactor Temperature, °C; F_{H_2} = Hydrogen Flow, Liters/Min; F_{TiCl_4} = Titanium Tetrachloride Flow, Liters/Min)

TABLE X

Multiple Regression and Correlation Analysis of Ti-Cr Alloy Depositions

Variable	Regression Coefficient	Observed T Value	T Value 95% Level
x_1	1.84×10^{-1}	4.45	2.36
x_2	4.62×10^{-3}	5.60	2.36
x_3	1.39×10^{-3}	2.69	2.36

Intercept: -5.43

Standard Error of Estimate: 0.17

Multiple Correlation Coefficient: 0.938

x_1 Total gas flow, l/min

x_2 Reactor temperature, °C

x_3 $TiCl_4$ flow, mg/min

TABLE XI

Factorial Analysis of Variance for Alloy Depositions

NUMBER OF VARIABLES 3

NUMBER OF REPLICATES 1

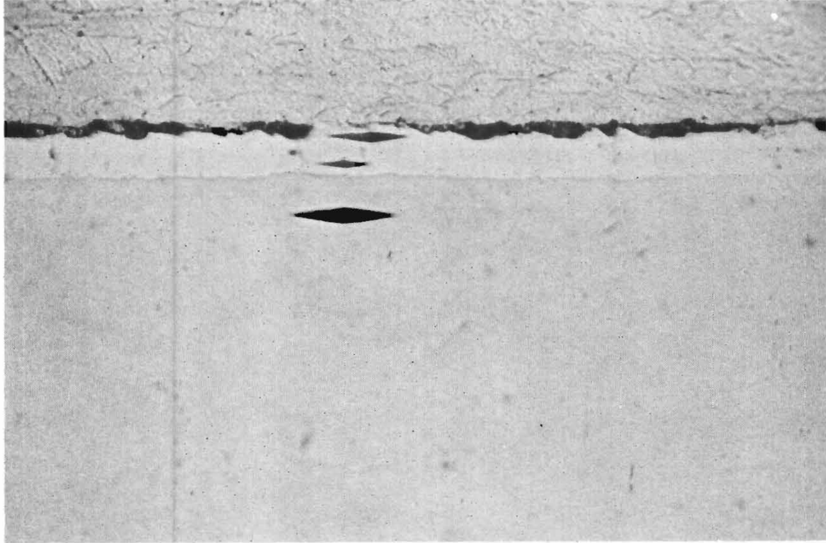
VARIABLE	NO. OF LEVELS
1	2
2	2
3	2

GRAND MEAN 1.49625

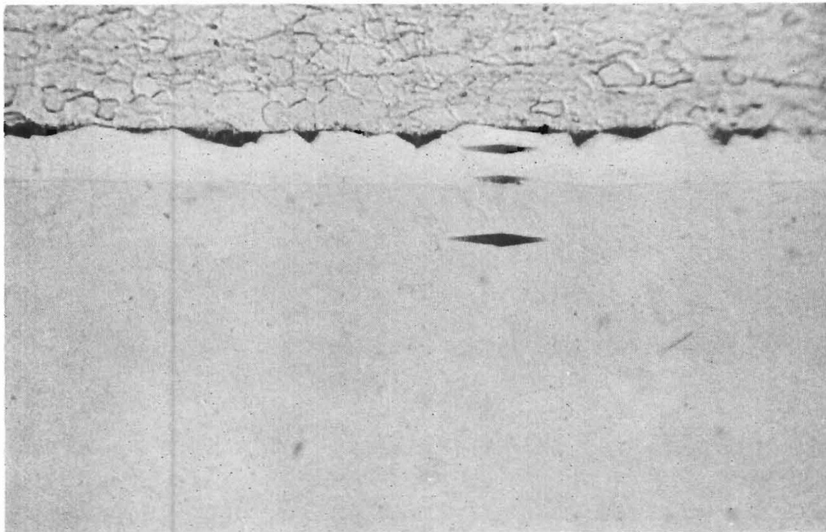
SOURCE OF VARIATION	DEGREES OF FREEDOM	SUMS OF SQUARES	F VALUE *	F REQUIRED **
1	1	0.21451	16.02	10.1
2	1	0.04061	3.03	
3	1	0.31601	23.57	
12	1	0.04351	3.25	
13	1	0.05281	3.91	
23	1	0.03781	2.81	
RESIDUAL	1	0.10351	7.72	10.1
TOTAL	7	0.80879		

* $\hat{\sigma}^2 = 0.0134$

** For 95% confidence level

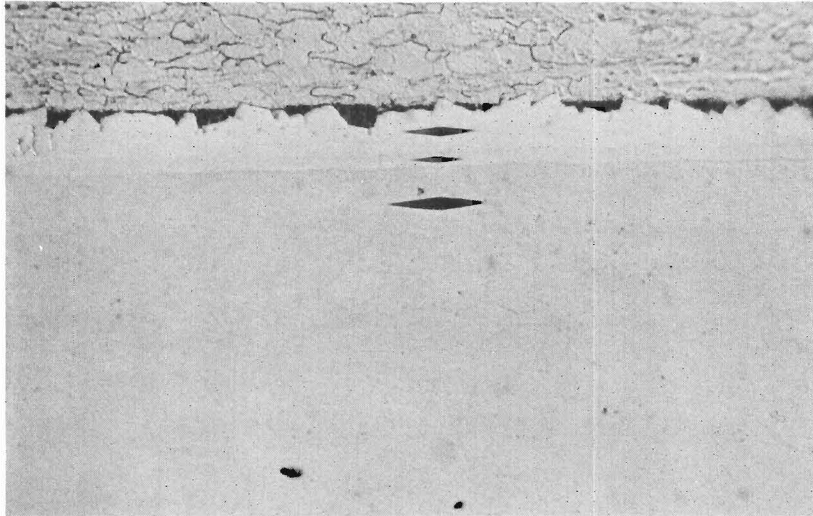


(a) Run 741

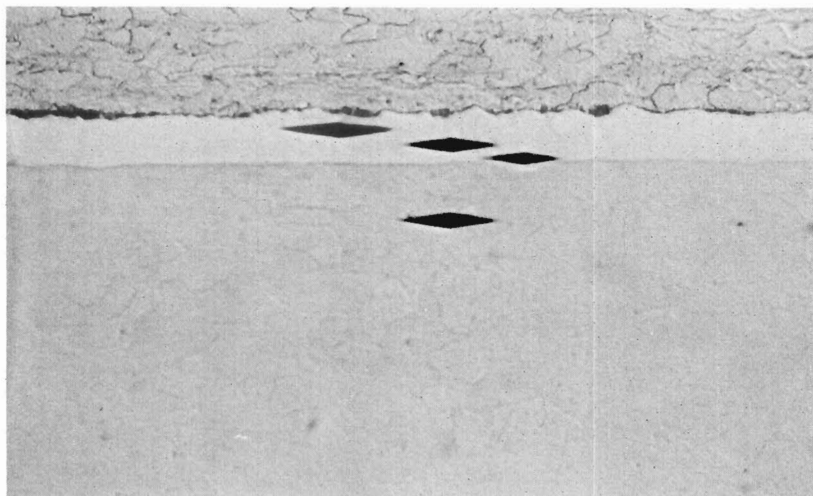


(b) Run 743

Figure 37 Codepositions of Titanium and Chromium (X500)

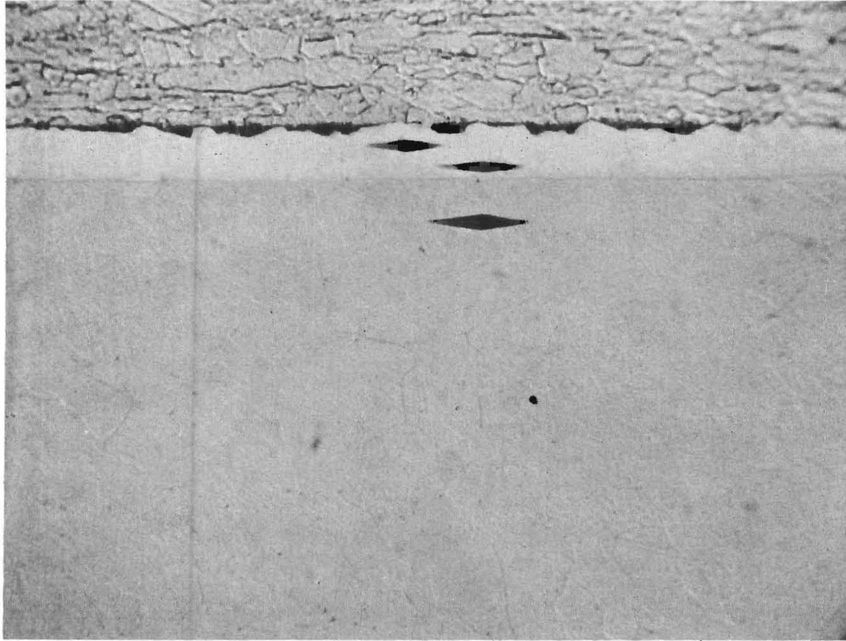


(c) Run 746



(d) Run 747

Figure 37 (continued)



(e) Run 745

Figure 37 (continued)

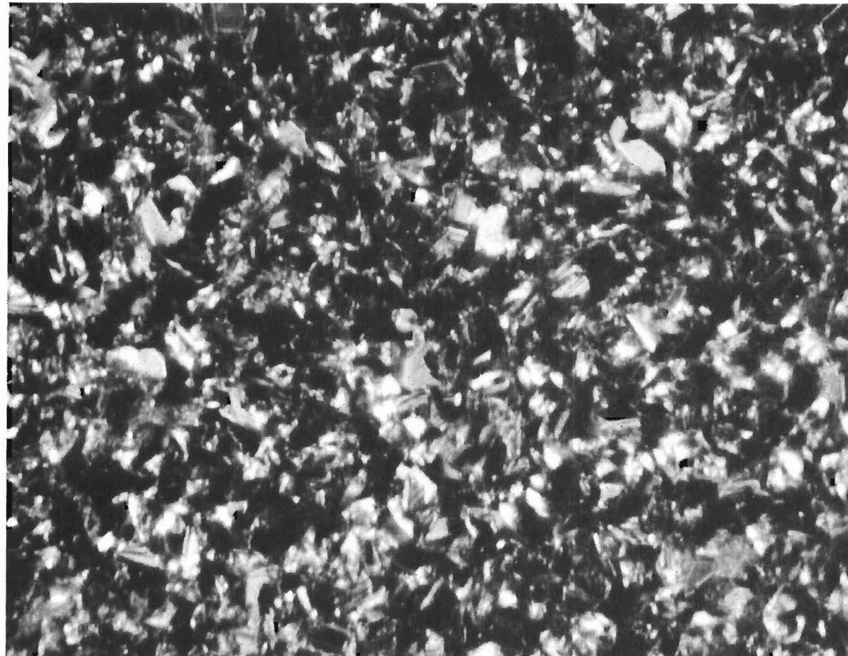
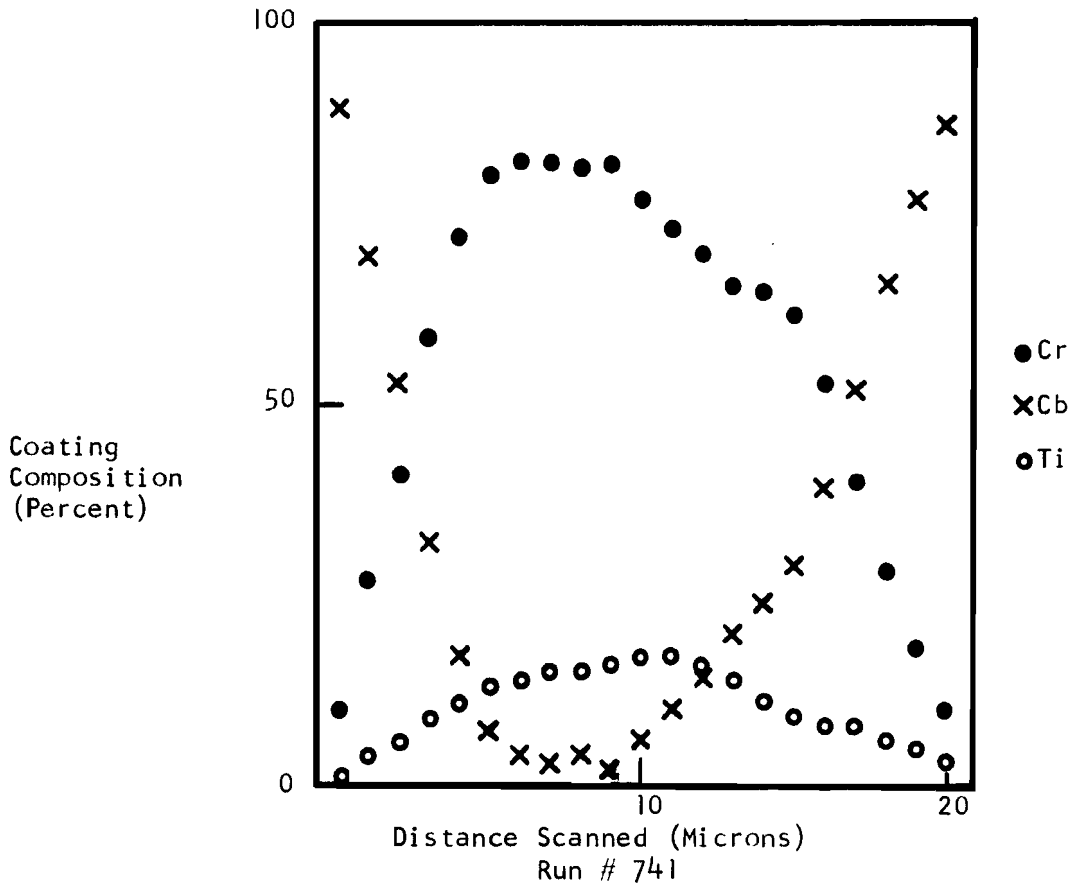


Figure 38 Surface Photograph of "as-deposited" Ti-Cr Alloy (X500)



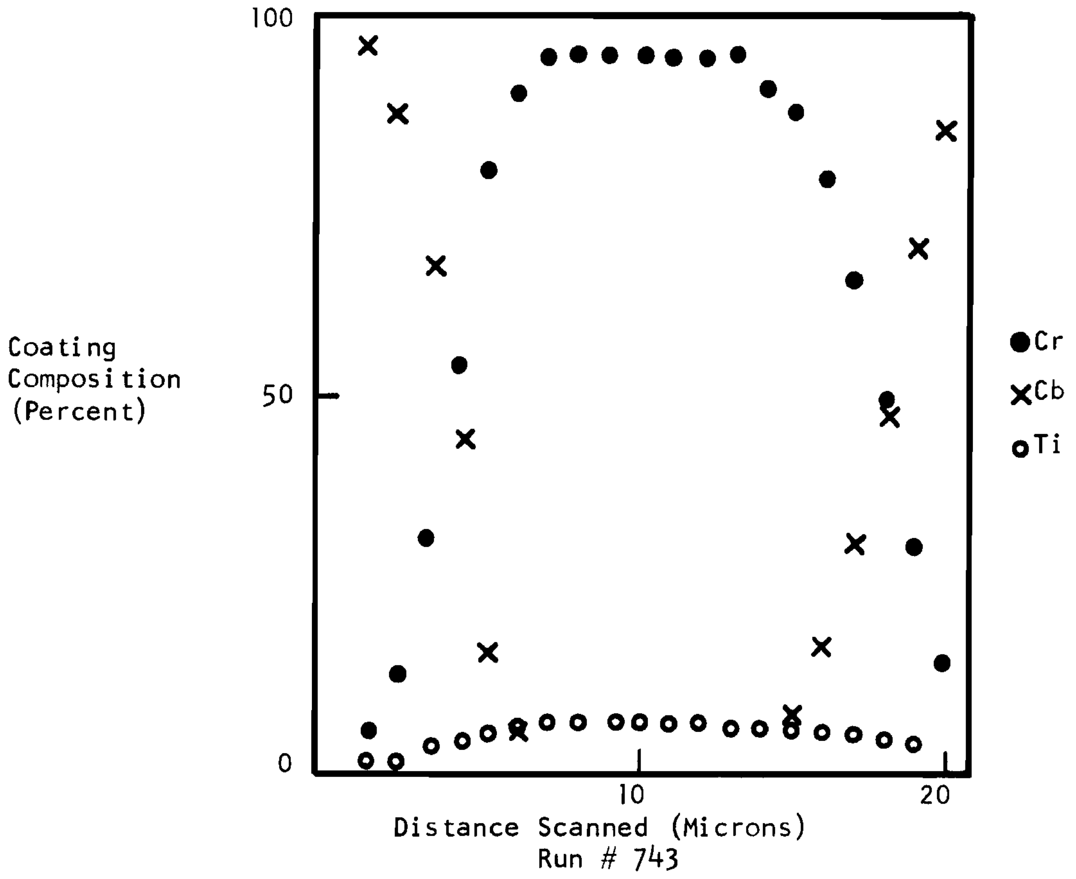
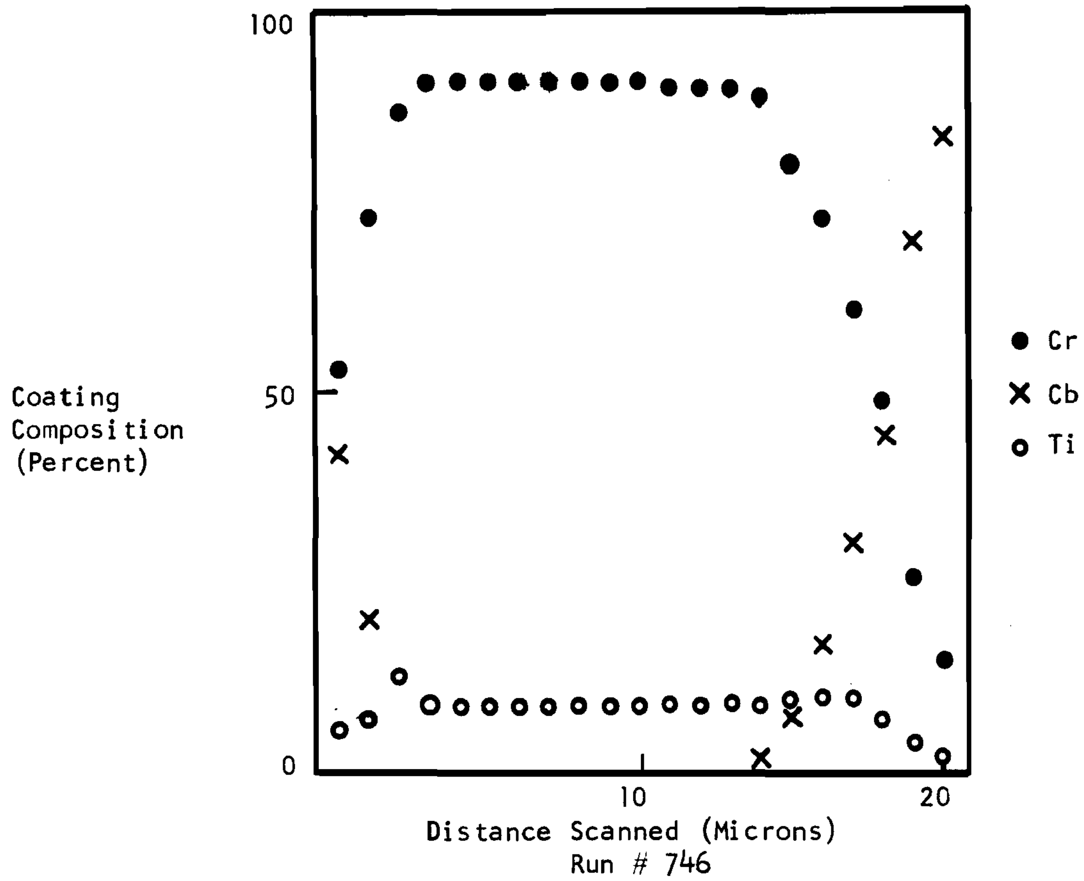
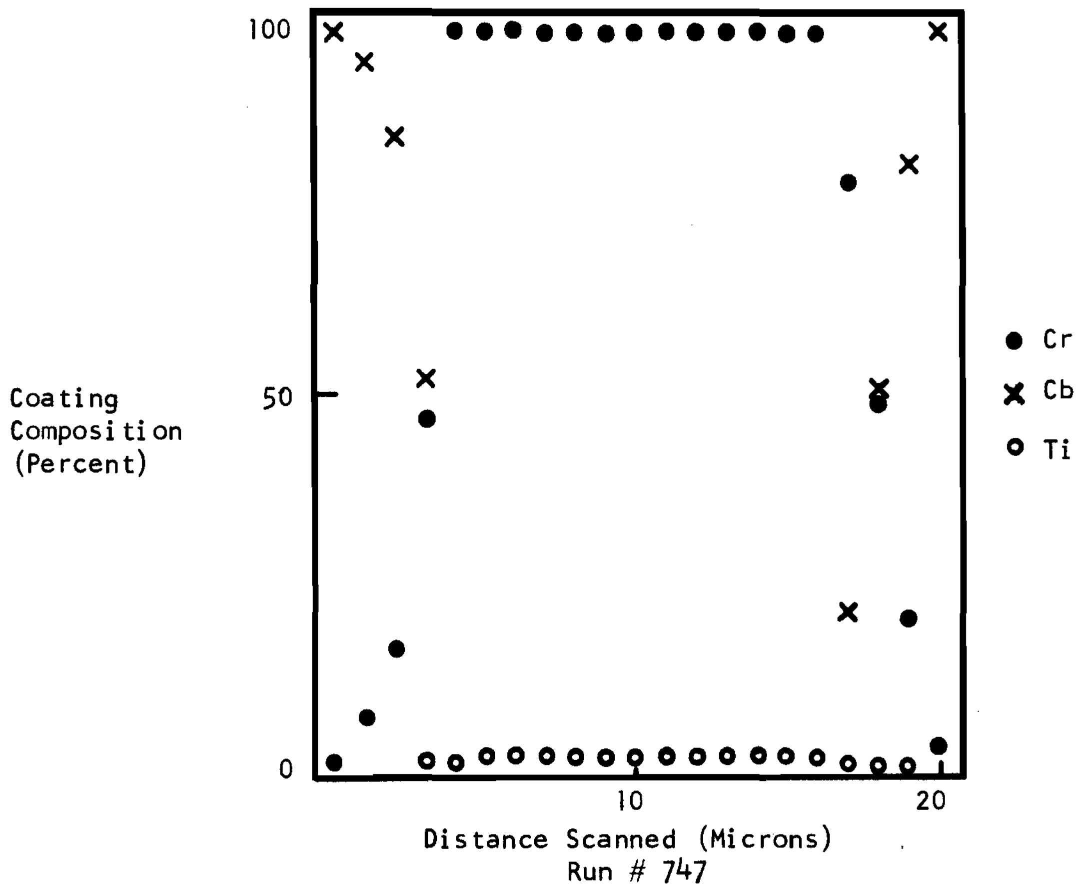


Figure 39 Profiles of Coating Composition Measured with an Electron Microprobe



Run # 746



Run # 747

Figure 39 (Continued)

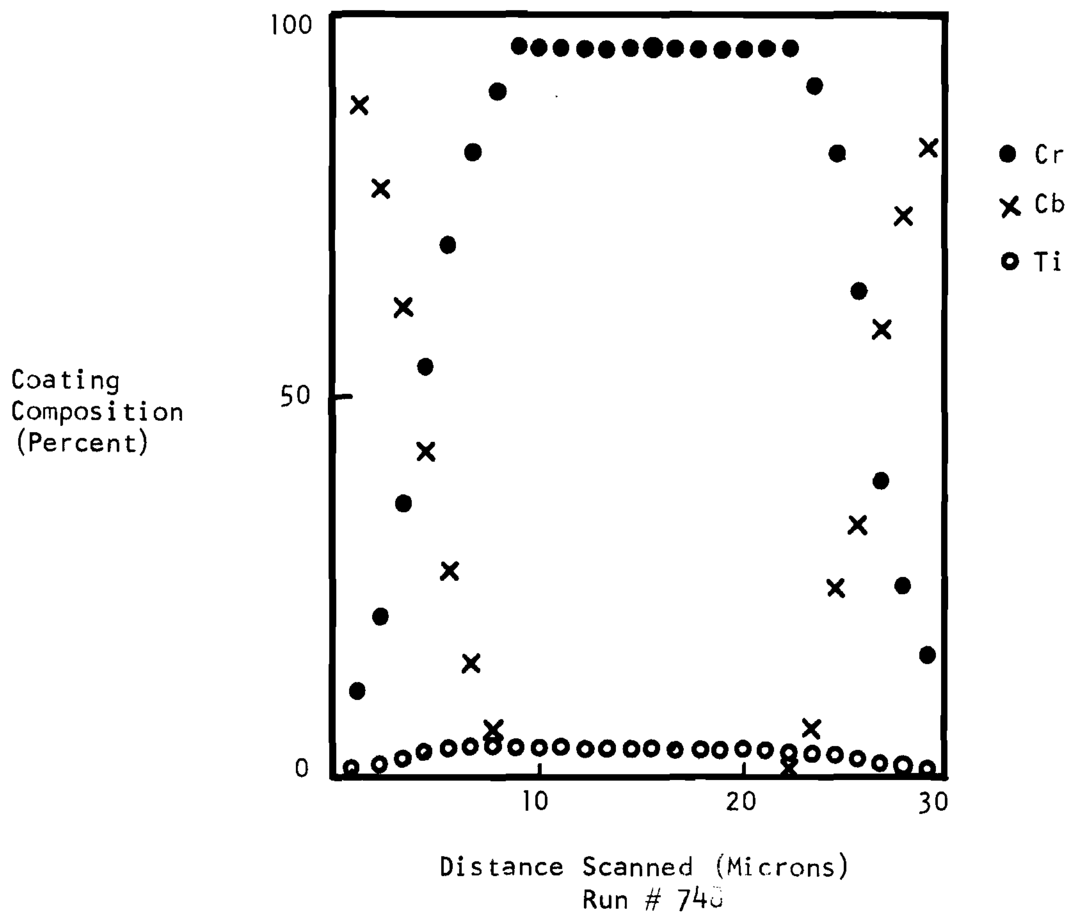


Figure 39 (Continued)

In general, concentrations were uniform through the coating, though for this particular series titanium concentrations were lower than desired. Alteration of the ratio of $TiCl_4$ flowing to the chromium and titanium compartments in the chloride generation chamber increased the titanium concentration in the deposits.

To test the reproducibility of the coating process, eight samples were coated on both sides. Each sample was coated on one side, removed from the reactor, weighed, then coated on the other side. The results, shown in Table XII, indicate fair reproducibility, with an average coating weight per side of 24.1 mg and an average deviation from this weight of ±10%. This appears satisfactory for the present level of process development.

This test series was also used to determine the effect of continuous operation on the performance of the coating equipment. Performance was generally satisfactory, except that the sample temperature increased slightly as the series progressed. An improved temperature controller was installed, and the method of attaching the thermocouple that controls sample temperature was improved to permit more precise control and to facilitate changing thermocouples. This increased overall precision and control of alloy deposition. A Pt-Pt10% Rh thermocouple with a quartz protection sleeve was embedded in the heater element.

Figure 40 shows cross sections of the coatings on two of the samples. These two samples were sheared to obtain bend-test specimens, which were subjected to the 4-T bend test. Both bent to 90 degrees without fracture of coating or substrate. X-ray analysis showed a body-centered cubic structure, quite close to the lattice parameter for chromium. This would be expected, since the body-centered cubic chromium phase would occur above 67% chromium. Microprobe analysis run on these samples is reported in the analysis section of this report.

TABLE XII

Alloy Deposition Reproducibility Series

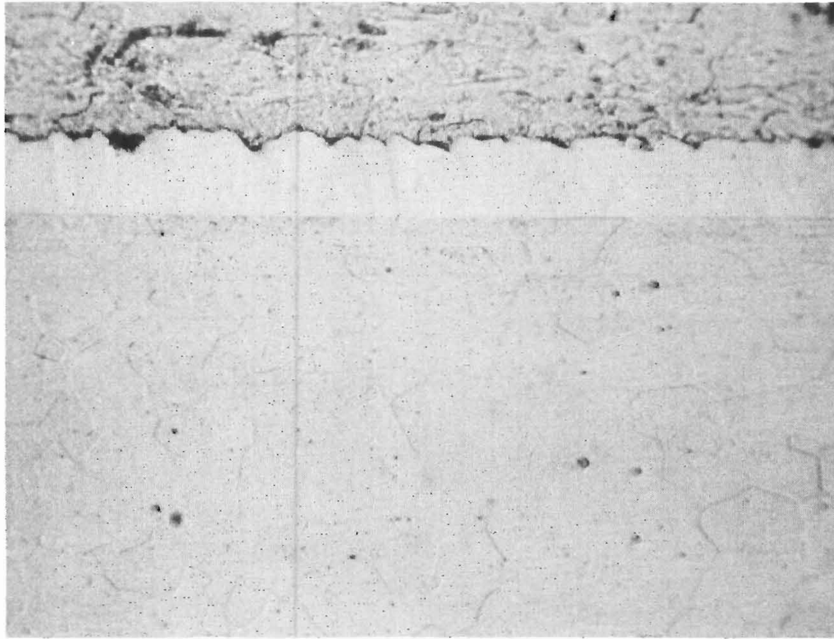
Run No.	Coating Weight	
	Side 1	Side 2
769	22.3	21.1
770	20.7	22.2
772	22.9	23.6
773	23.6	24.9
774	25.2	26.5
775	15.9	28.2
776	26.9	27.1
777	27.6	26.7

Average Weight Gain: 24.1 mg

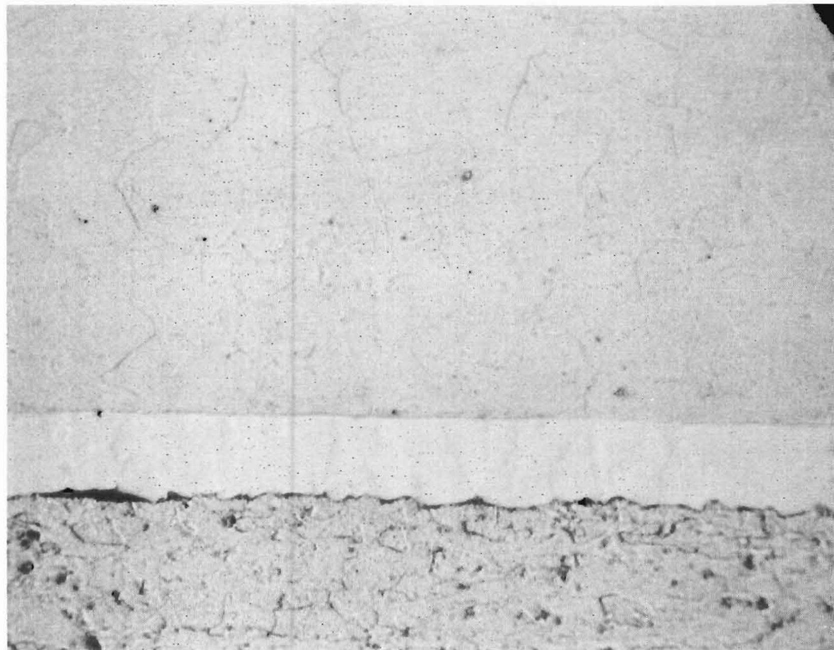
Average Deviation: 2.5 mg

Experimental Parameters:

Temperature	1300°C
Hydrogen Flow	4.0 ℓ/min
Argon Flow	4.0 ℓ/min
Chromium-Titanium Temperature	750°C
Deposition Time	10 minutes

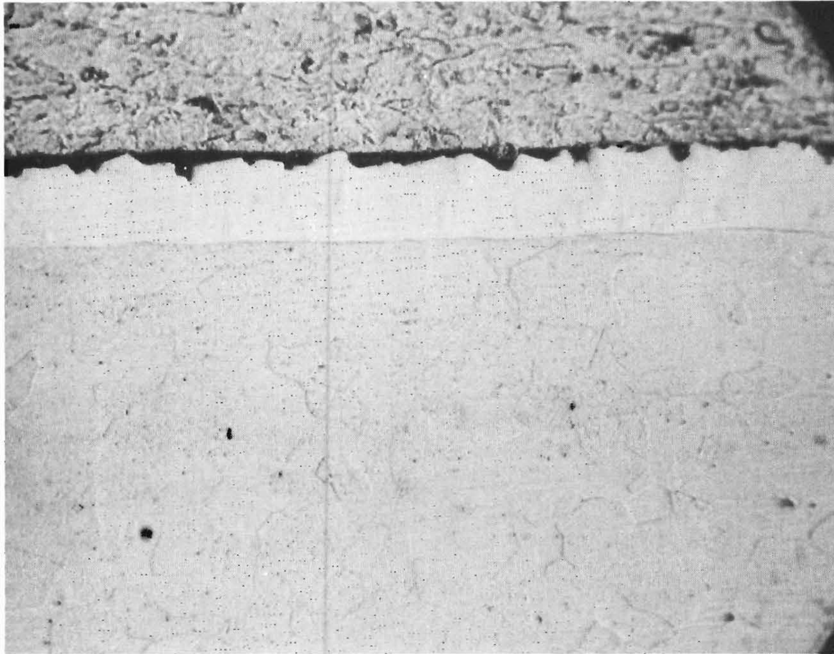


776
500 X

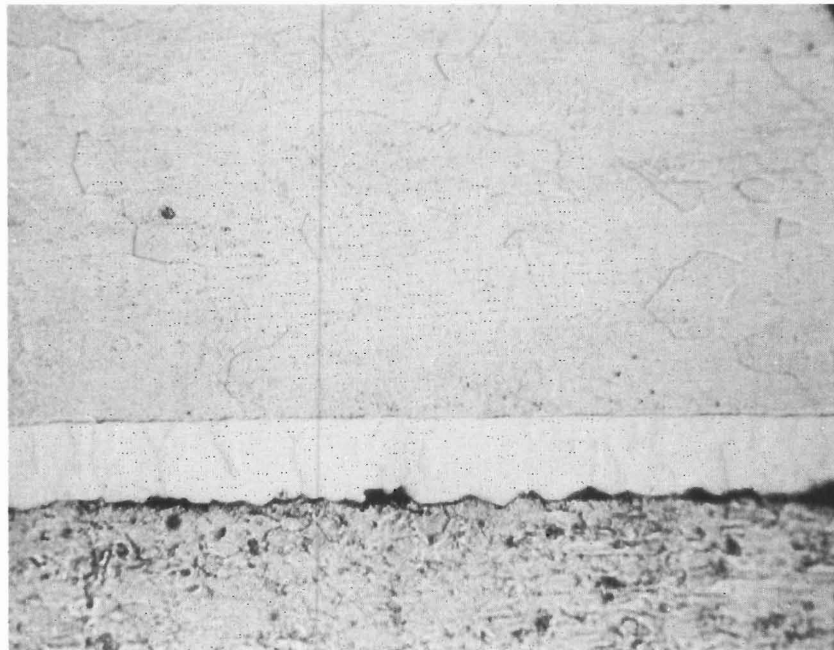


776
500 X

Figure 40 Ti-Cr Coatings on Two Sides of B-66 Substrates
(Mag. 500 X)



777
500 X
1 in = 2 mils



777
500 X
1 in = 2 mils

Figure 40 (Continued)

E. Relationship of the Gas-Phase Concentration to Deposit Compositions

The investigations of codeposition of titanium-chromium alloys have further elucidated the gas-phase composition required to obtain coatings having specified metal concentrations.

Data obtained comparing alloy deposit composition and gas-phase compositions were analyzed. The plot in Figure 41 summarizes these results. The concentration of titanium is about 14 times greater in the gas than in the coating for the range of experimental variables investigated. This is to be expected in view of the relative thermodynamic stability of the chlorides. Deposit composition was slightly temperature-dependent at any gas composition, within the limits noted on the plot. In general, higher temperatures favored a higher titanium composition, which implies a higher "effective" entropy change for the titanium reduction than for the chromium reduction.

F. Silicon Deposition Process

Deposition of silicon was an established process and thus required little preliminary investigation. To check the process, deposits of silicon were made on several substrate materials by the hydrogen reduction of silicon tetrachloride. Runs 800 through 814 listed in the appendix were made in this way. Figure 42 is a cross section of silicon on tantalum; Figure 43, silicon on molybdenum; and Figure 44, silicon on titanium-chromium alloy deposit from Run 773, which before siliciding would have had a cross section similar to the Run 776 figure. Only on the Ti-Cr alloy did the silicon interact extensively with the substrates, as evidenced by the existence of several zones in the coating. Silicon content of this coating was approximately 10 mg/cm^2. The standard silicon deposition process was satisfactory for preparation of coatings, though the best diffusion time to interact the silicon with the alloy coating was not investigated.

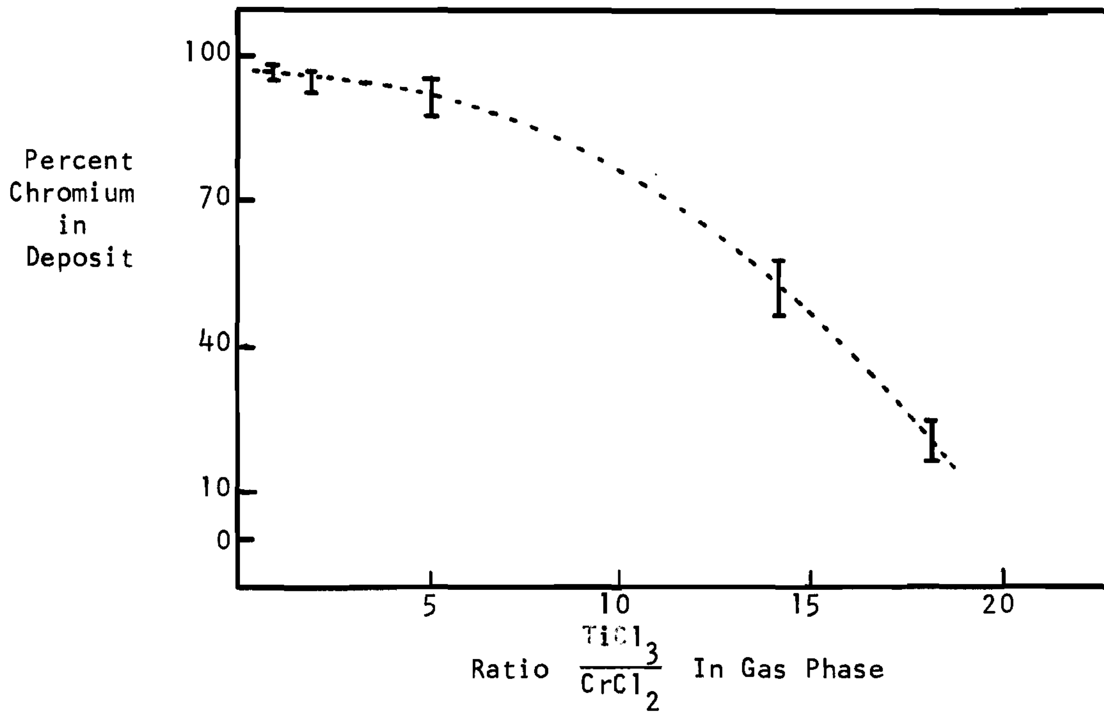


Figure 41 Composition of Coating Deposit Versus Concentration of Gas Phase for Codeposition of Titanium-Chromium Alloys

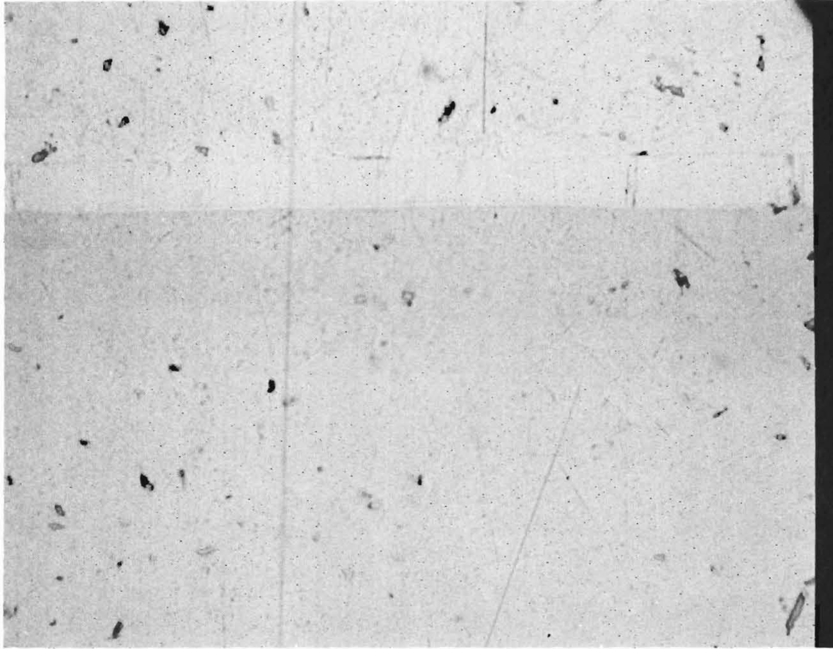


Figure 42 Silicon Coating on Tantalum (Run 808, 500X)

Figure 43 Silicon Coating on Molybdenum (Run 806, 500X)

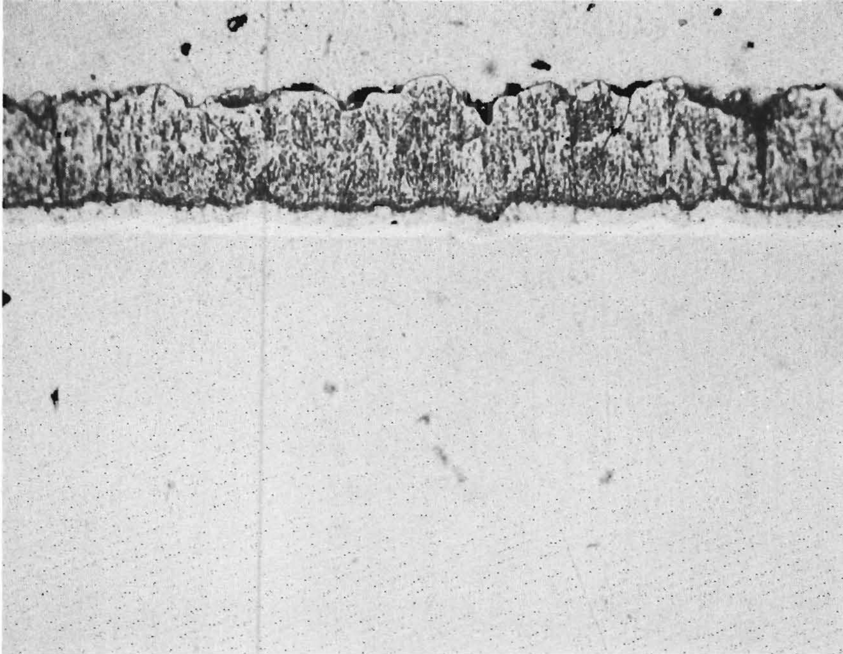


Figure 44 Titanium-Chromium-Silicon Coating on B-66 (X500)

SECTION IV

COATING PROTECTIVENESS STUDIES

The purpose of this phase of the work was to prepare and evaluate coatings to determine the applicability of the CVD process for preparing the titanium-chromium-silicon coating. Previous efforts (Phase I) had resulted in several processes by which the metal alloy coatings could be prepared. To obtain the maximum range of possible compositions, the two-chamber process was selected for the alloy deposition. In this process the titanium-to-chromium ratio is adjusted mechanically and thus remains constant throughout a series.

The overall plan was to evaluate a number of series, each containing several samples. This approach yielded a more realistic view of the relation of performance to coating procedure and also served to test the capability to prepare coatings reproducibly. Six samples were coated in each series and subjected to test and evaluation as follows:

Sample No.	
1	Retained for Reference
2	Oxidation Test 2300°F
3	Oxidation Test 2500°F
4	Cross Section Analysis
5	Oxidation Test 2300°F
6	Oxidation Test 2500°F

The coating was formed by depositing the desired alloy coating on one side, removing and weighing the sample, then alloy coating the other side. The samples were then siliconized by depositing and reacting silicon using hydrogen reduction of $SiCl_4$.

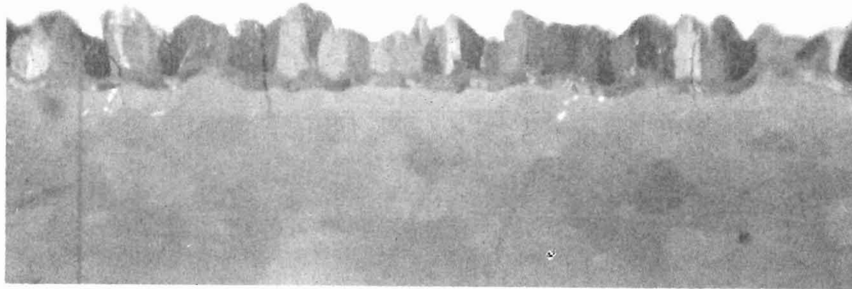
Samples were oxidized in a silicon carbide element electric form or in slowly moving air. They were supported on Leco zirconia boats in a mullite tube. The boat was inserted into the hot furnace, rapidly removed at approximately 1 hour intervals during the day for visual examination and weighing,

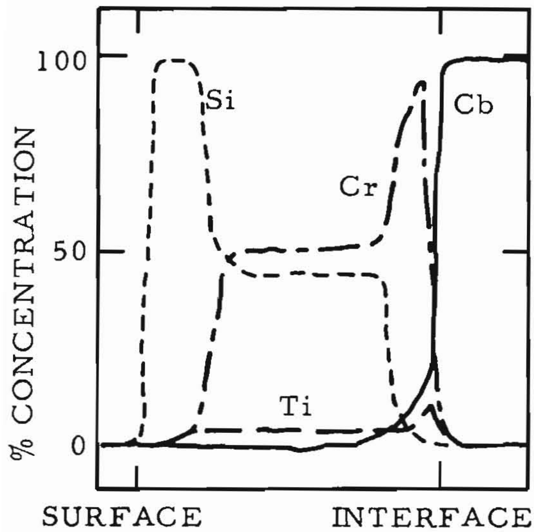
then returned to the hot furnace. The samples were allowed to soak overnight at the test temperature.

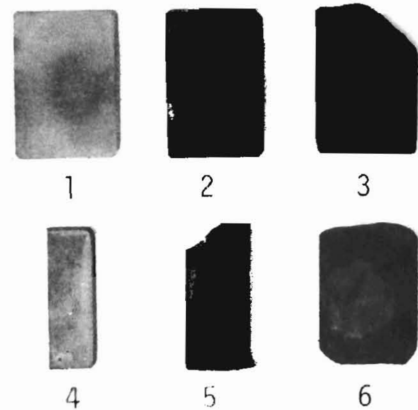
Results of the evaluation for each series are shown in the following pages and are summarized in Table XIII.

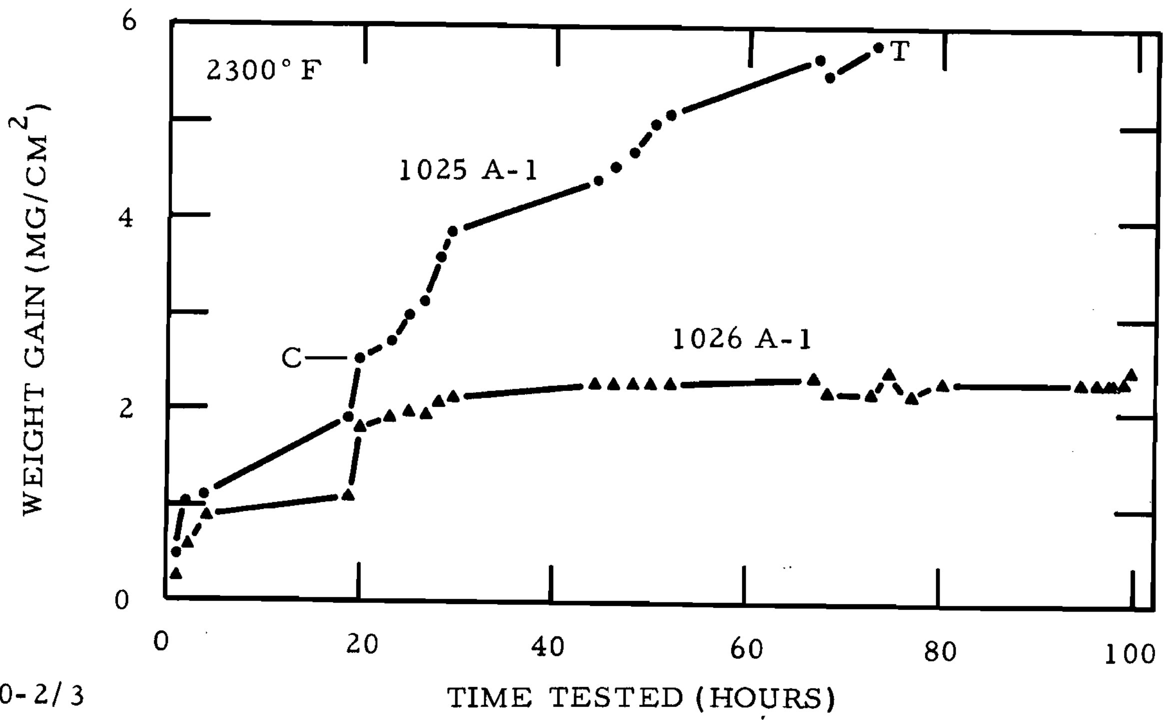
SERIES A-1

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1023	18.4	15.0		
2	1026	17.6	8.2	2300	100
3	1028	18.6	8.0	2500	70
4	1027	18.6	9.0		
5	1025	19.0	8.6	2300	74
6	1024	19.2	7.1	2500	89









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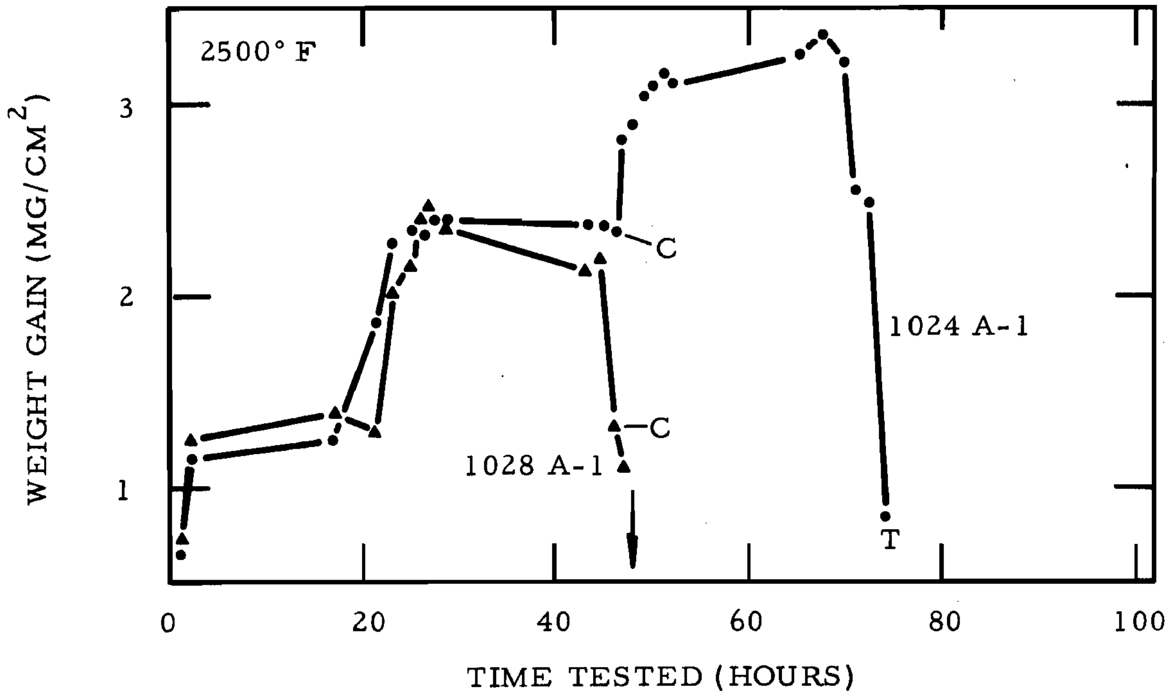
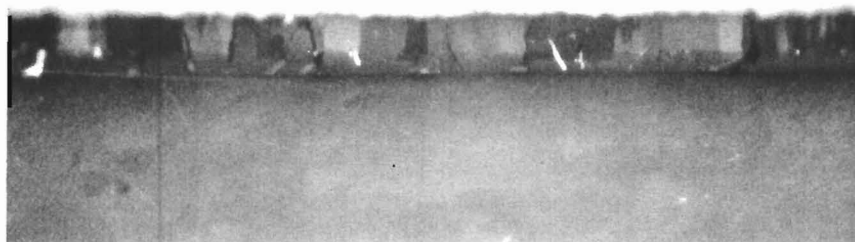
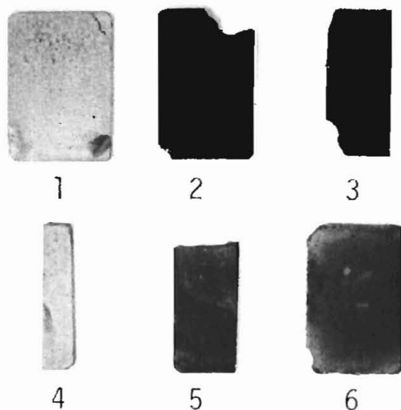


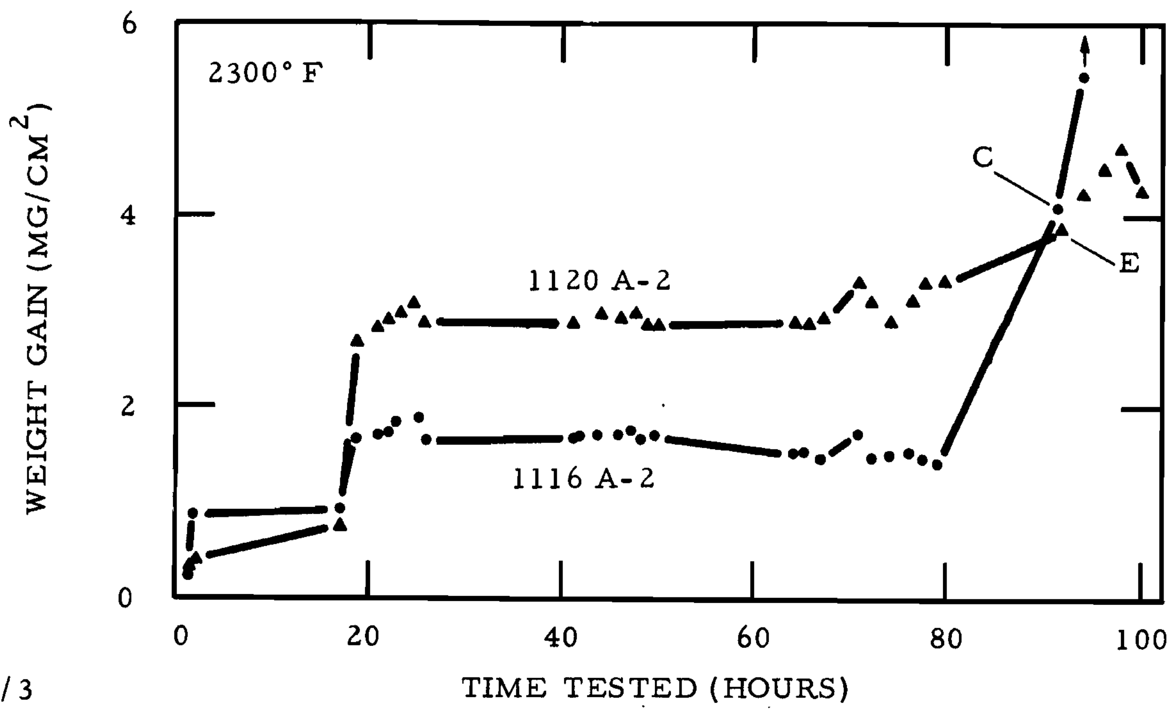
Weight Gain of Coatings in Air for Series A-1

SERIES A-2

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1119	6.8	8.3		
2	1120	6.3	7.4	2300	100
3	1118	6.0	9.8	2500	100
4	1115	5.9	9.1		
5	1116	6.0	9.1	2300	100
6	1117	6.2	10.4	2500	100







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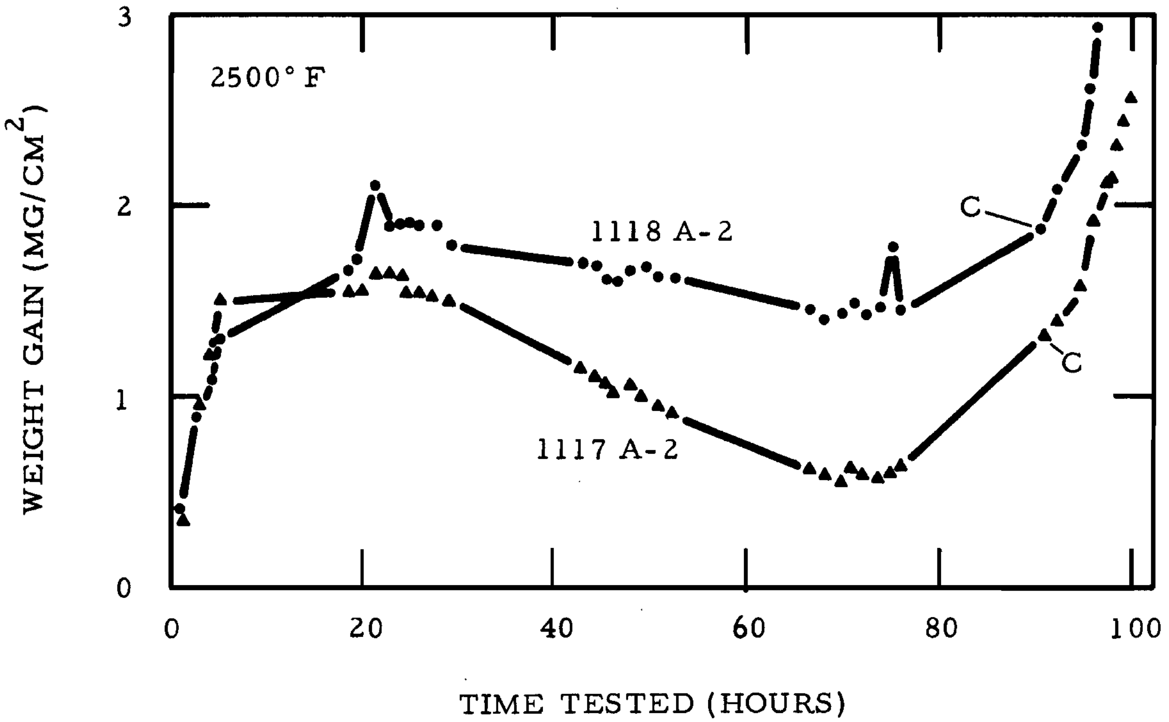
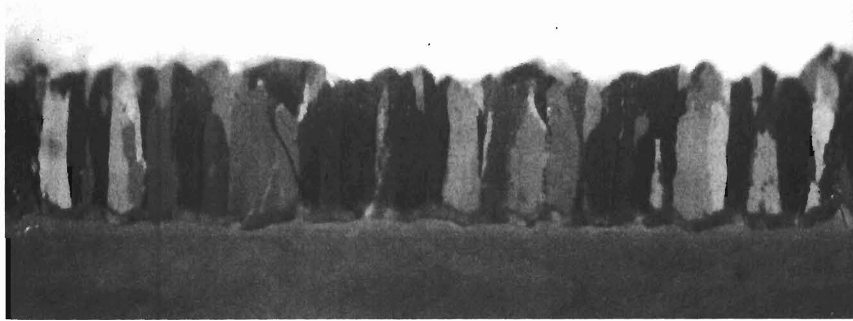
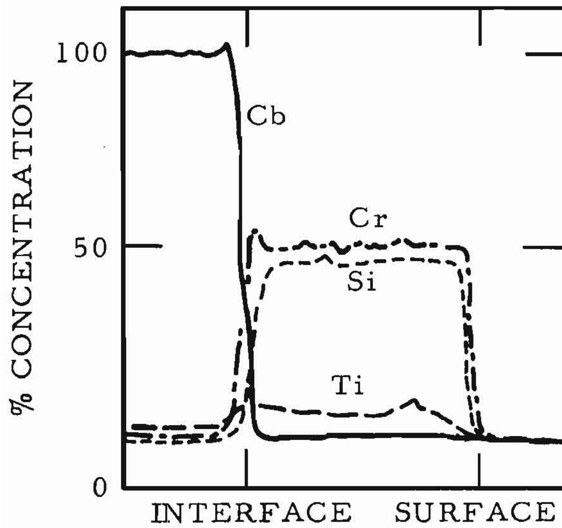


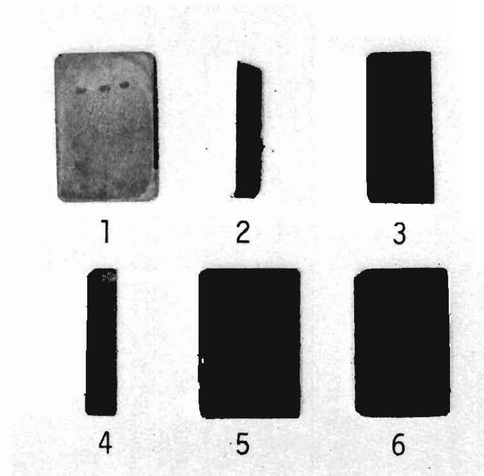
Weight Gain of Coatings in Air for Series A-2

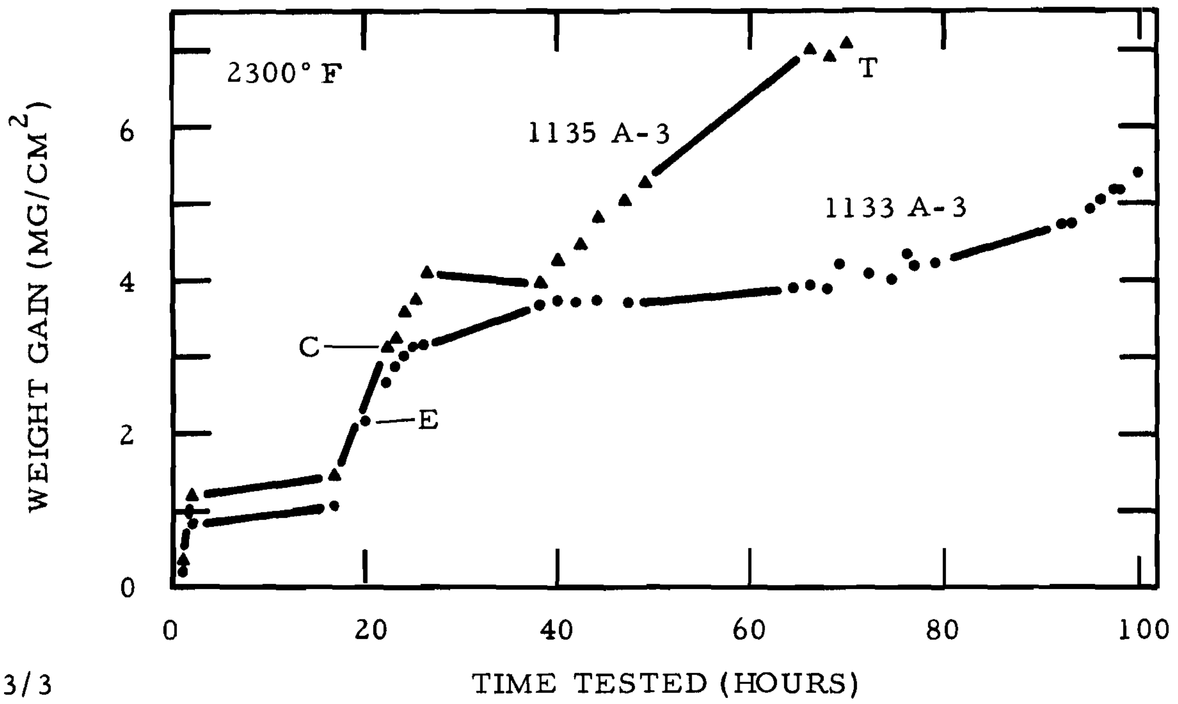
SERIES A-3

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1131	11.0	12.8		
2	1135	11.8	13.8	2300	70
3	1136	10.7	13.4	2500	100
4	1137	11.3	13.6		
5	1133	10.7	12.8	2300	100
6	1129	10.3	12.0	2500	100









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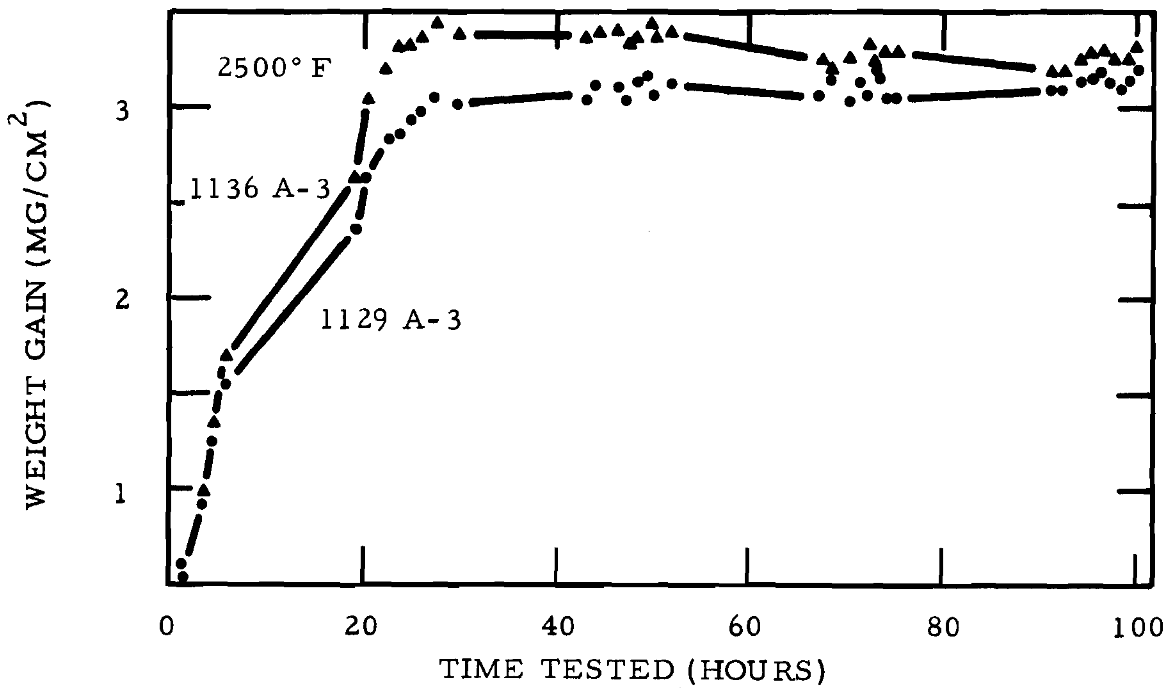
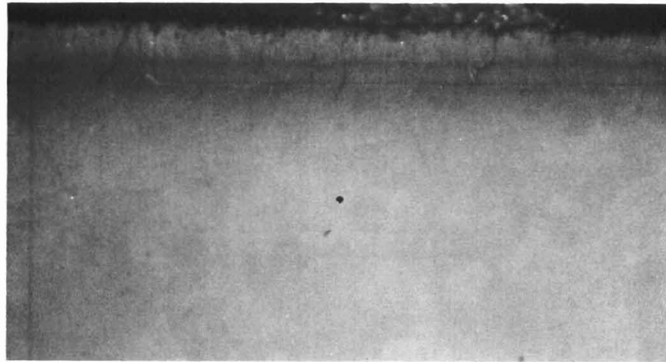
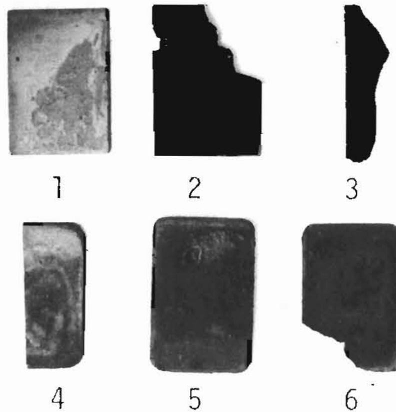


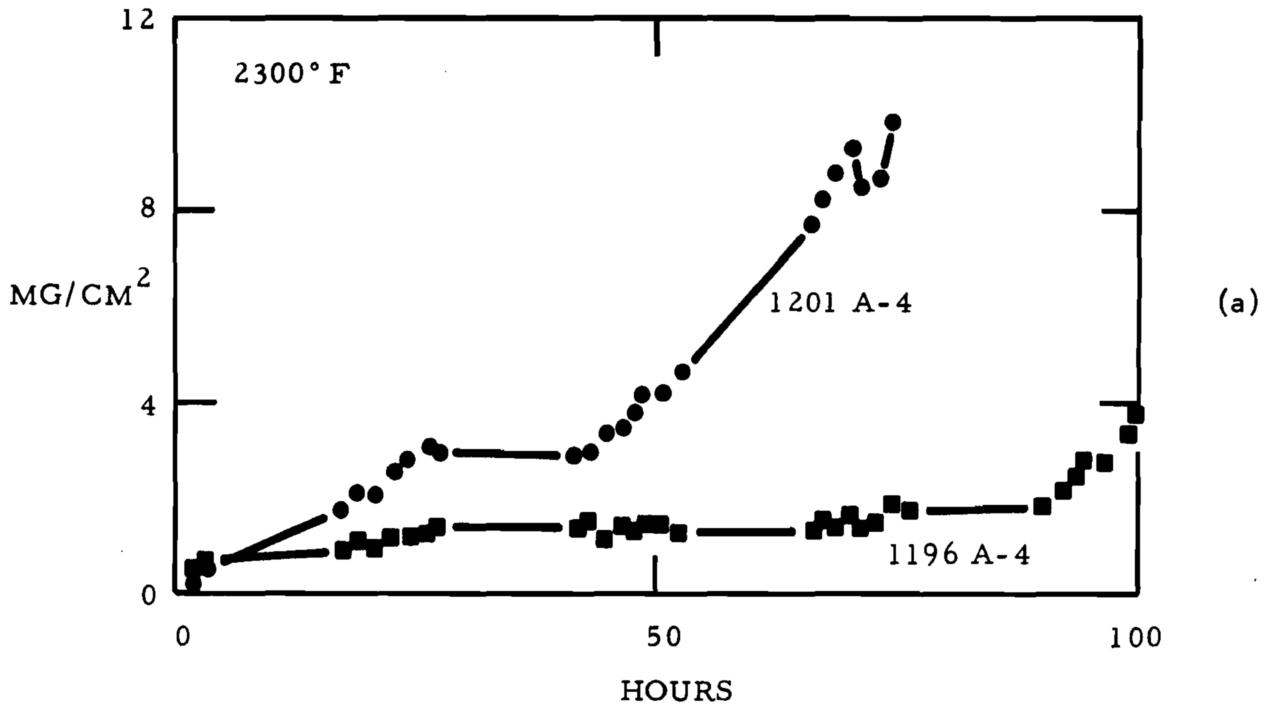
Weight Gain of Coatings in Air
Series A-3

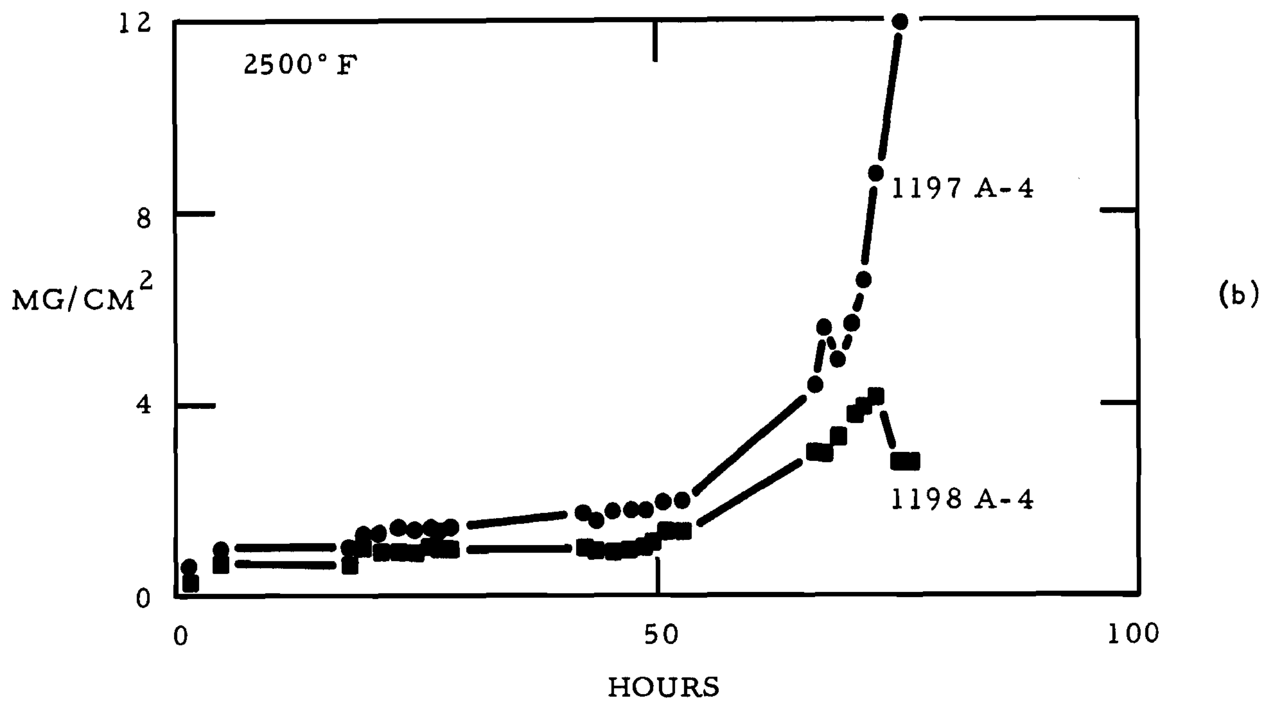
SERIES A-4

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1200	8.0	8.2		
2	1201	6.6	9.1	2300	75
3	1198	8.4	10.9	2500	90
4	1199	9.1	7.5		
5	1196	6.1	9.1	2300	100
6	1197	7.8	9.5	2500	76





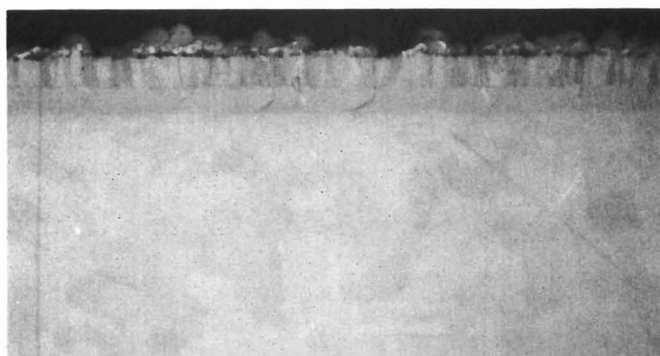


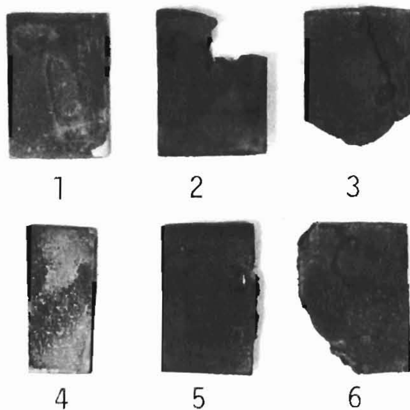


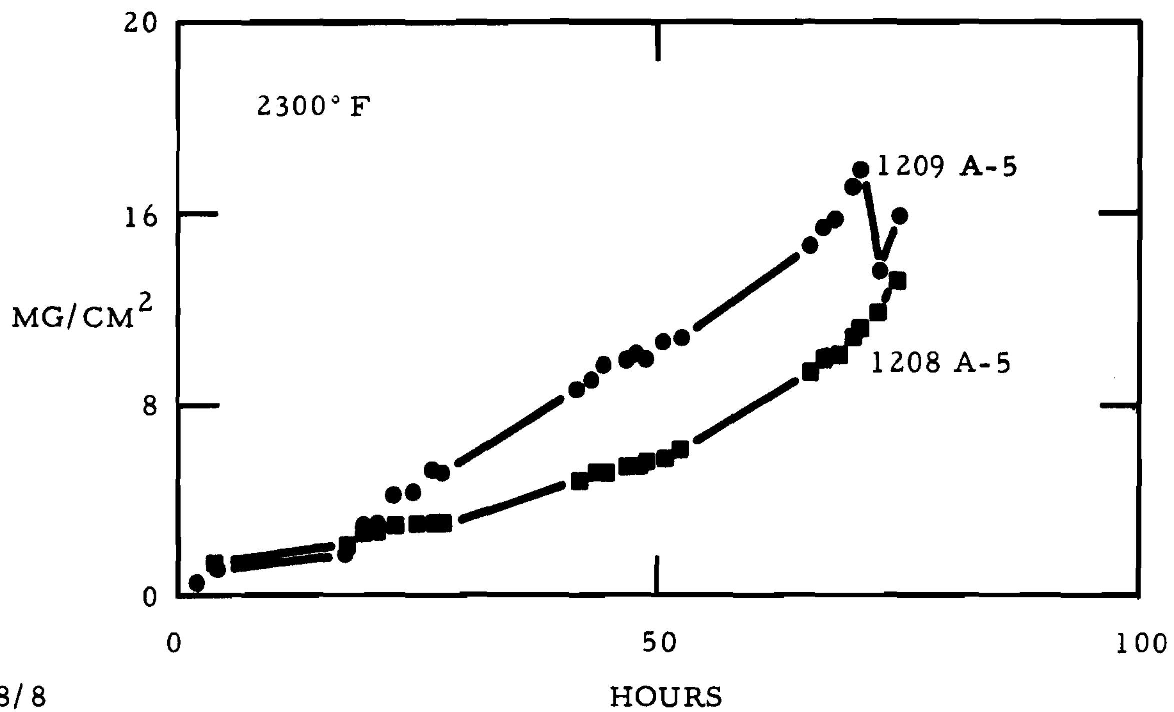
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-4

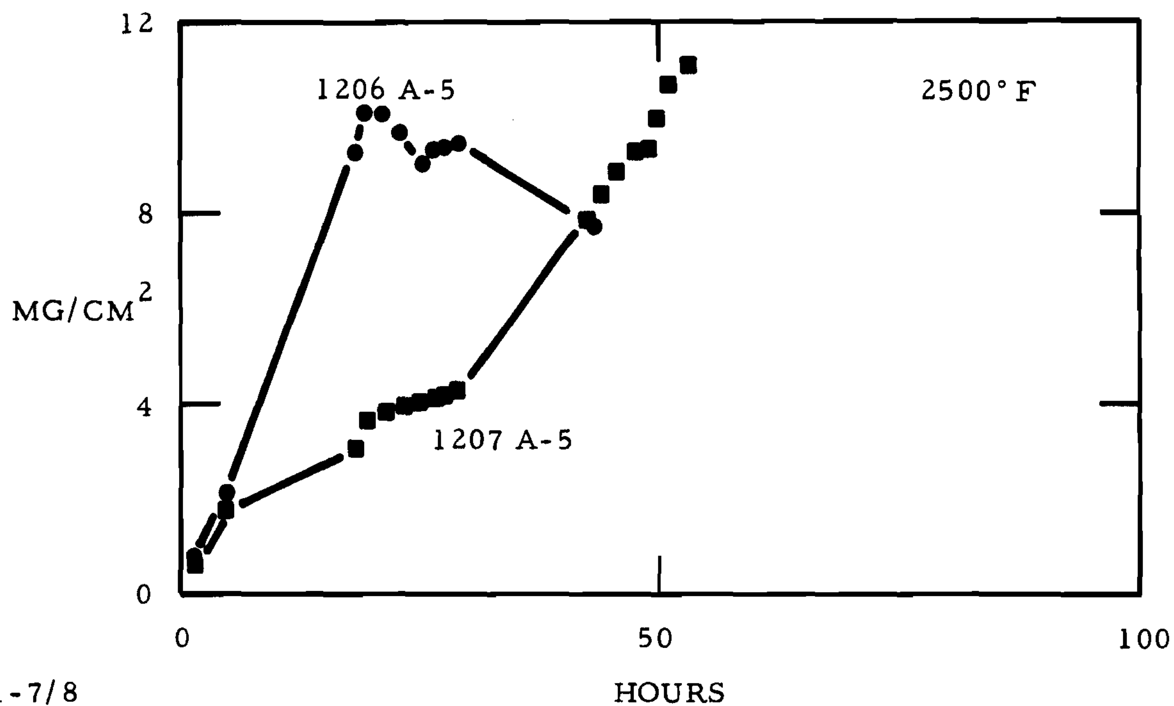
SERIES A-5

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1204	12.6	7.4		
2	1209	10.7	10.4	2300	76
3	1207	11.6	12.5	2500	67
4	1205	14.2	13.2		
5	1208	10.3	8.8	2300	76
6	1206	14.0	15.0	2500	44





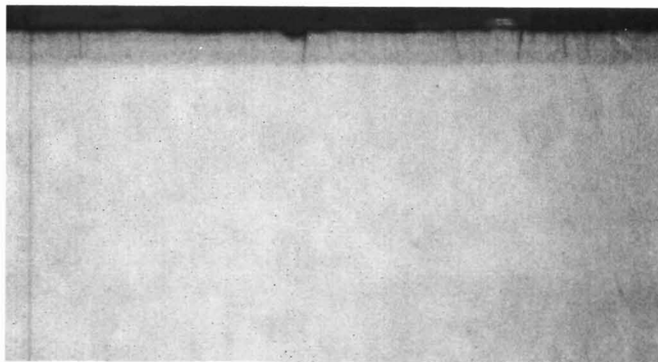


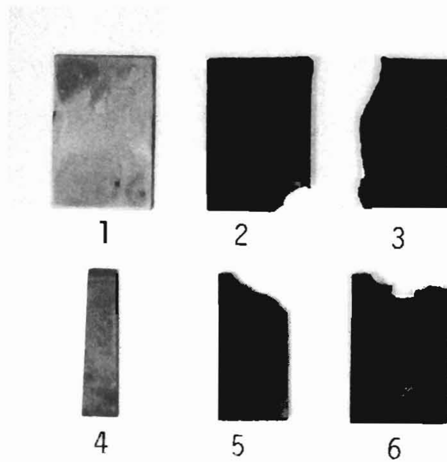


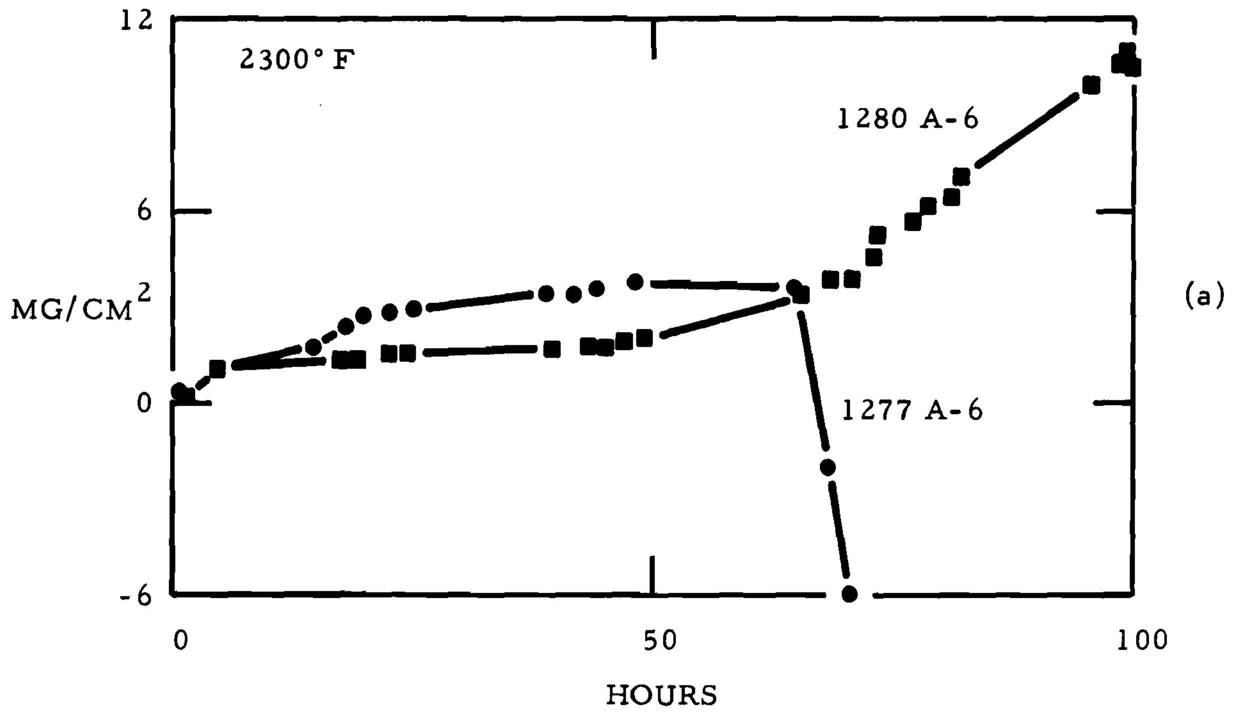
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-5

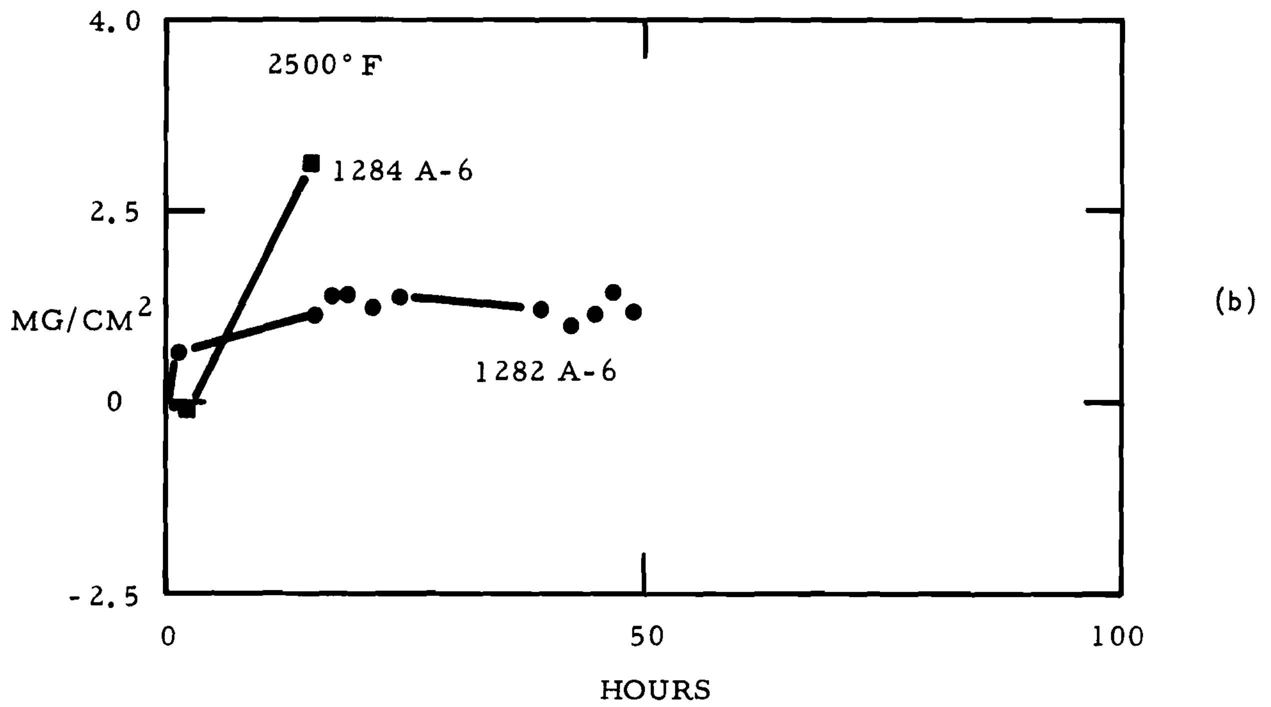
SERIES A-6

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1281	9.0	5.6		
2	1280	10.1	5.8	2300	100
3	1284	10.1	6.4	2500	15
4	1283	12.0	6.3		
5	1277	10.0	7.4	2300	70
6	1282	9.4	8.0	2500	49





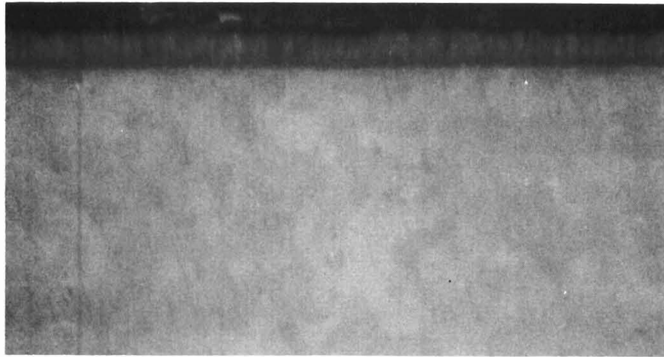


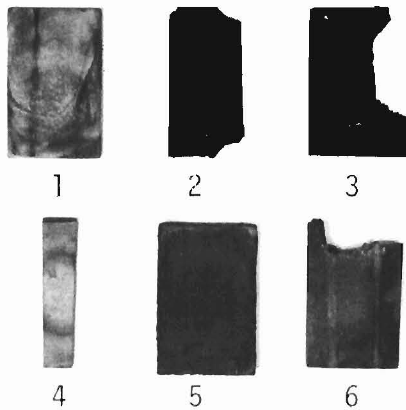


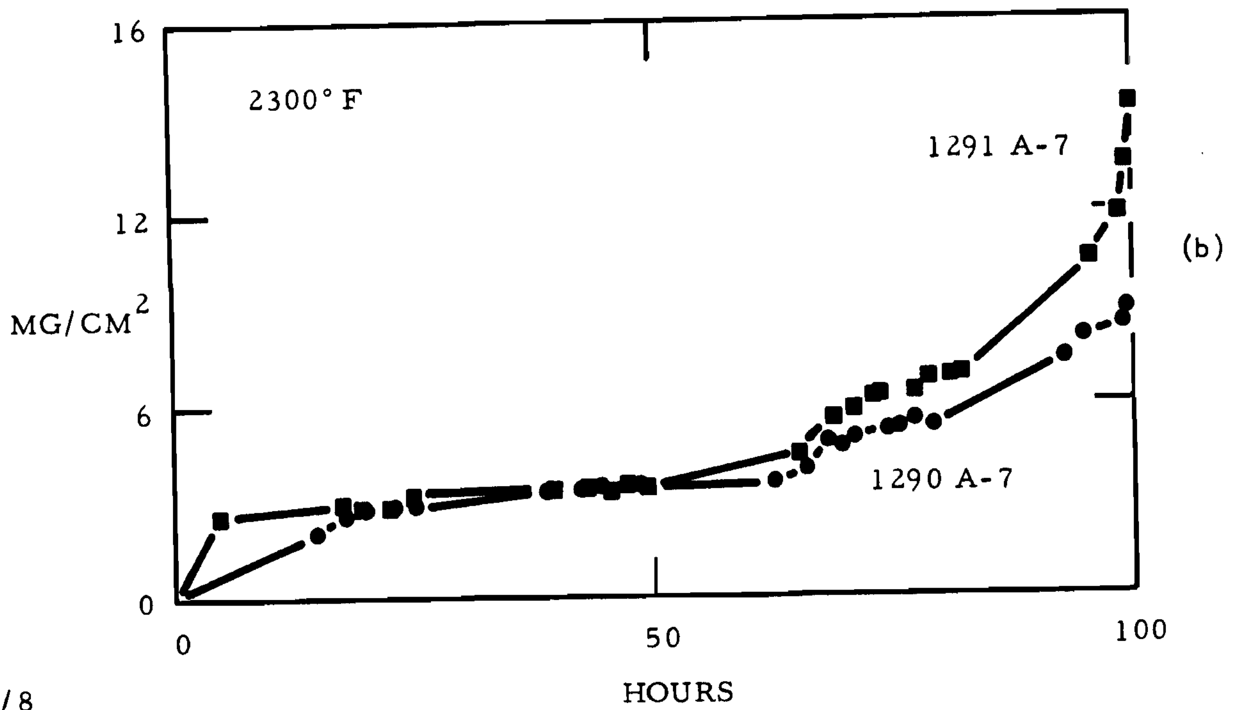
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-6

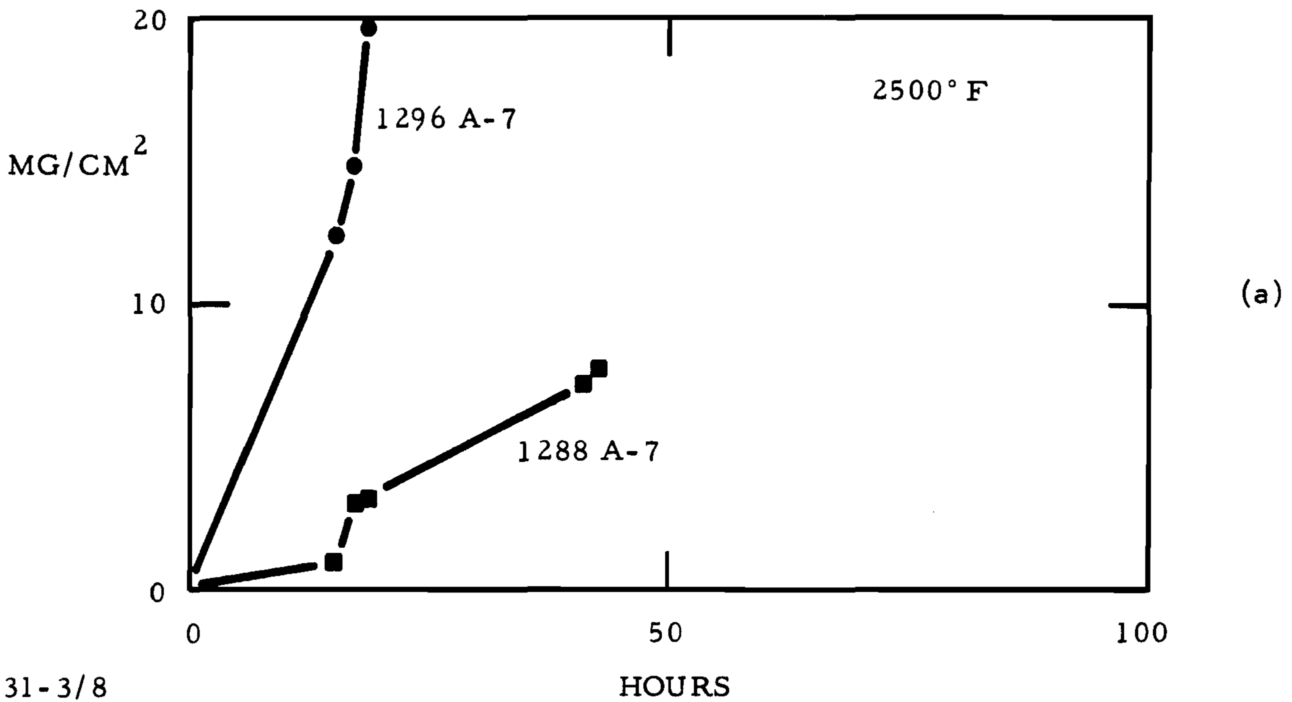
SERIES A-7

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1289	10.4	5.4		
2	1291	8.8	10.2	2300	100
3	1296	9.8	11.5	2500	18
4	1286	10.8	5.5		
5	1290	9.0	9.6	2300	100
6	1288	11.7	6.8	2500	43





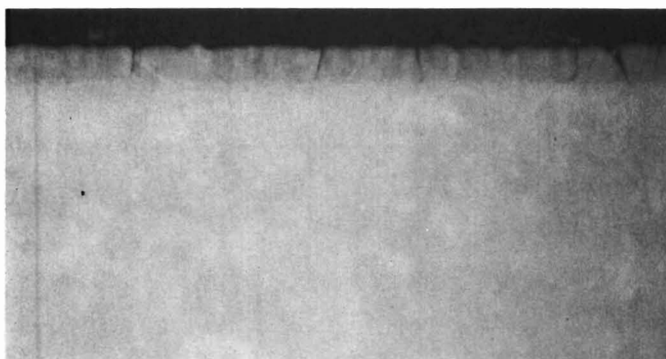


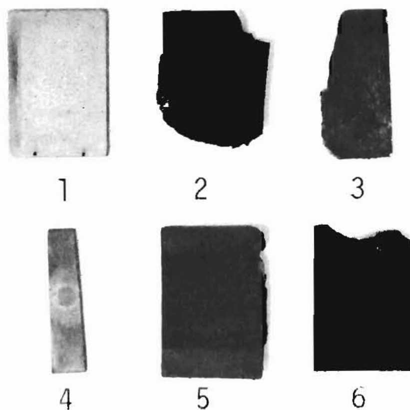


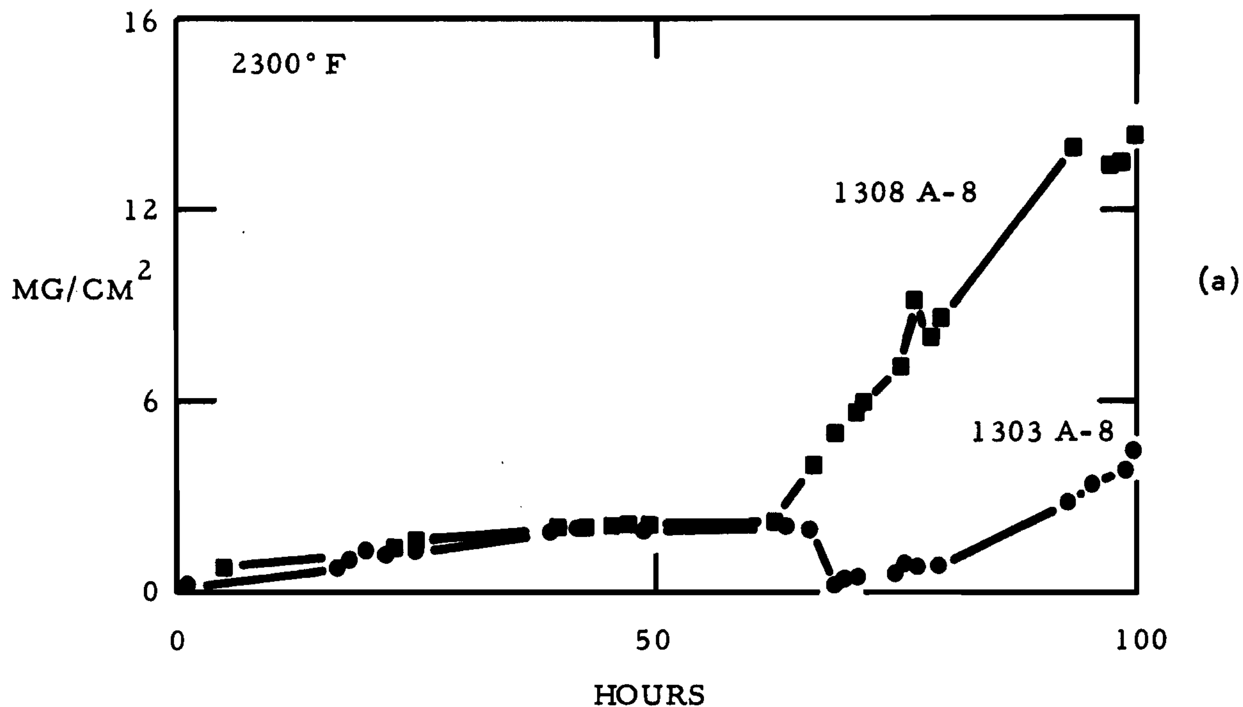
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-7

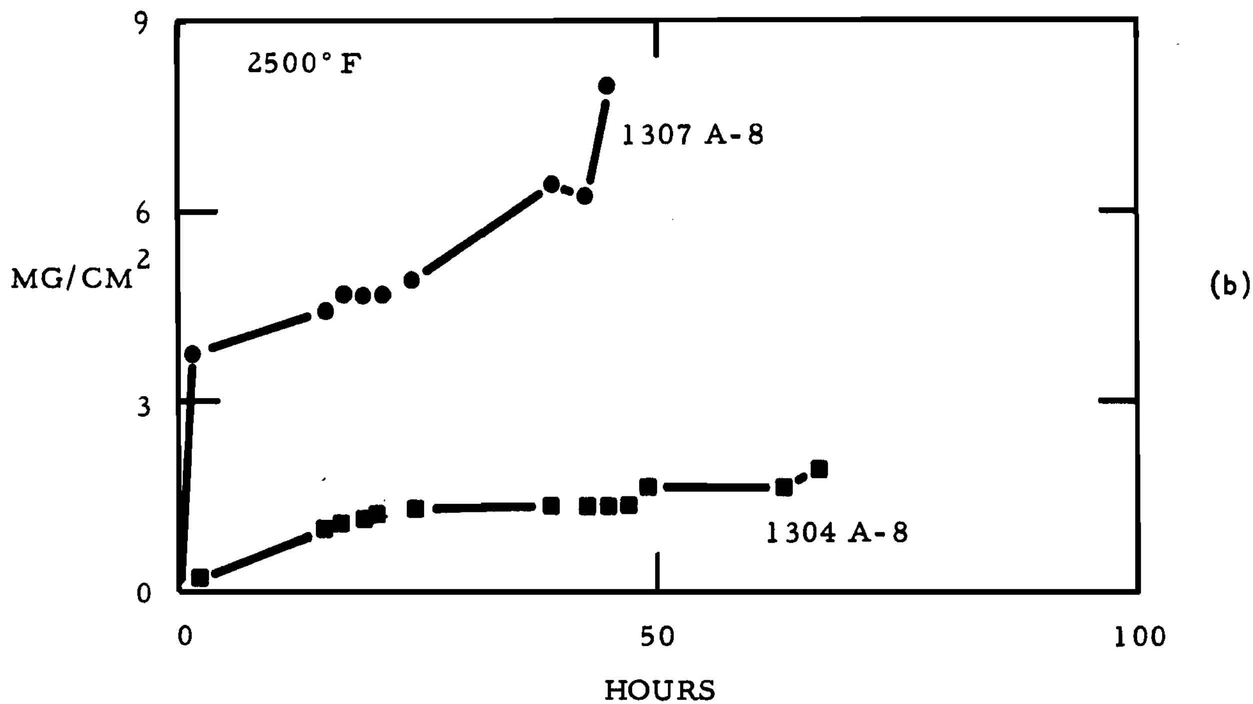
SERIES A-8

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1301	8.0	7.4		
2	1308	8.6	7.6	2300	100
3	1307	9.2	8.4	2500	49
4	1309	8.8	7.4		
5	1303	8.6	9.9	2300	100
6	1304	8.6	9.2	2500	67





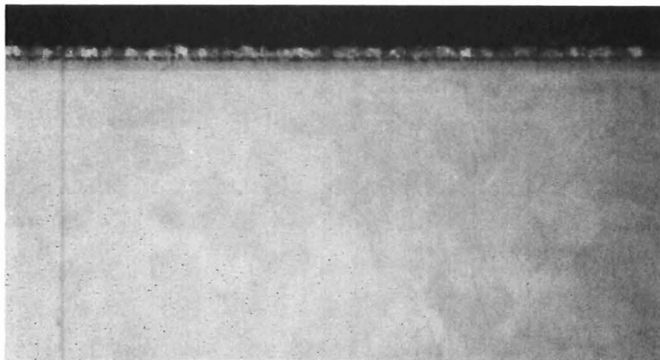


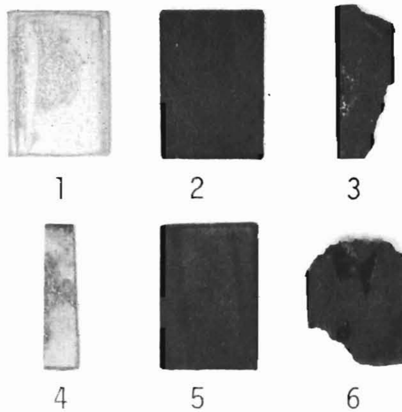


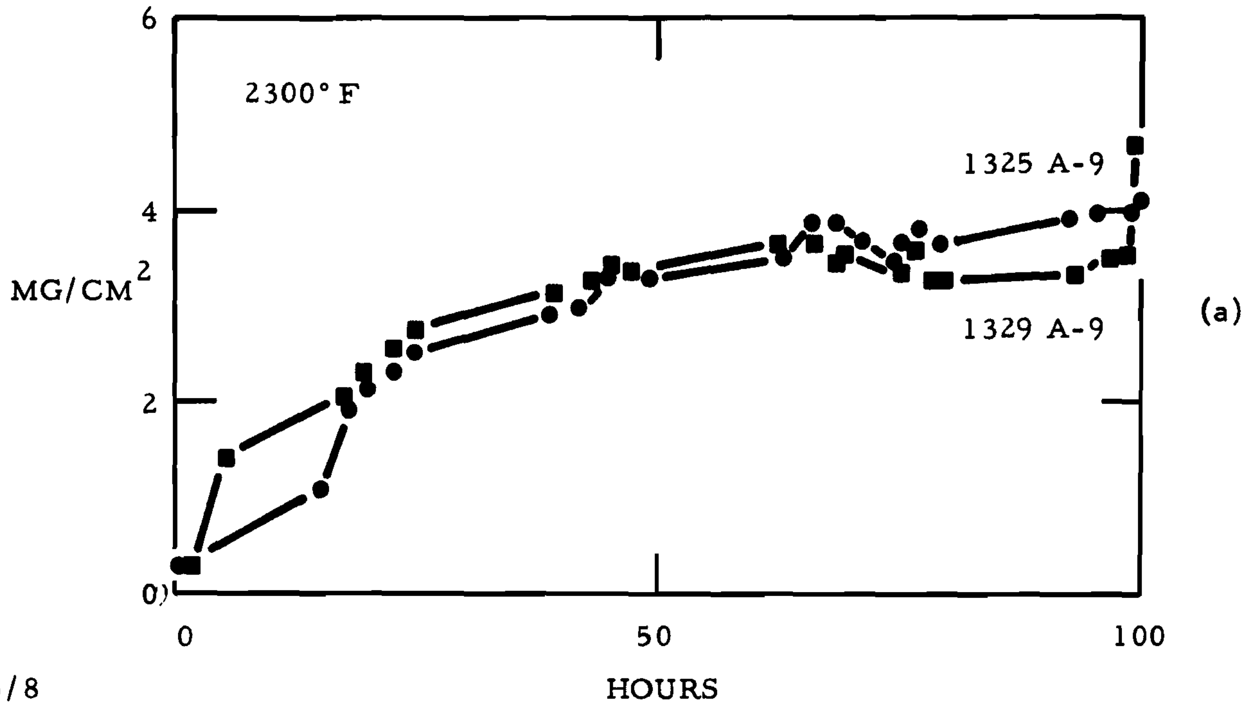
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-8

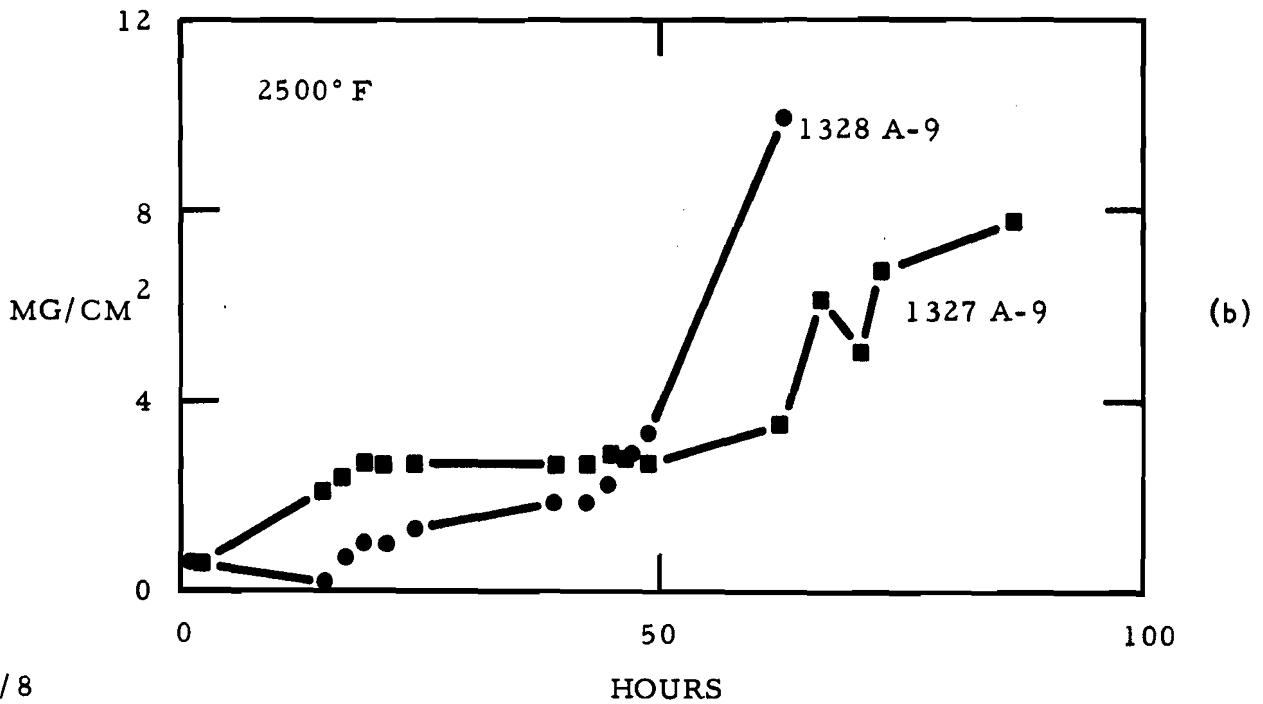
SERIES A-9

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1324	9.5	8.6		
2	1329	10.9	8.5	2300	100
3	1328	10.7	8.8	2500	63
4	1326	10.1	8.3		
5	1325	10.4	8.3	2300	100
6	1327	10.5	9.1	2500	88





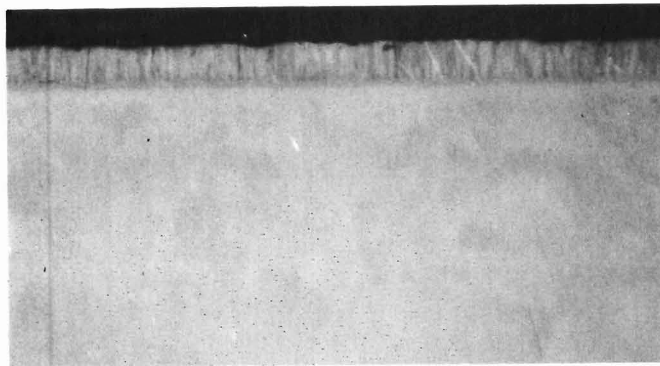


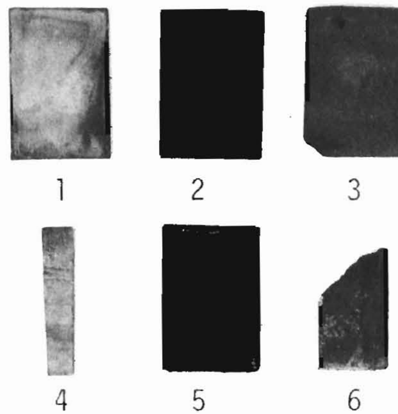


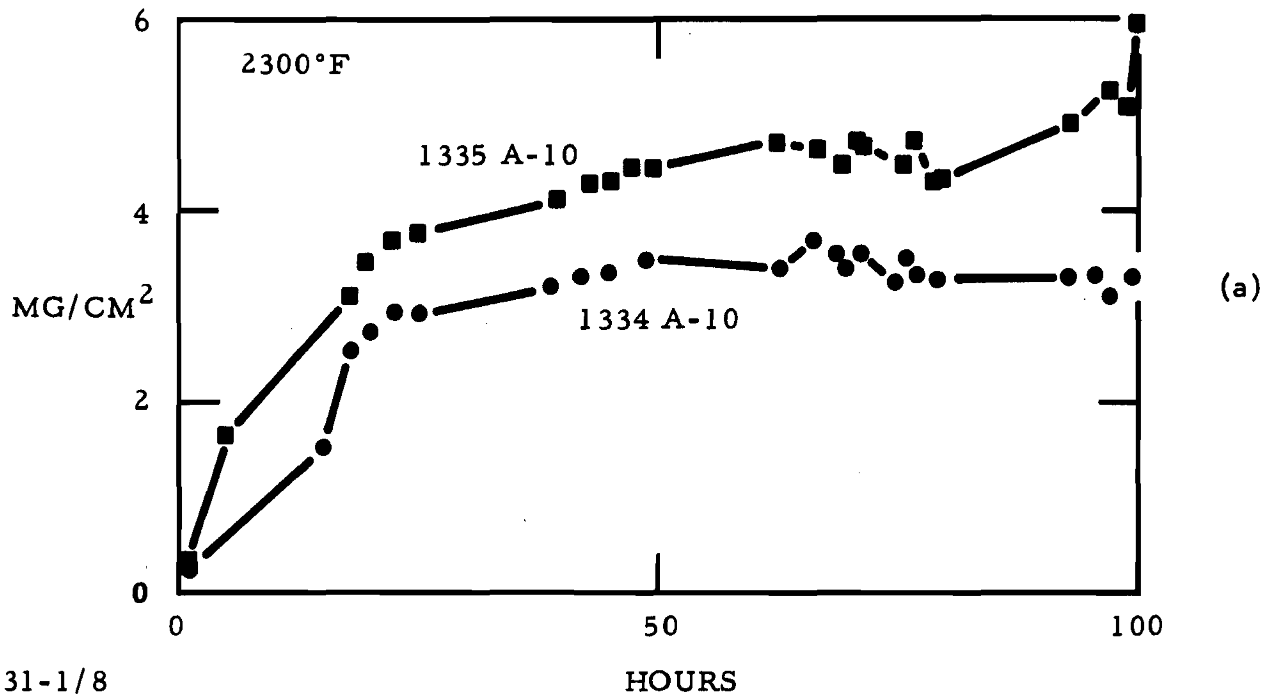
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-9

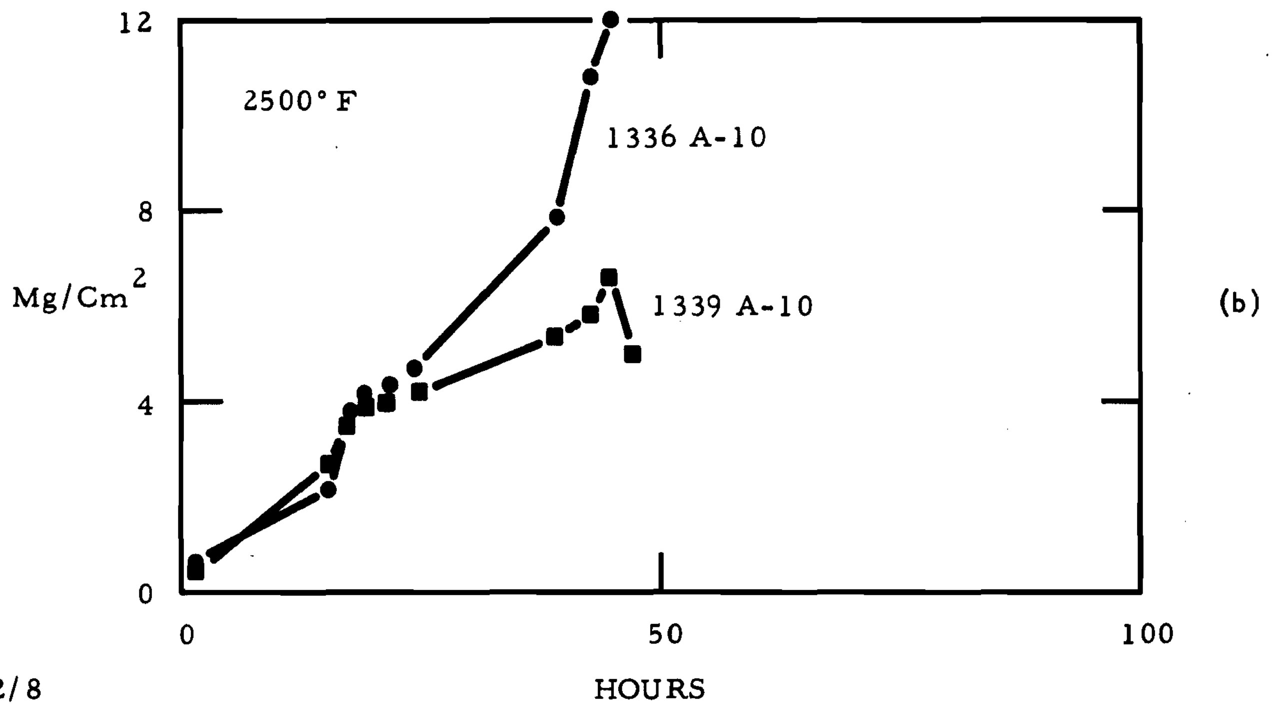
SERIES A-10

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1337	13.4	7.9		
2	1335	14.3	11.9	2300	100
3	1339	12.2	16.4	2500	63
4	1340	11.7	11.3		
5	1334	15.9	10.5	2300	100
6	1336	12.7	16.4	2500	63





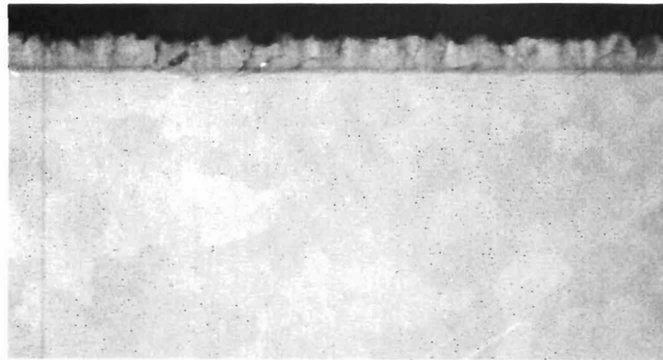


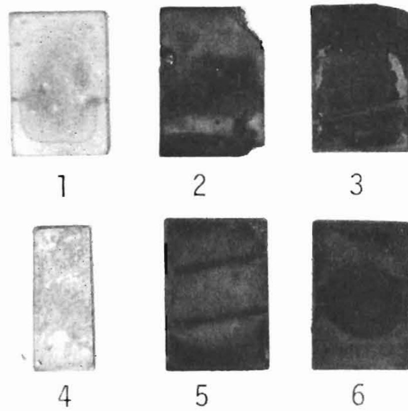


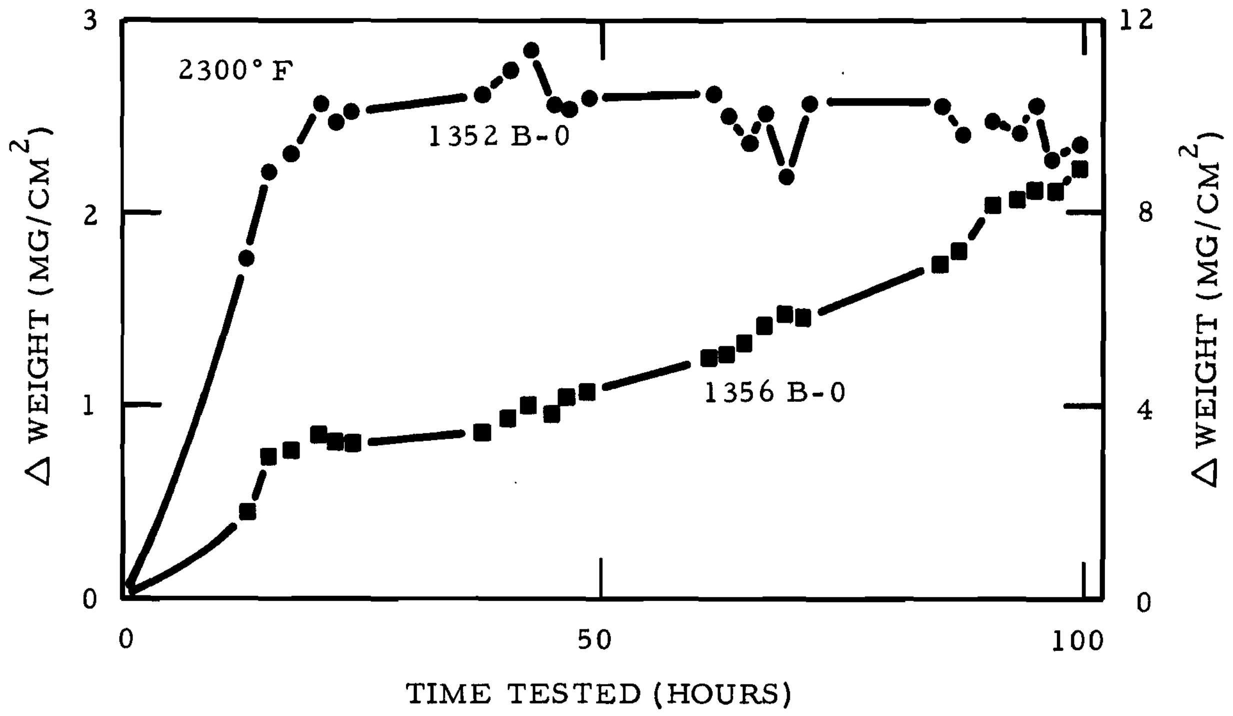
Oxidation Test Results for Ti-Cr-Si Coating (Weight Gain vs Time) Series A-10

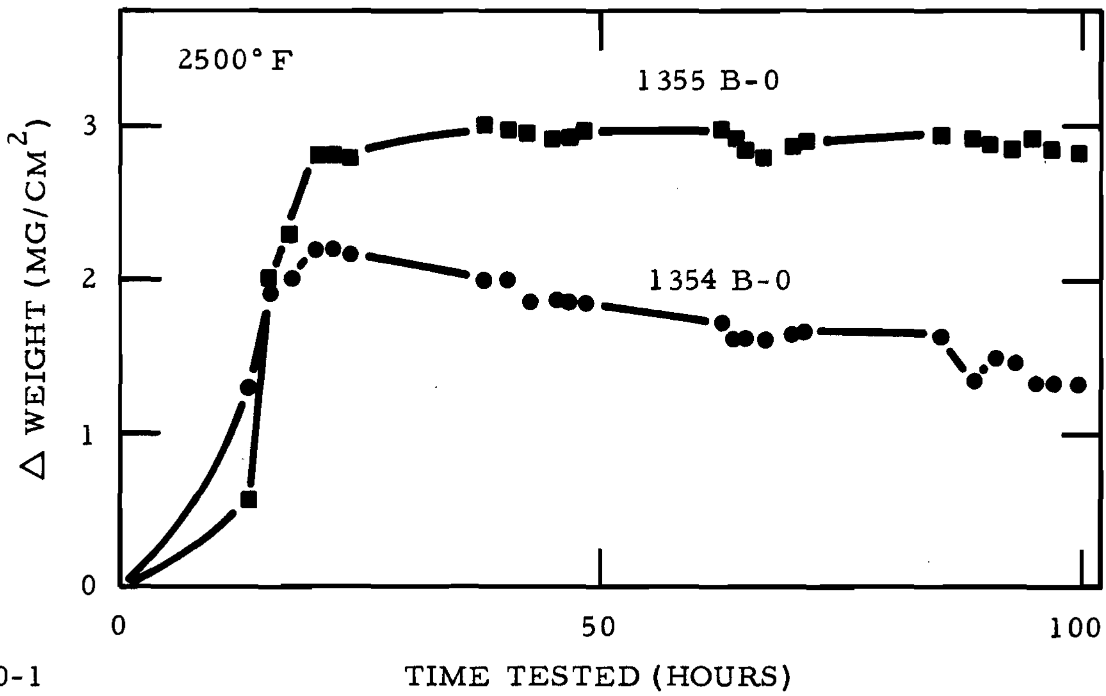
SERIES B-0

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1357	11.7	10.3		
2	1356	11.1	8.9	2300	100
3	1355	11.6	6.7	2500	100
4	1353	10.8	5.9		
5	1352	13.0	6.7	2300	100
6	1354	10.3	7.5	2500	100





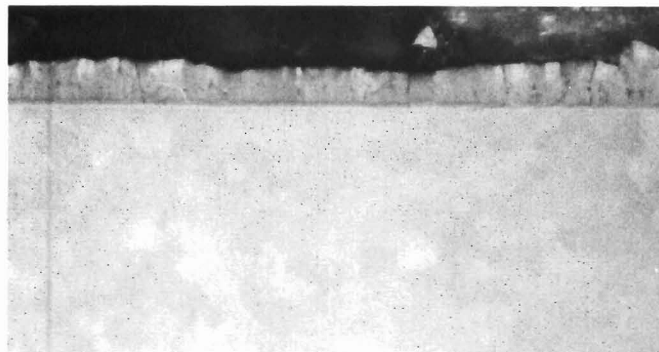


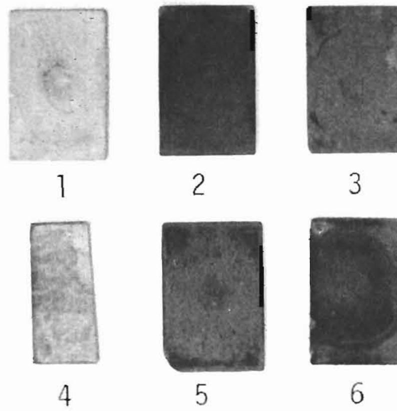


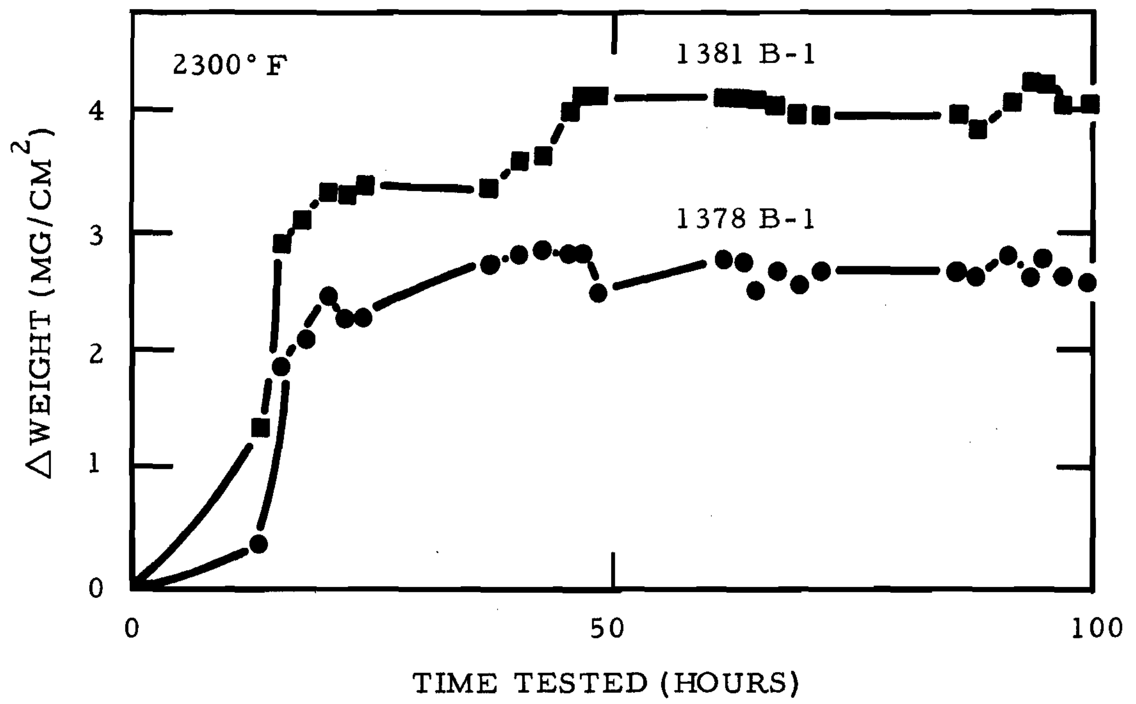
04670-1

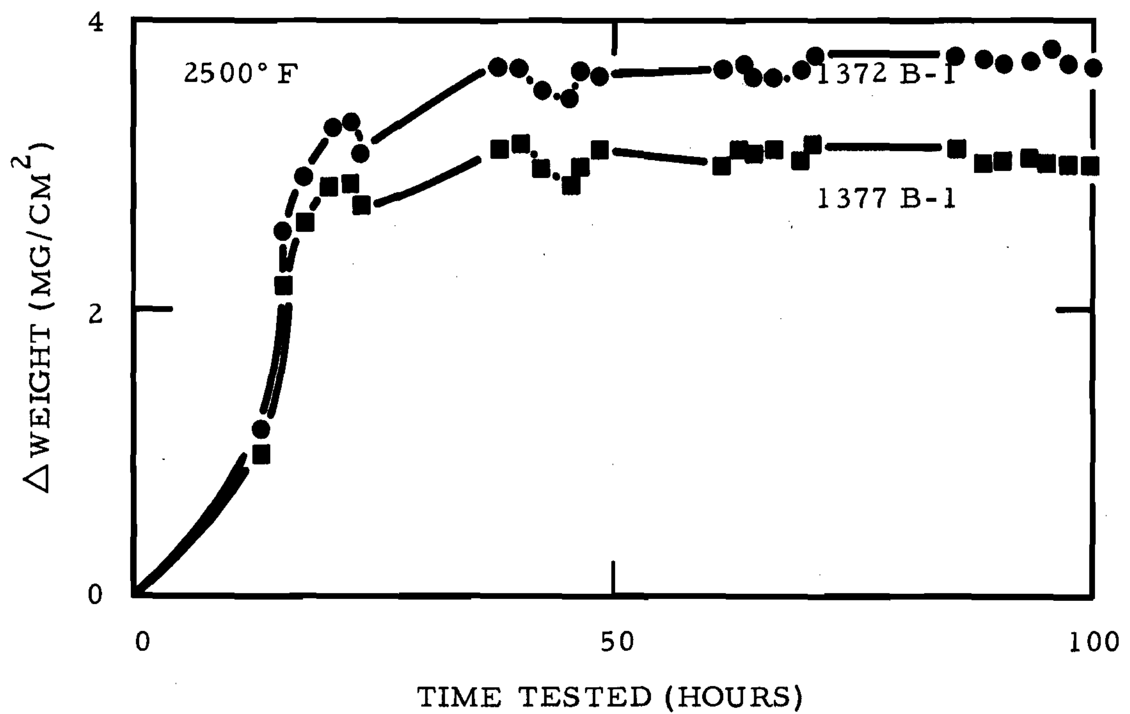
SERIES B-1

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1380	13.6	8.4		
2	1381	13.0	8.0	2300	100
3	1377	12.4	7.0	2500	100
4	1379	12.8	8.0		
5	1378	12.7	8.3	2300	100
6	1372	13.6	7.8	2500	100





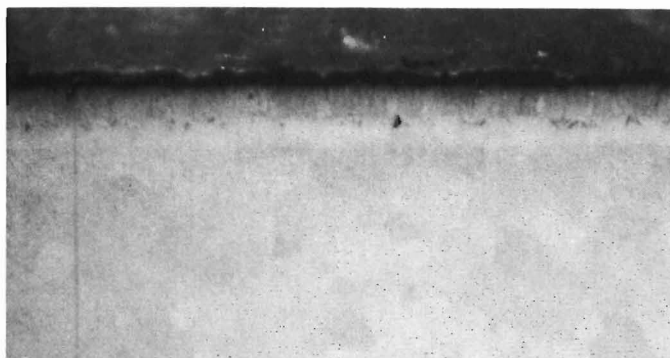


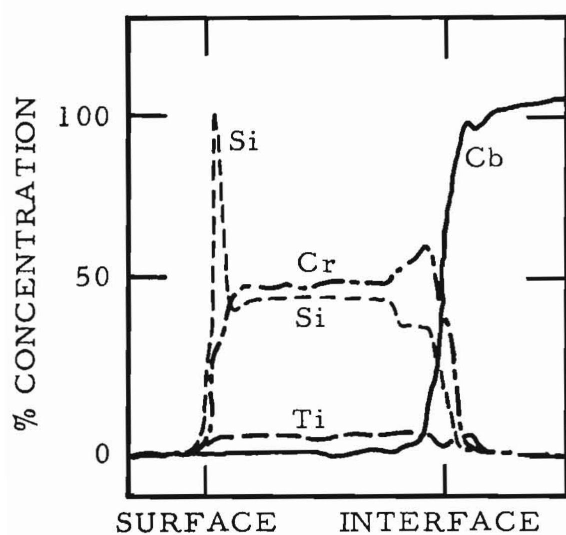


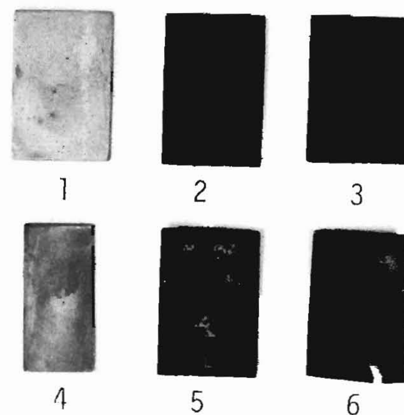
04670-2

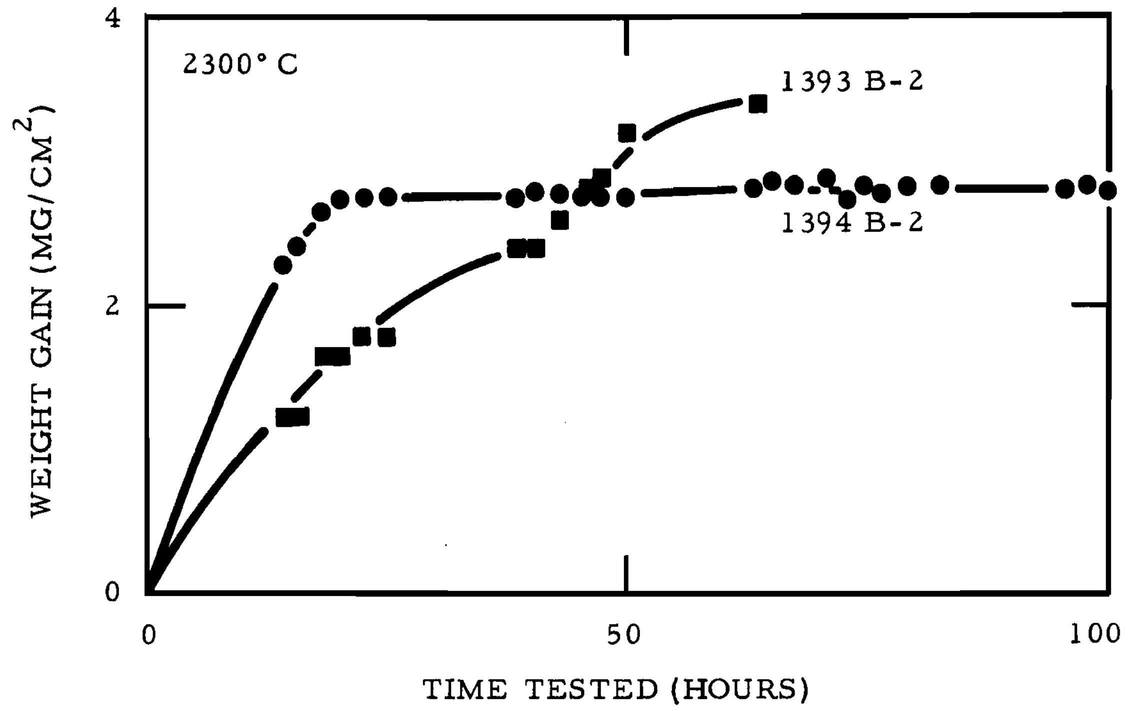
SERIES B-2

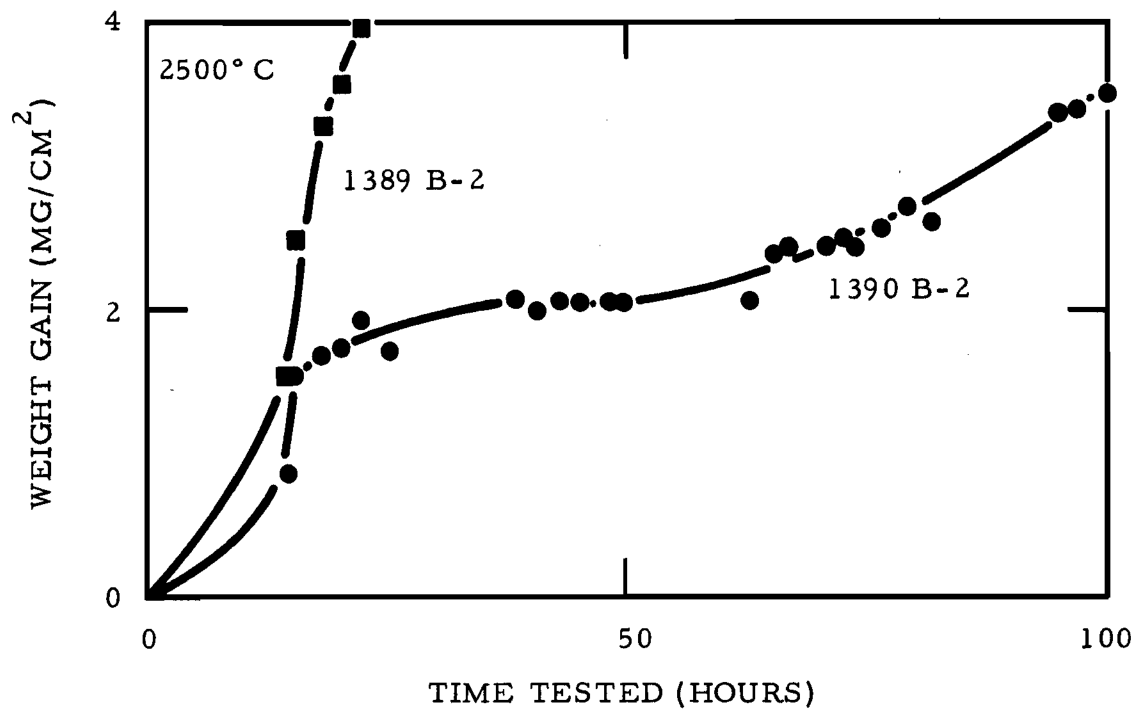
No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1395	15.0	10.4		
2	1394	12.6	8.7	2300	100
3	1390	13.4	7.3	2500	100
4	1391	12.0	7.8		
5	1393	10.2	6.7	2300	68
6	1389	8.8	7.4	2500	38







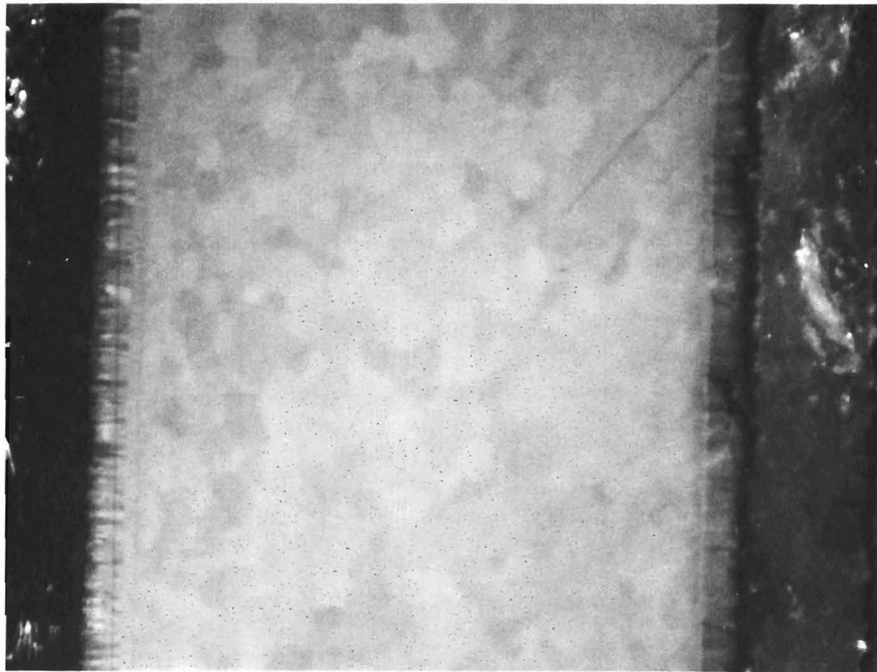


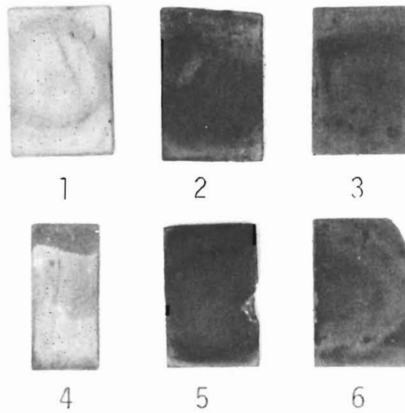


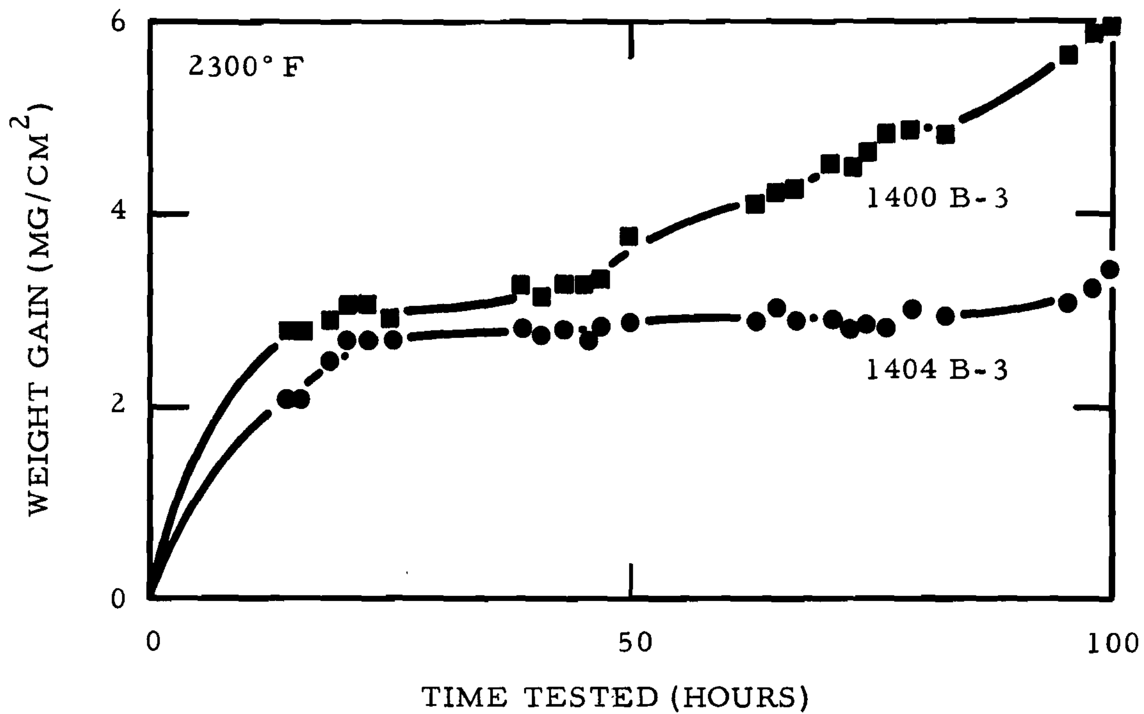
04670-3

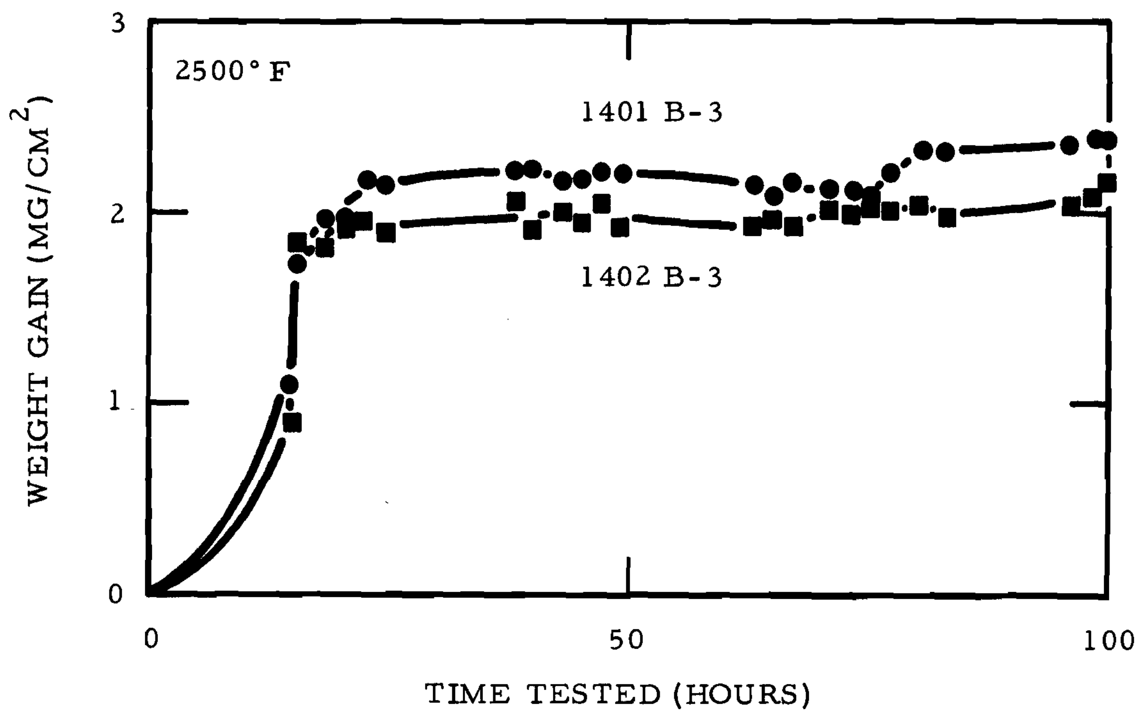
SERIES B-3

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1403	9.6	10.5		
2	1404	10.2	11.5	2300	100
3	1402	8.4	8.1	2500	100
4	1398	9.0	10.7		
5	1400	8.4	9.1	2300	100
6	1401	11.4	7.0	2500	100





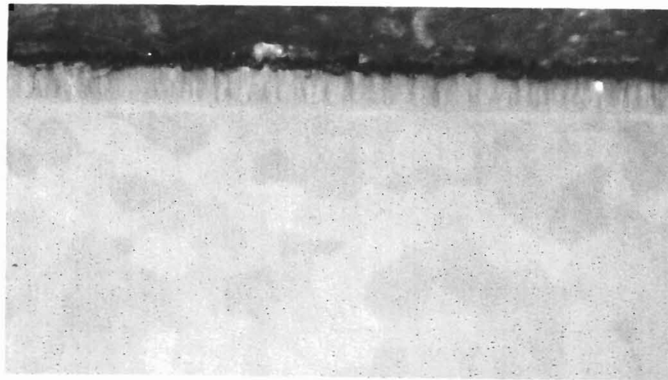


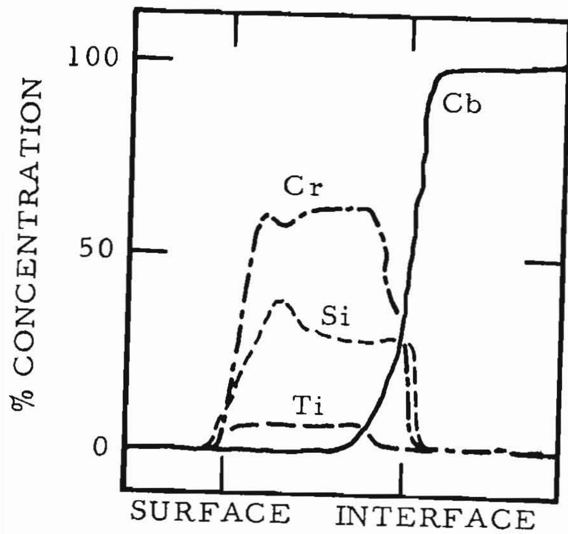


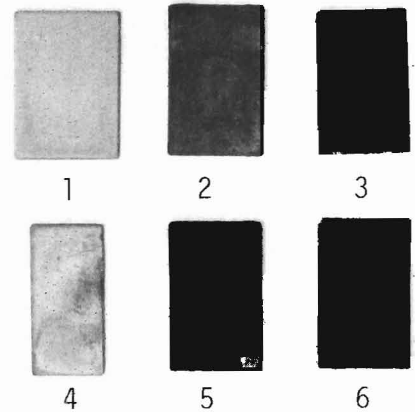
04670-4

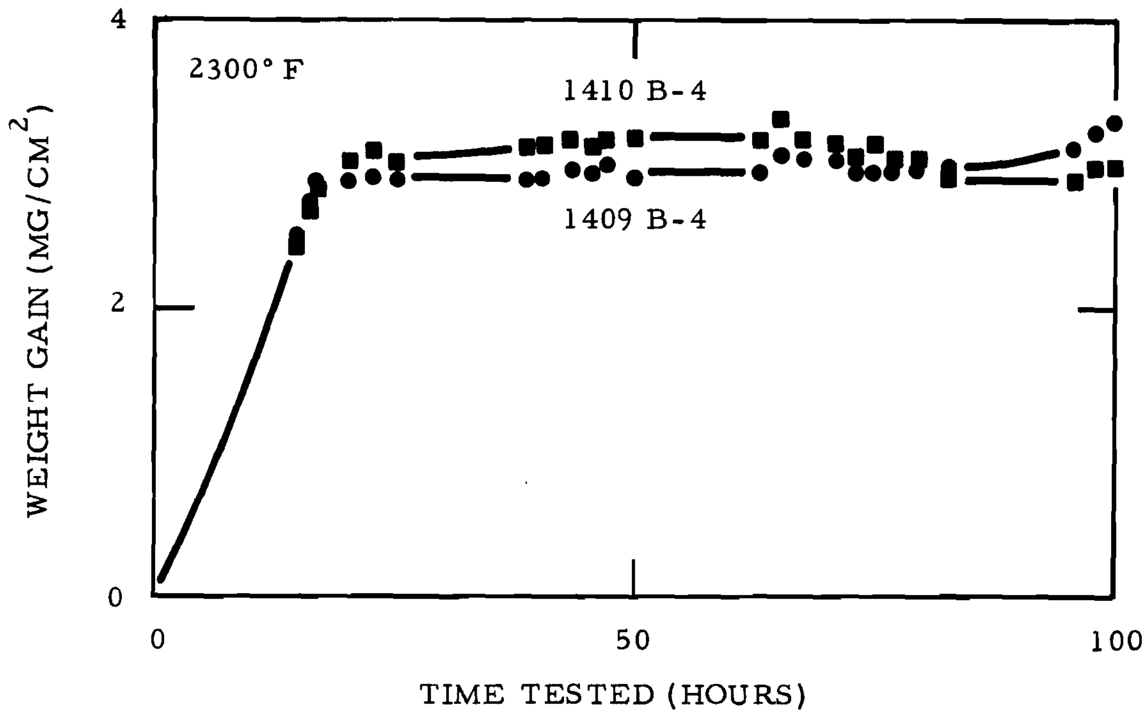
SERIES B-4

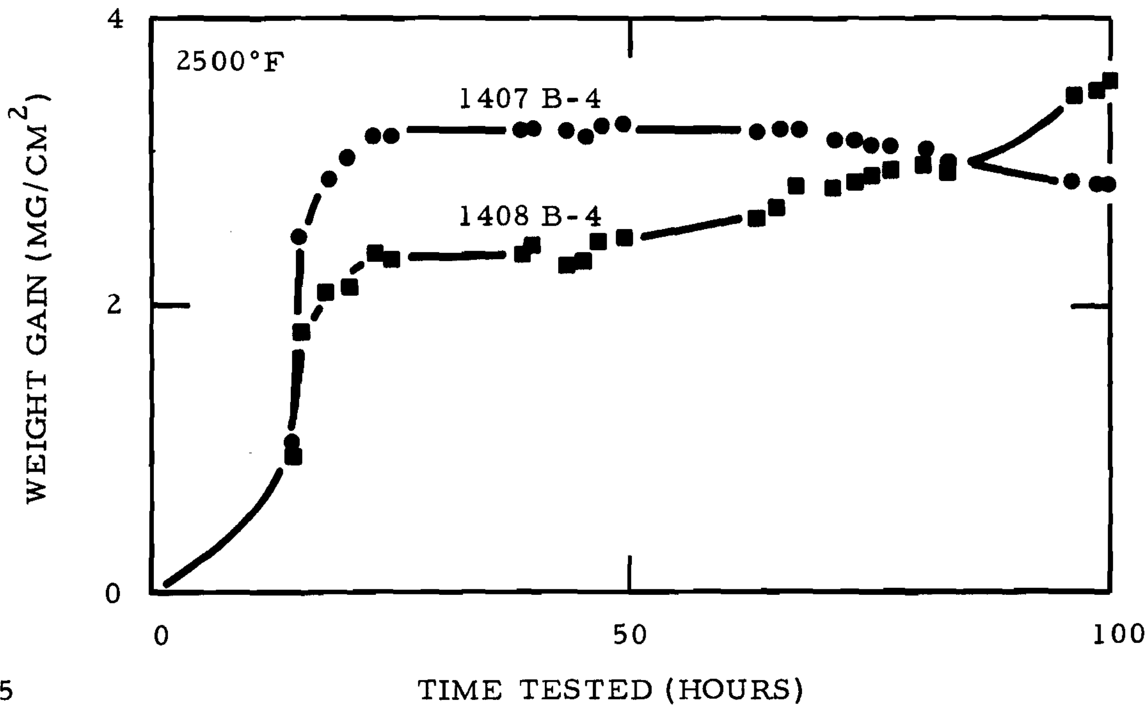
No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1412	10.6	10.1		
2	1410	9.8	10.1	2300	100
3	1408	8.8	10.1	2500	100
4	1411	10.5	7.6		
5	1409	9.5	11.6	2300	100
6	1407	10.3	8.6	2500	100







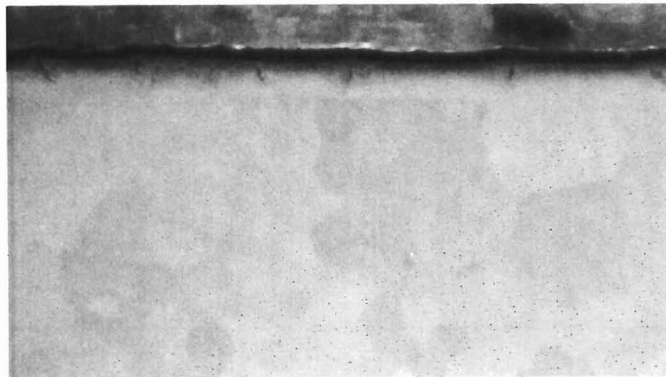


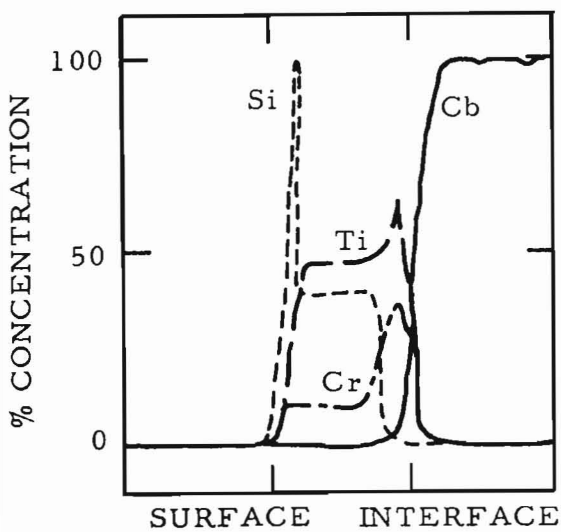


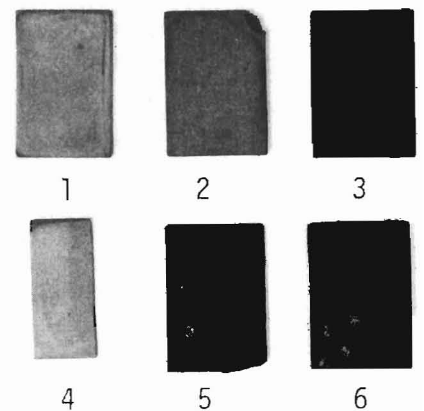
04670-5

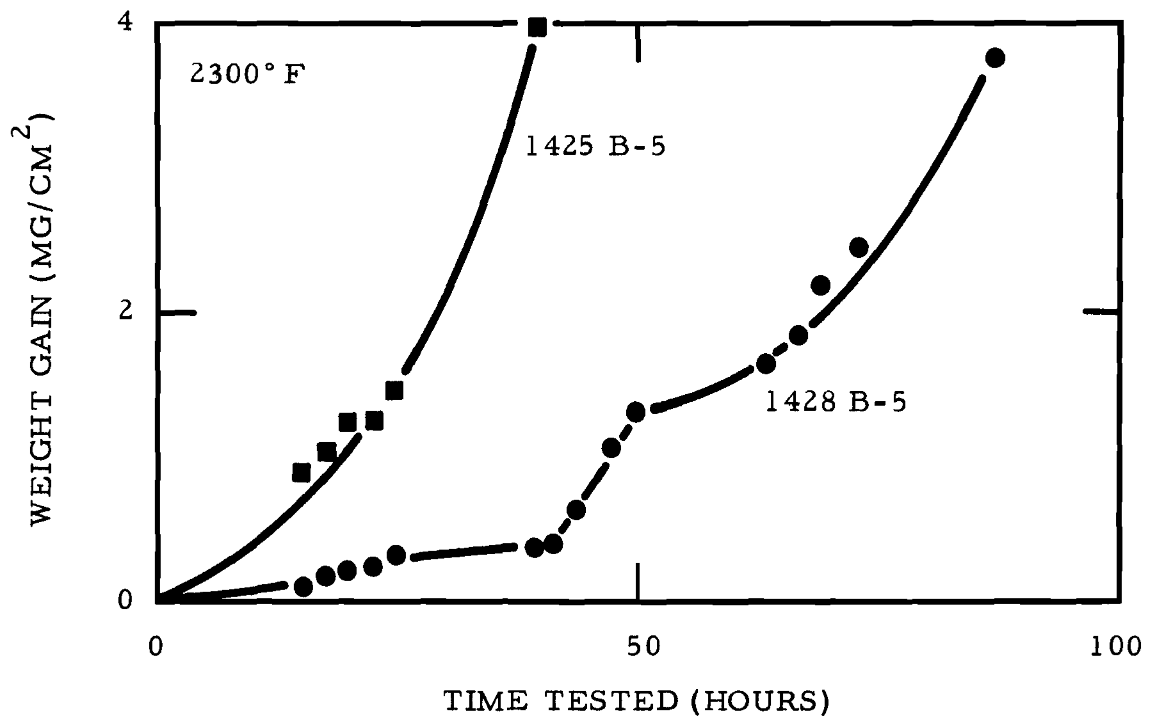
SERIES B-5

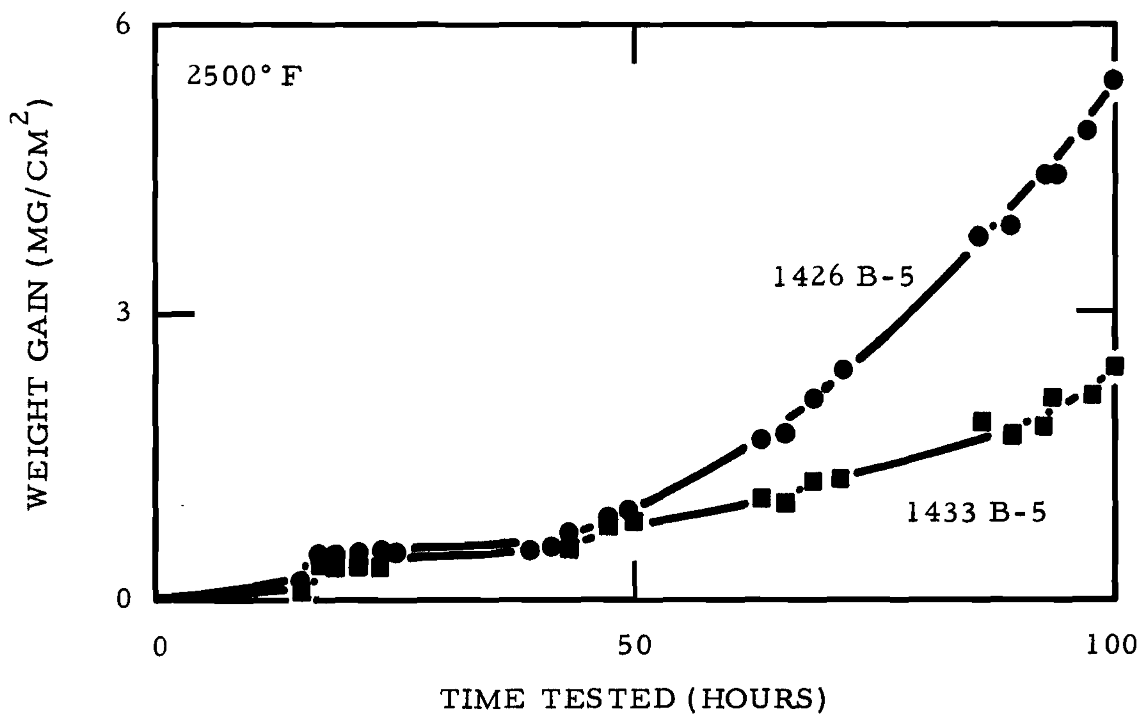
No.	Run No.	Average Weight Cr-Ti (mg/cm²)	Average Weight Si (mg/cm²)	Test Temperature (°C)	Time Tested (hours)
1	1427	9.2	4.4		
2	1428	9.7	5.2	2300	87
3	1433	10.8	6.8	2500	100
4	1434	8.4	3.2		
5	1425	10.3	5.8	2300	40
6	1426	9.4	7.4	2500	100







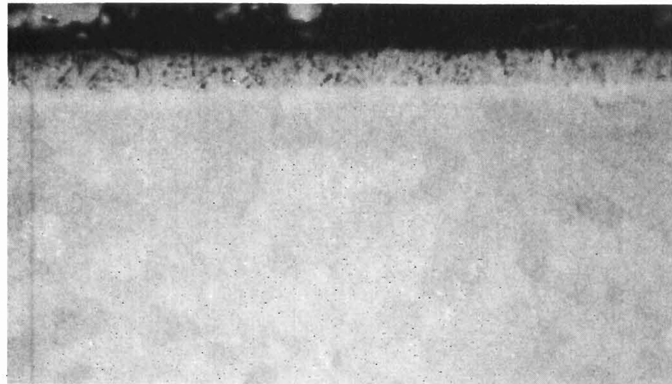


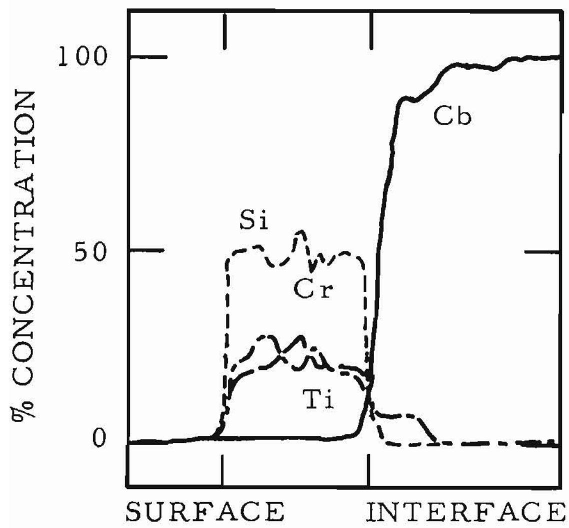


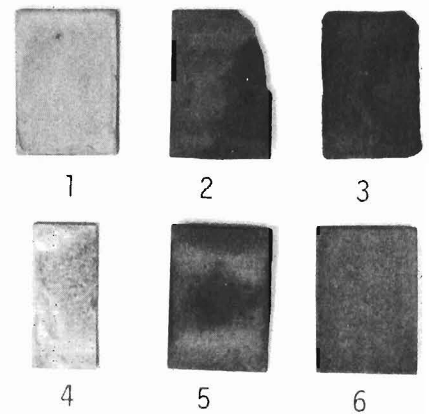
04670-6

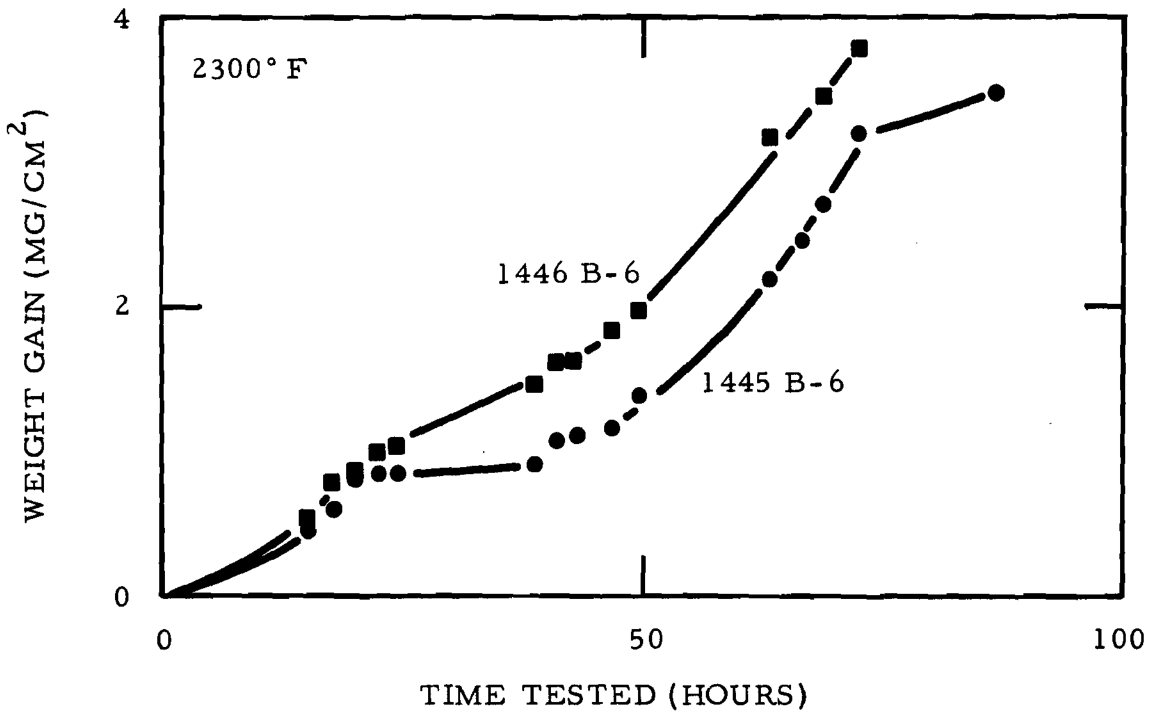
SERIES B-6

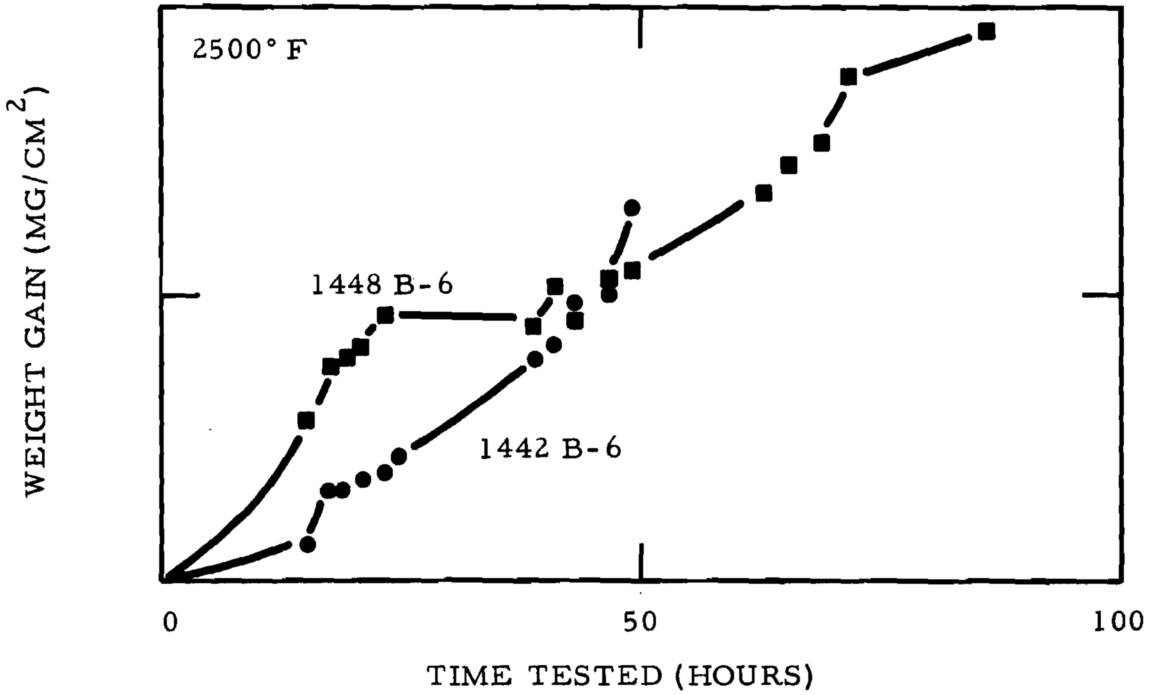
No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1443	10.4	3.8		
2	1446	8.2	6.3	2300	86
3	1448	8.3	8.6	2500	86
4	1444	10.1	4.6		
5	1445	8.3	8.4	2300	92
6	1442	9.9	6.9	2500	63







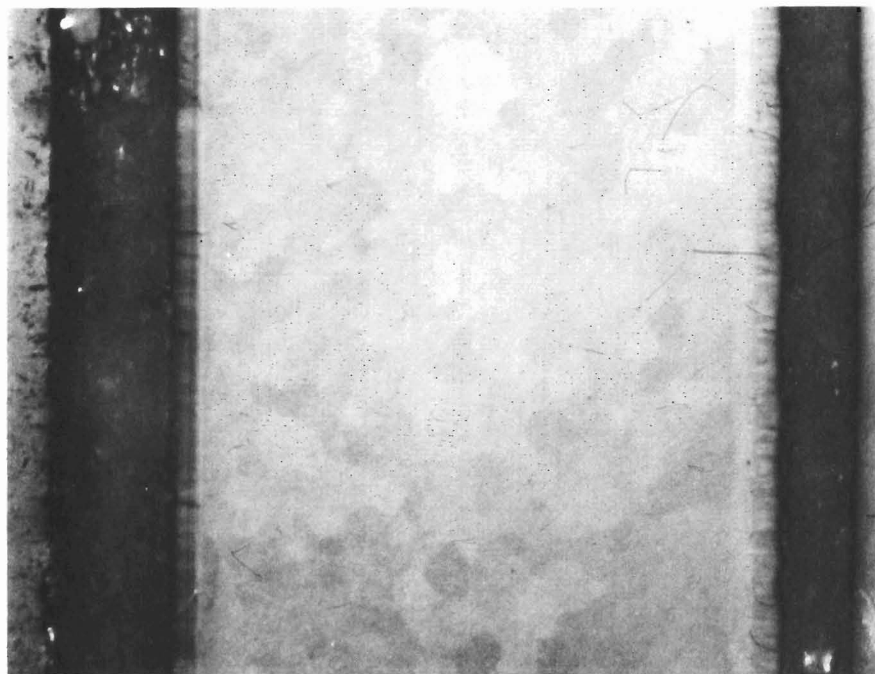


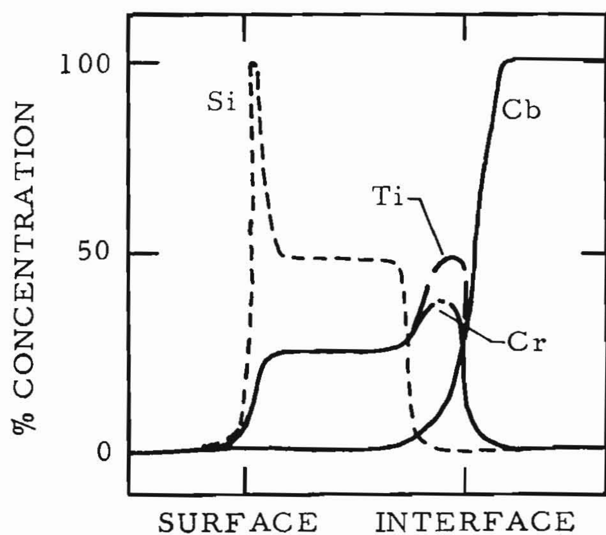


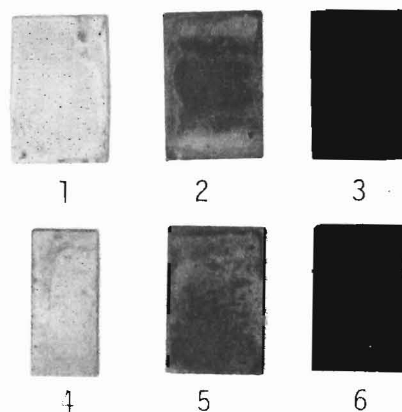
04670-7

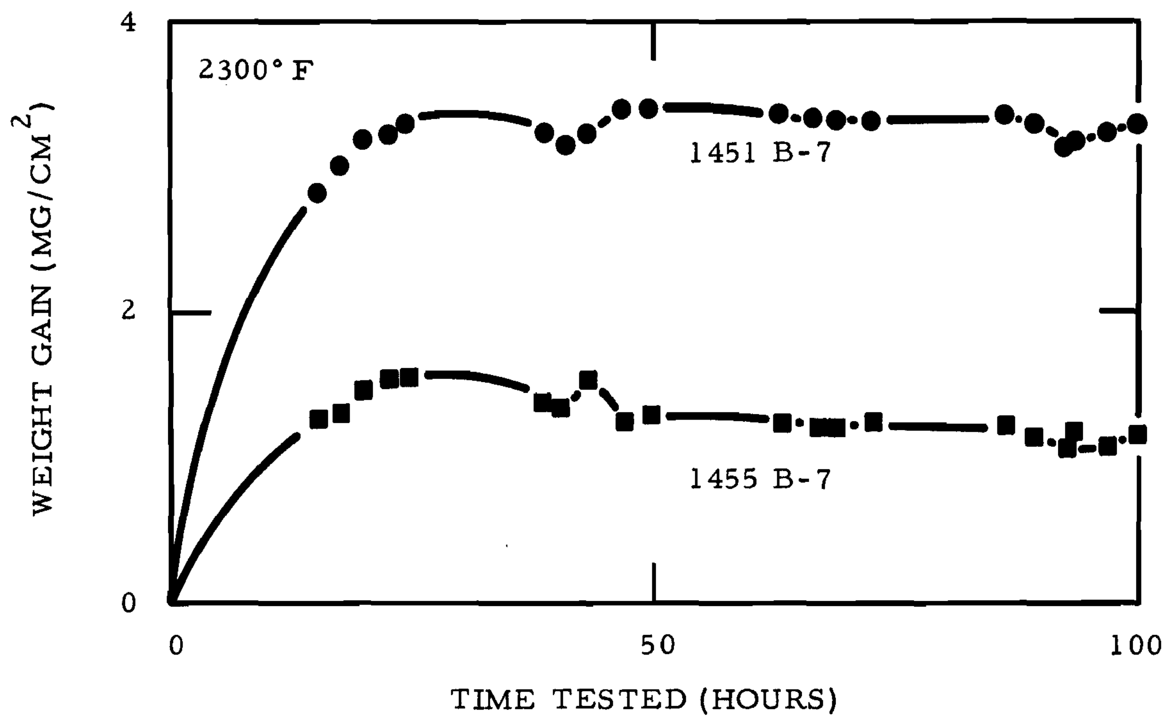
SERIES B-7

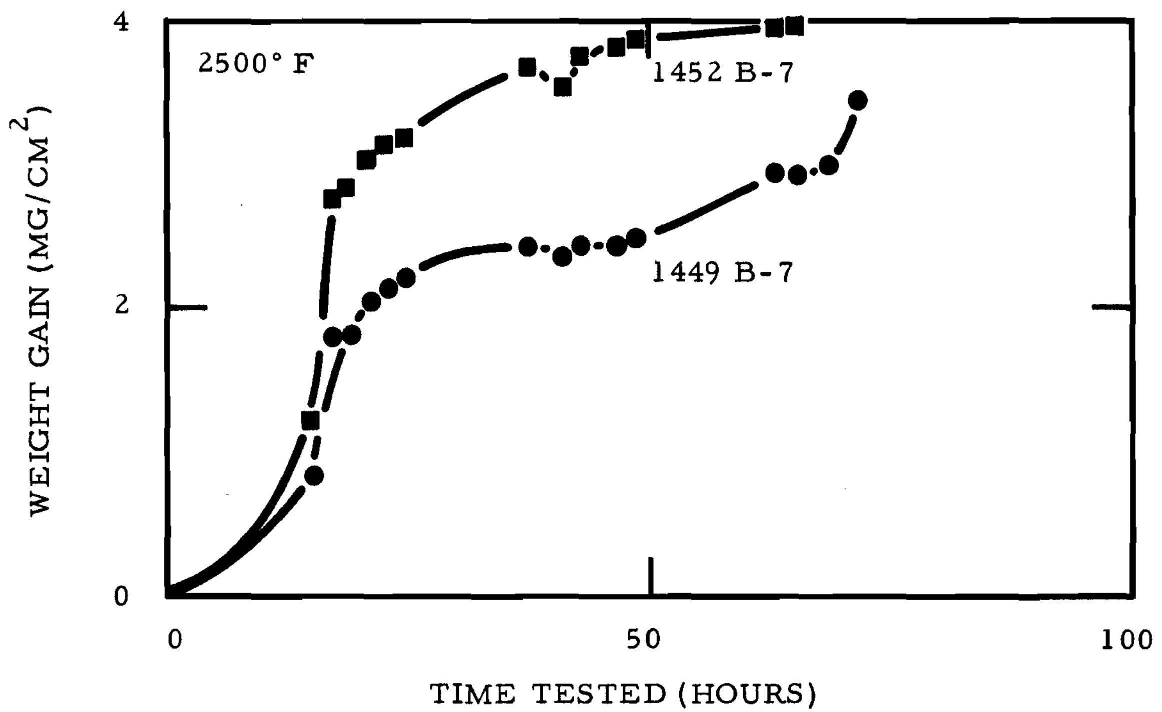
No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1454	9.0	5.2		
2	1455	8.9	6.7	2300	100
3	1452	10.3	9.1	2500	86
4	1453	9.5	6.8		
5	1451	8.9	11.2	2300	100
6	1449	8.1	7.4	2500	86







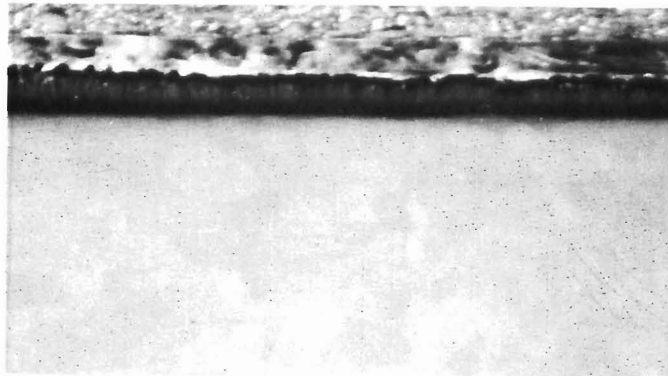


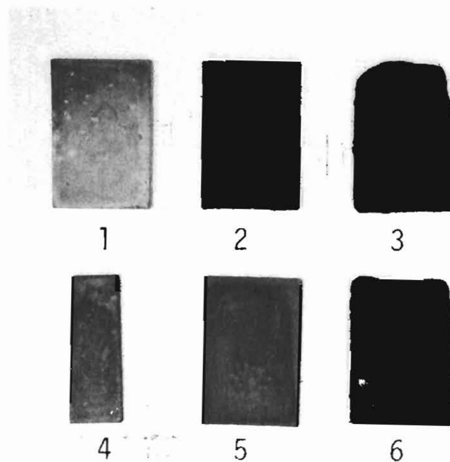


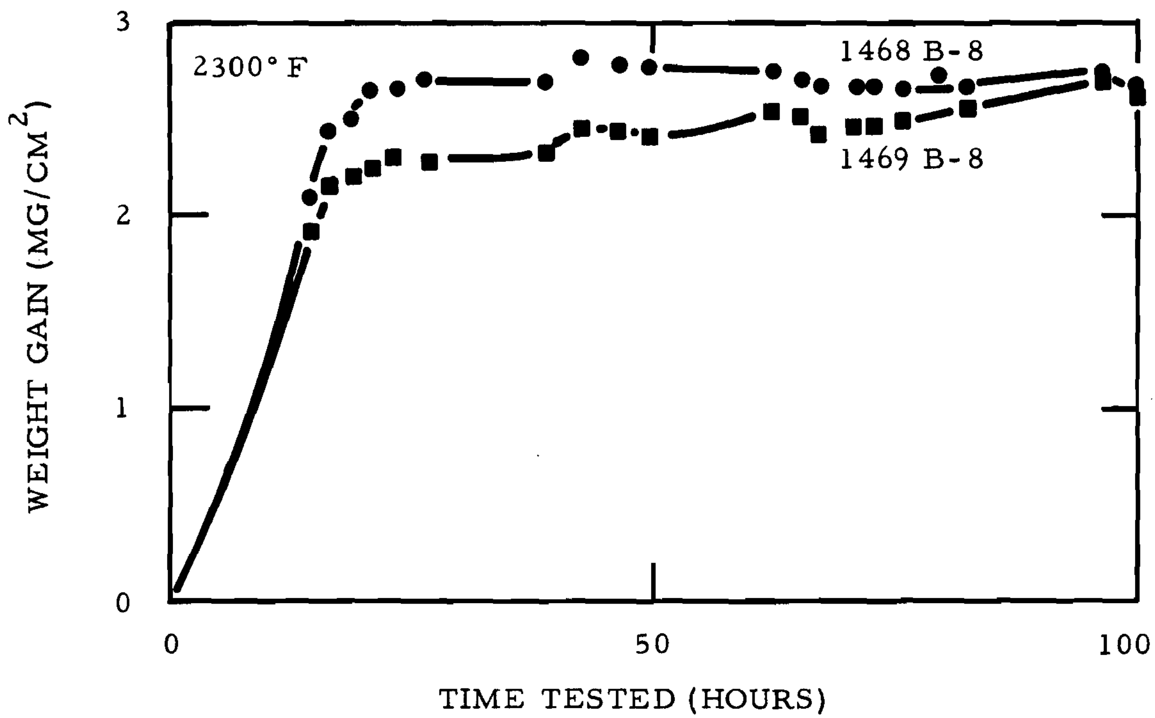
04670-8

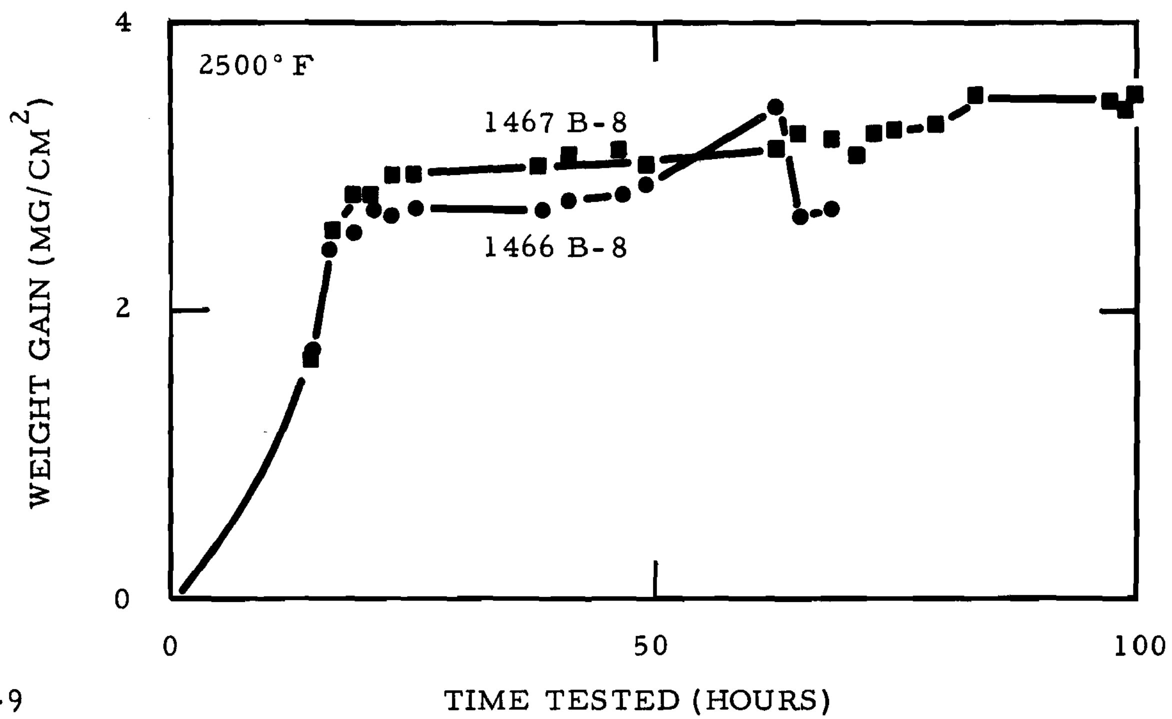
SERIES B-8

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1465	10.0	8.7		
2	1469	8.0	7.9	2300	100
3	1466	8.8	9.1	2500	73
4	1464	10.0	5.1		
5	1468	9.3	8.1	2300	100
6	1467	8.1	8.3	2500	100





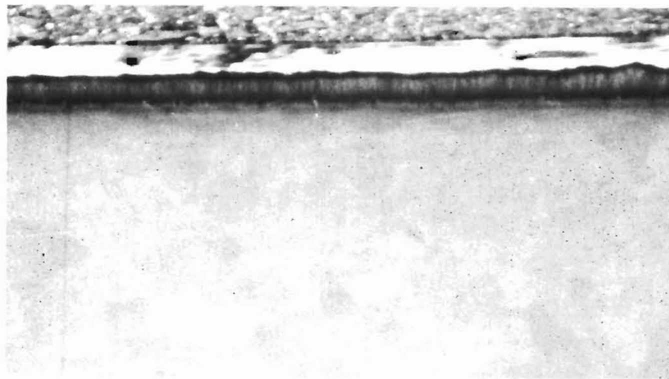


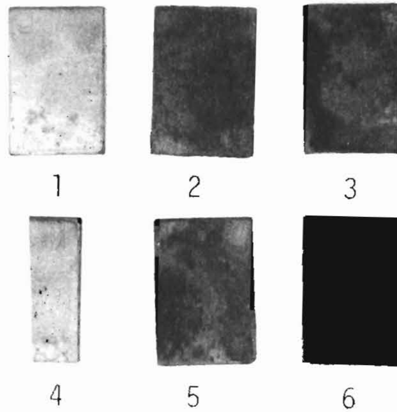


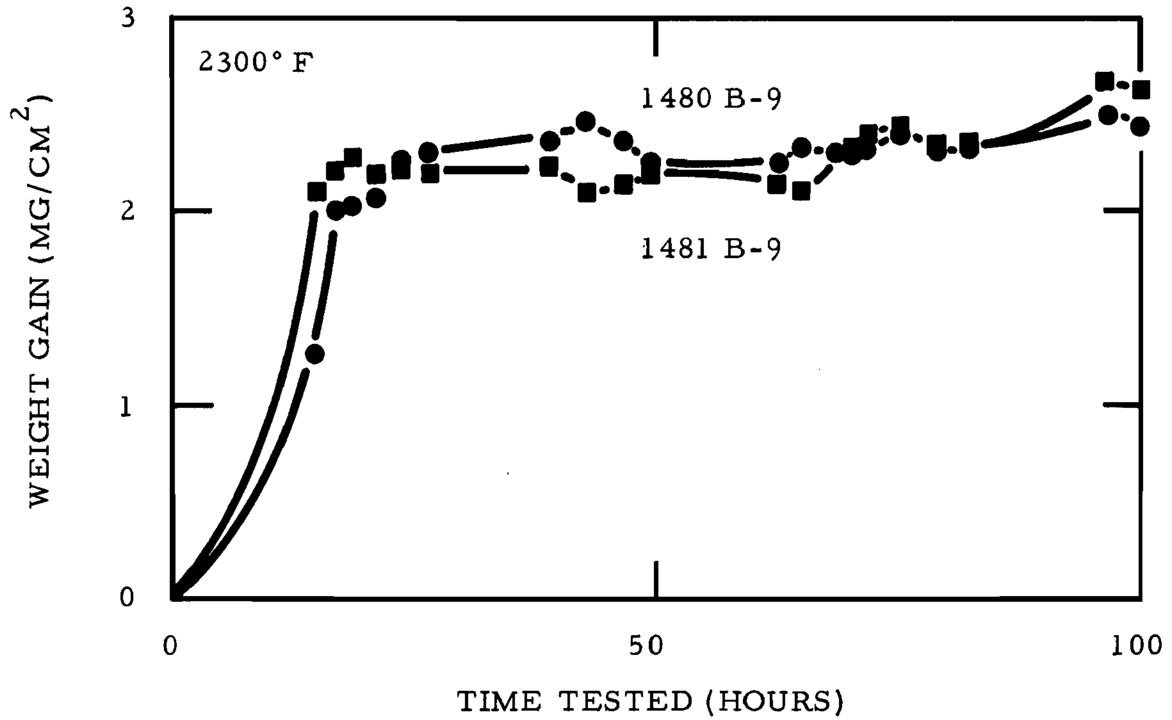
04670-9

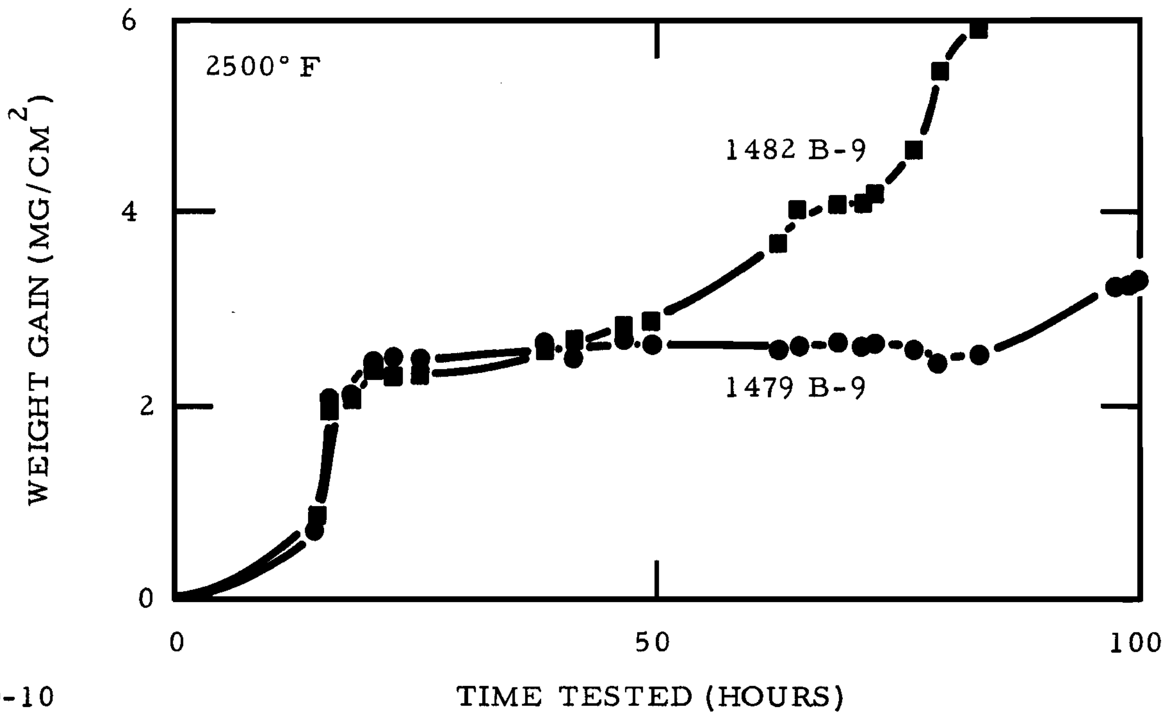
<u>SERIES B-9</u>

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1476	8.0	3.1		
2	1481	8.1	7.7	2300	100
3	1482	8.2	7.8	2500	83
4	1478	9.6	4.6		
5	1480	8.8	6.9	2300	100
6	1479	8.4	6.6	2500	100





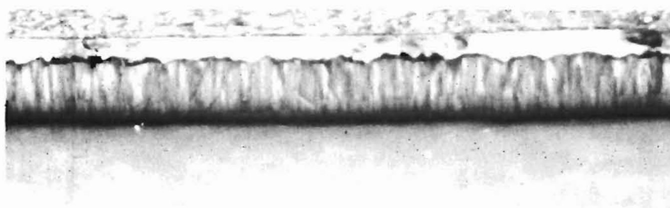


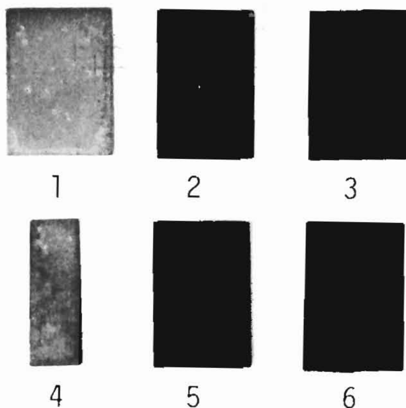


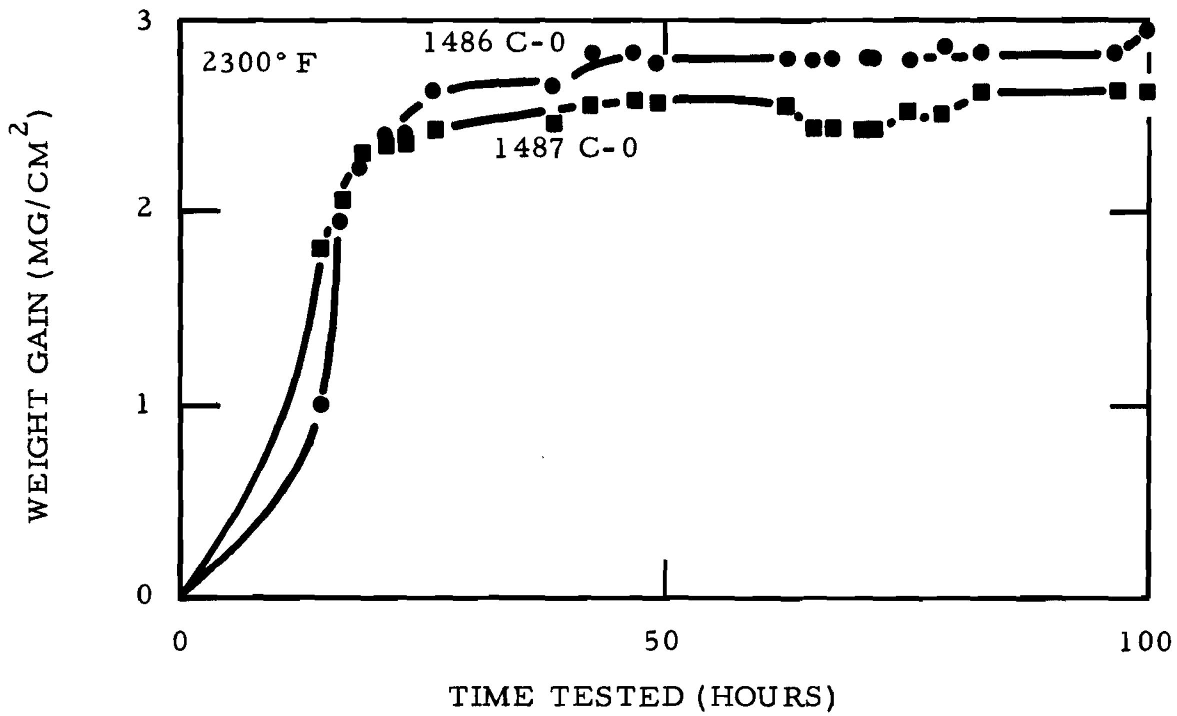
04670-10

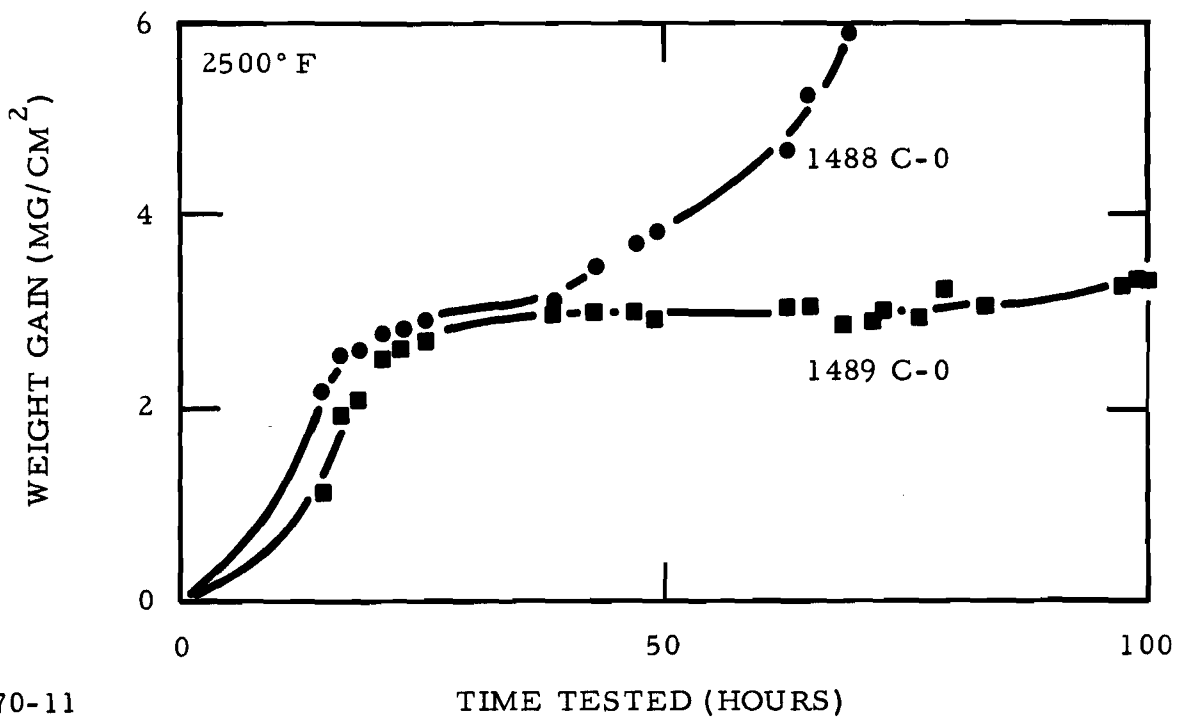
SERIES C-0

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1484	10.8	11.3		
2	1487	8.9	9 9	2300	100
3	1489	8.5	11.7	2500	100
4	1485	9.7	9.3		
5	1486	9.3	9.8	2300	100
6	1488	9.0	9.8	2500	73





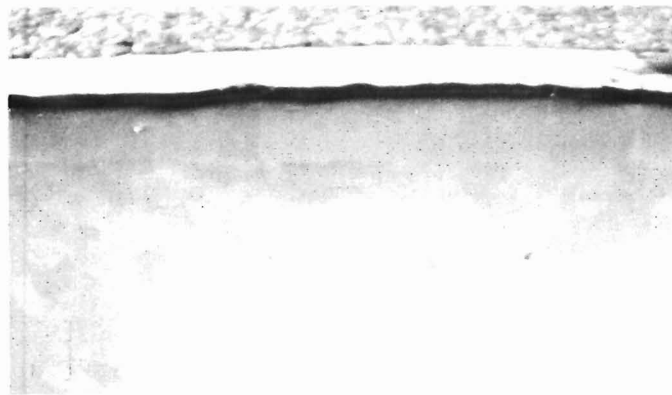


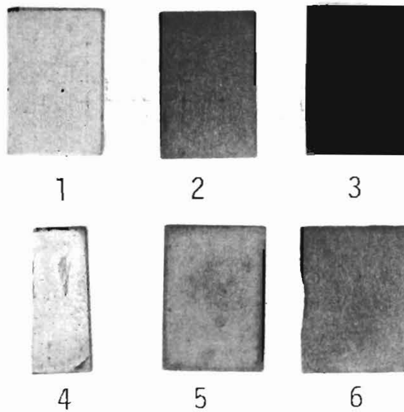


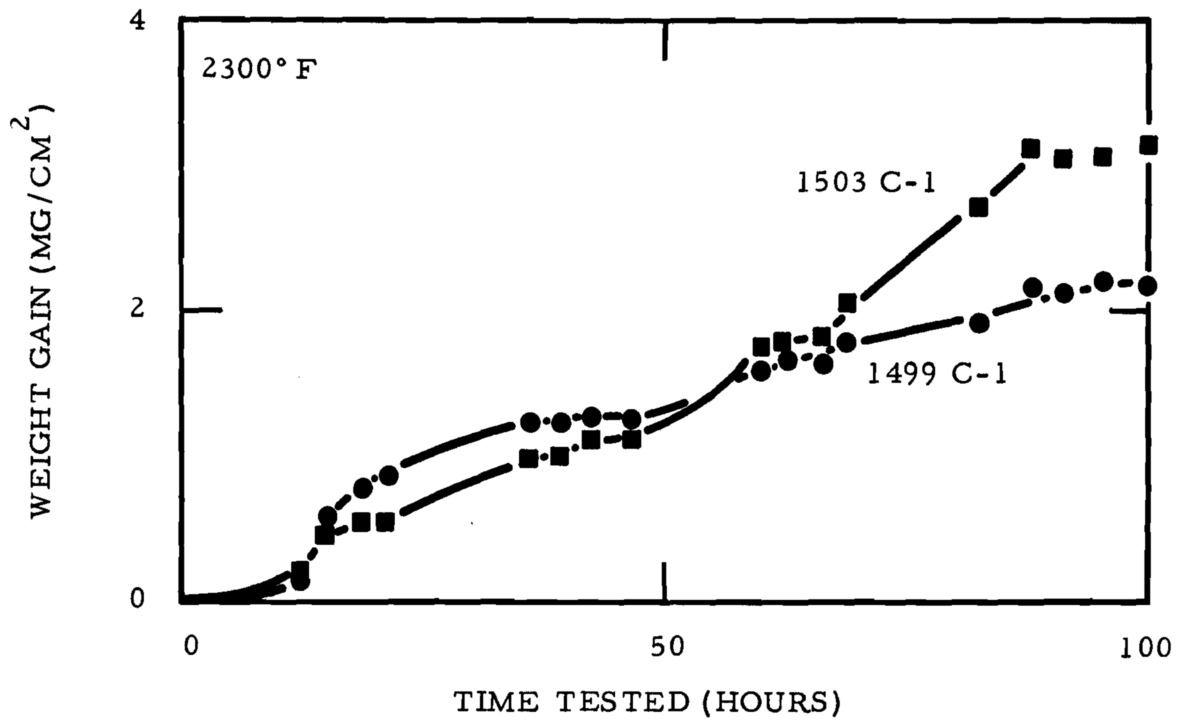
04670-11

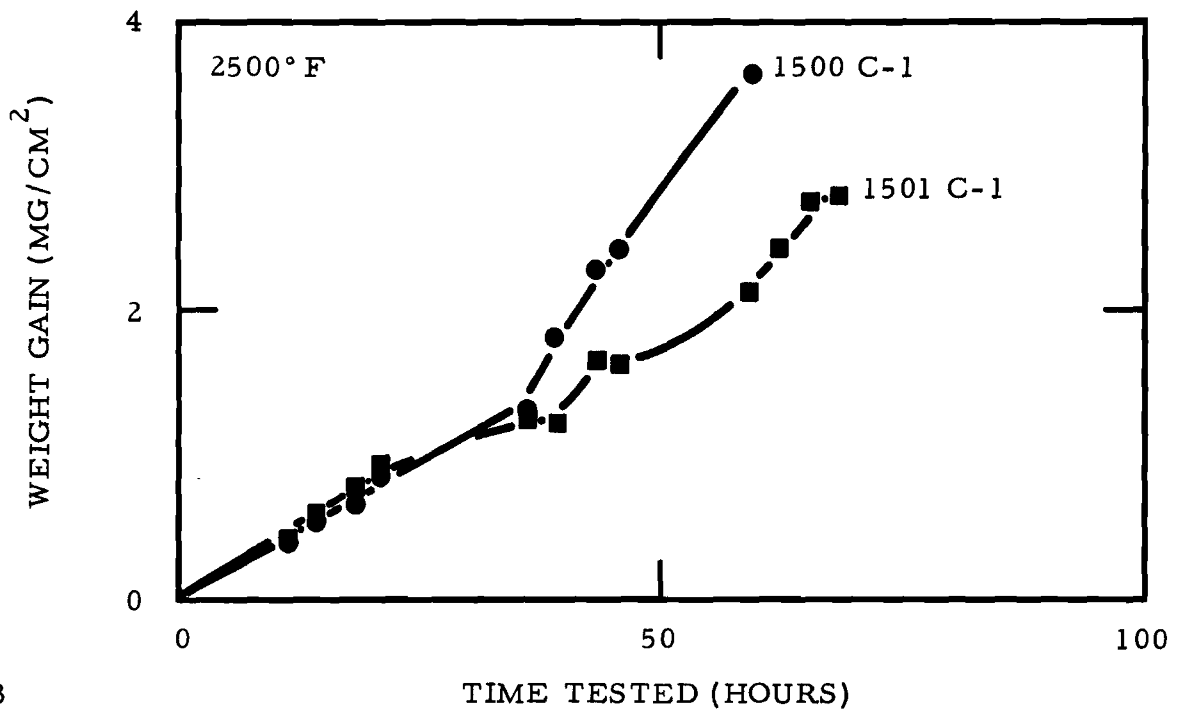
SERIES C-1

No.	Run No.	Average Weight Cr-Ti (mg/cm²)	Average Weight Si (mg/cm²)	Test Temperature (°C)	Time Tested (hours)
1	1502	7.5	3.5		
2	1503	6.6	2.5	2300	100
3	1501	8.7	5.3	2500	83
4	1498	9.8	4.3		
5	1499	9.6	4.2	2300	100
6	1500	9.5	5.2	2500	60





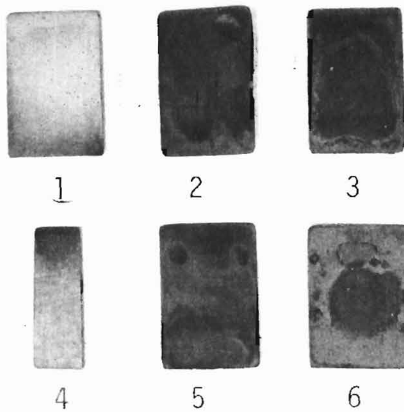


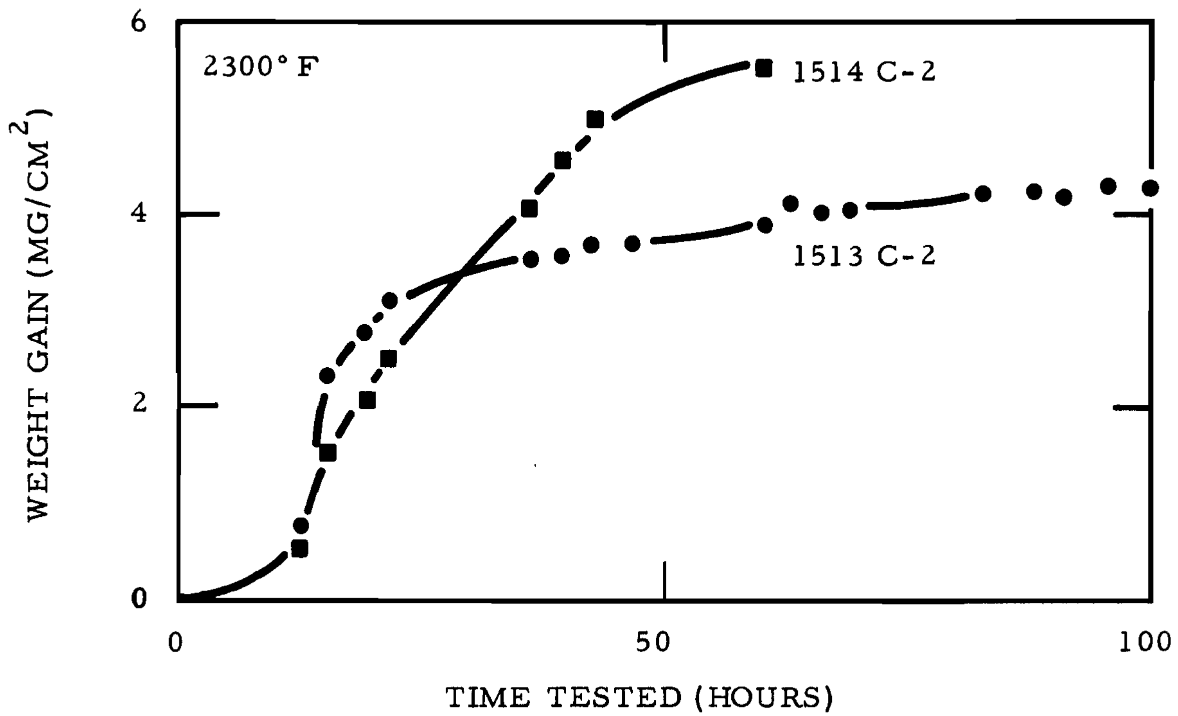


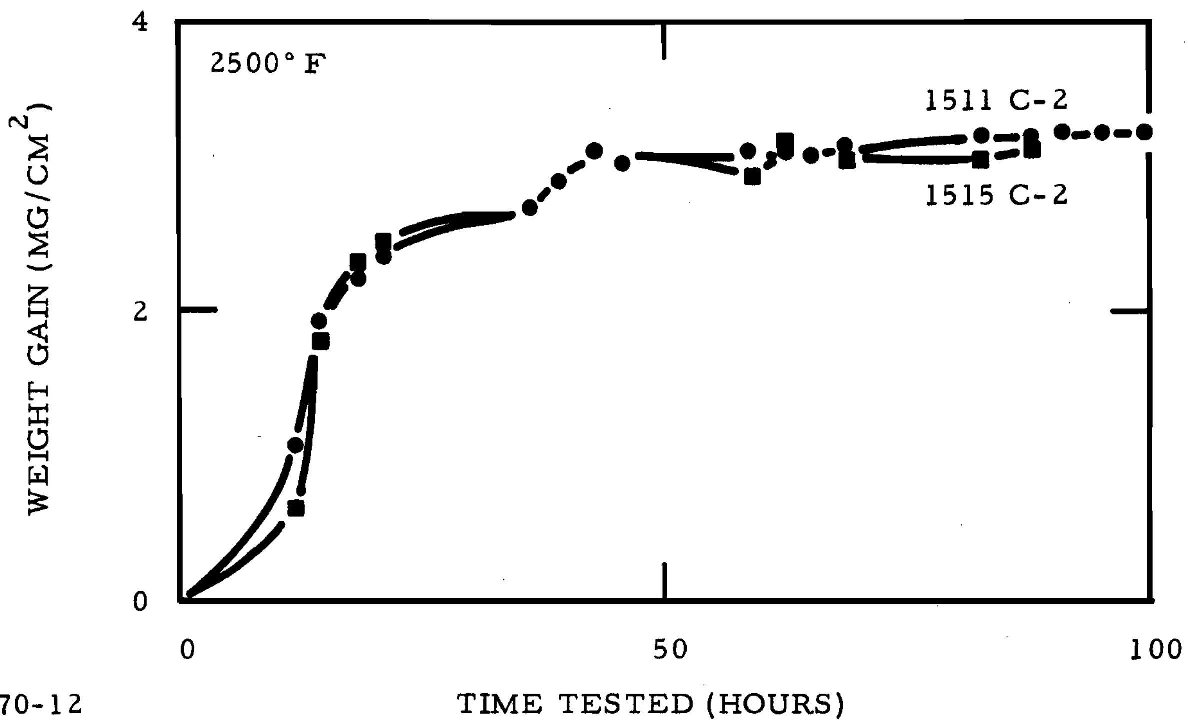
04670-13

SERIES C-2

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1510	10.3	5.6		
2	1514	13.0	6.3	2300	51
3	1515	13.2	8.1	2500	100
4	1512	12.6	6.9		
5	1513	13.2	7.8	2300	100
6	1511	13.2	6.6	2500	100



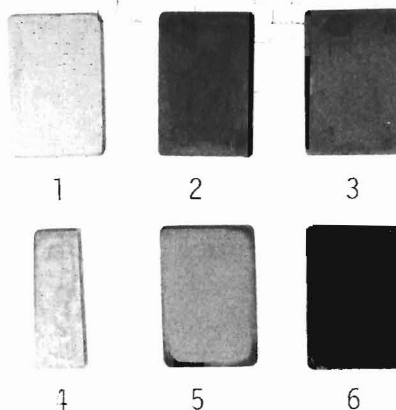


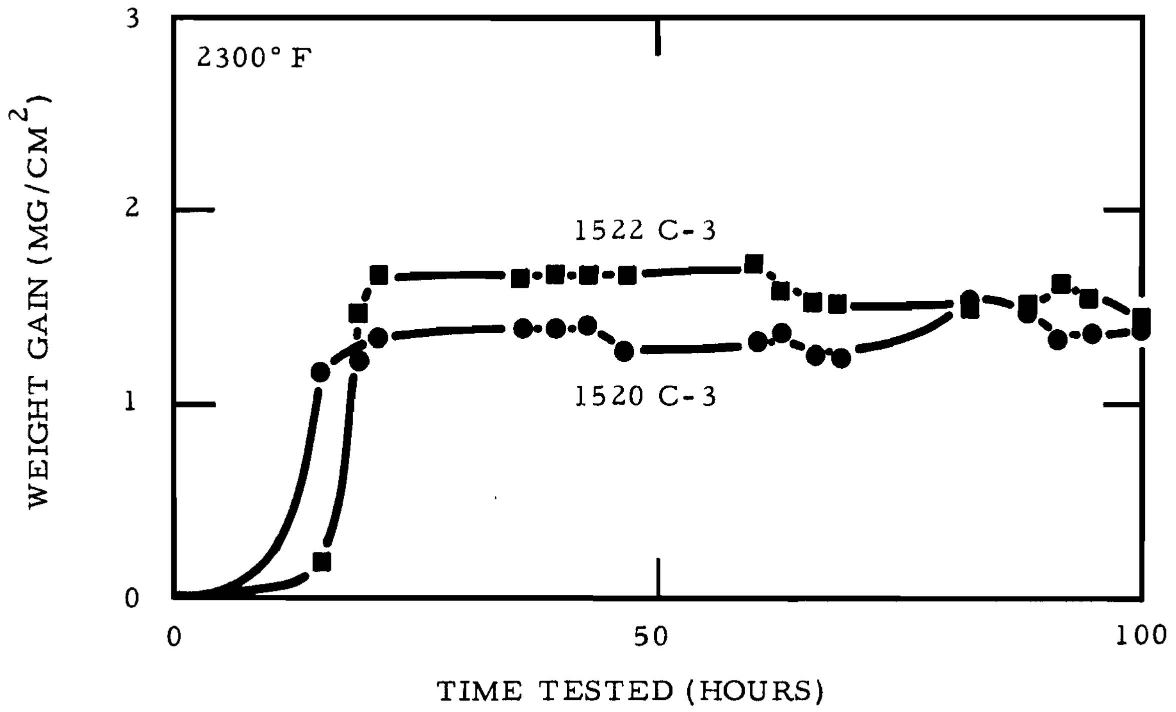


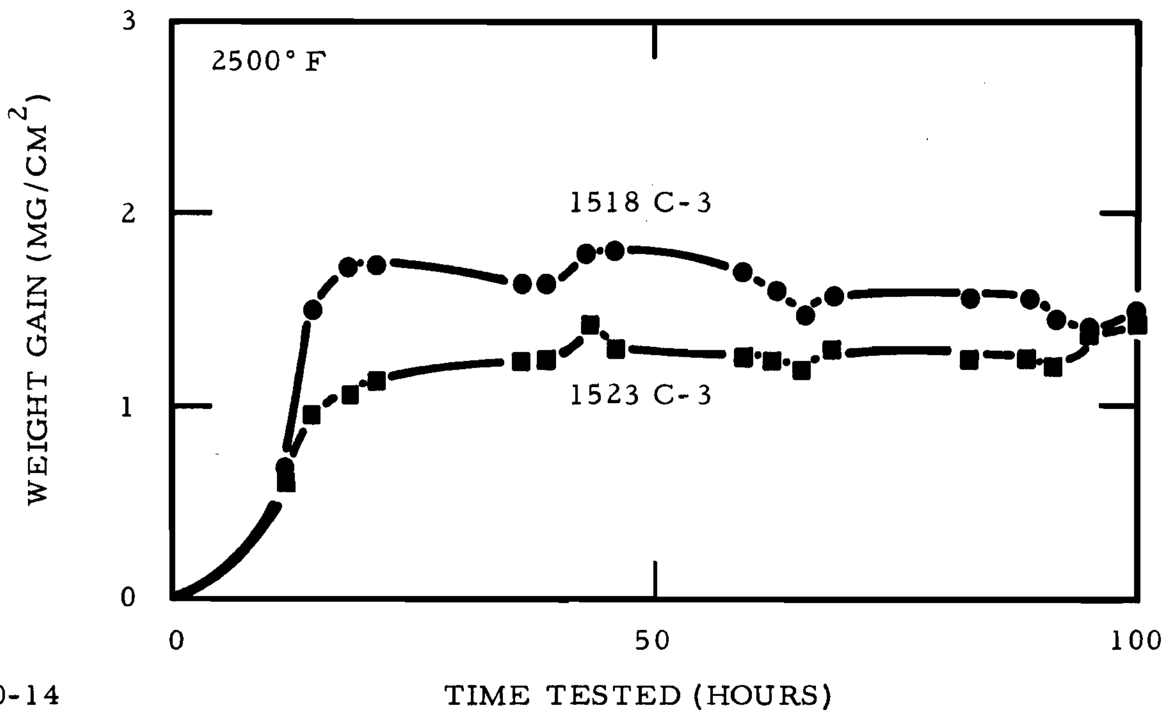
04670-12

SERIES C-3

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1519	10.2	1.8		
2	1522	8.9	5.7	2300	100
3	1523	9.3	6.0	2500	100
4	1521	9.3	2.5		
5	1520	10.5	2.2	2300	100
6	1518	9.5	3.8	2500	100



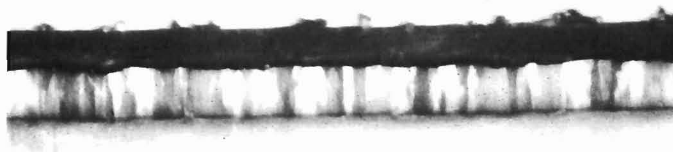


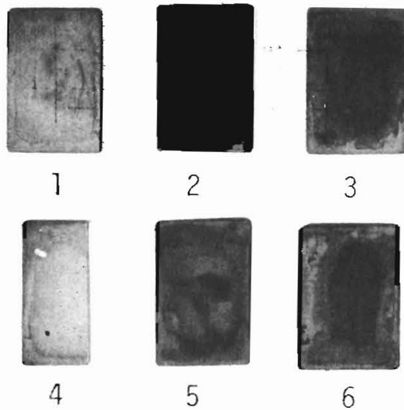


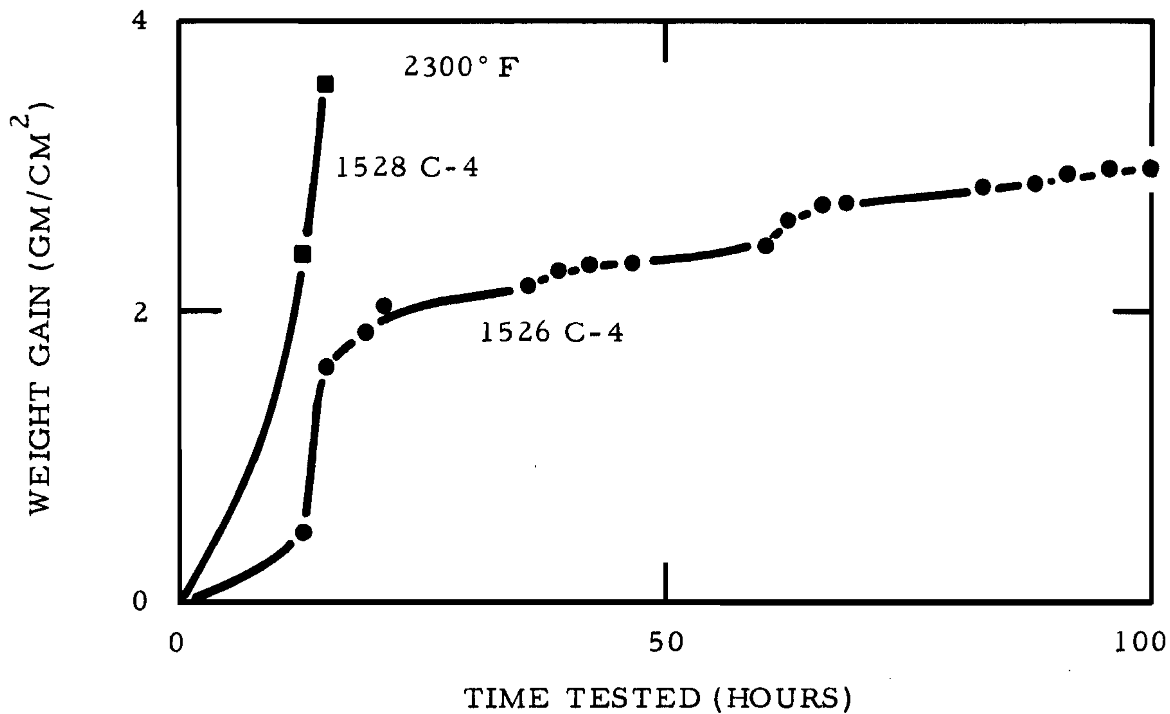
04670-14

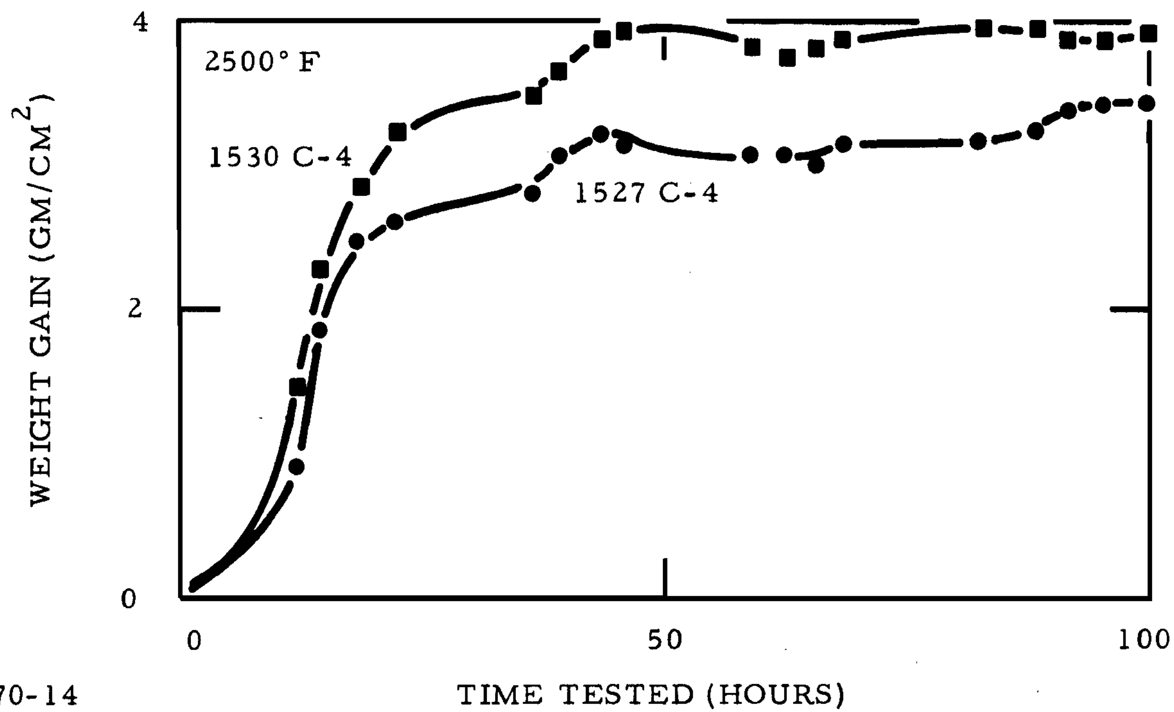
SERIES C-4

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1524	13.4	5.7		
2	1526	14.8	9.2	2300	100
3	1527	14.9	11.0	2500	100
4	1525	15.6	7.1		
5	1528	15.2	7.0	2300	19
6	1530	15.8	10.9	2500	100





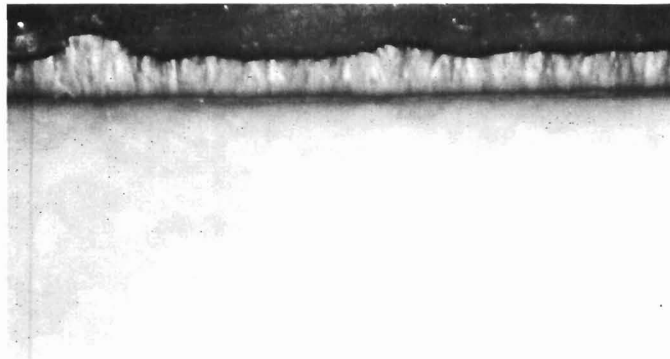


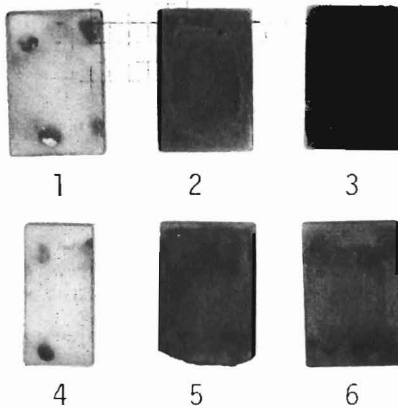


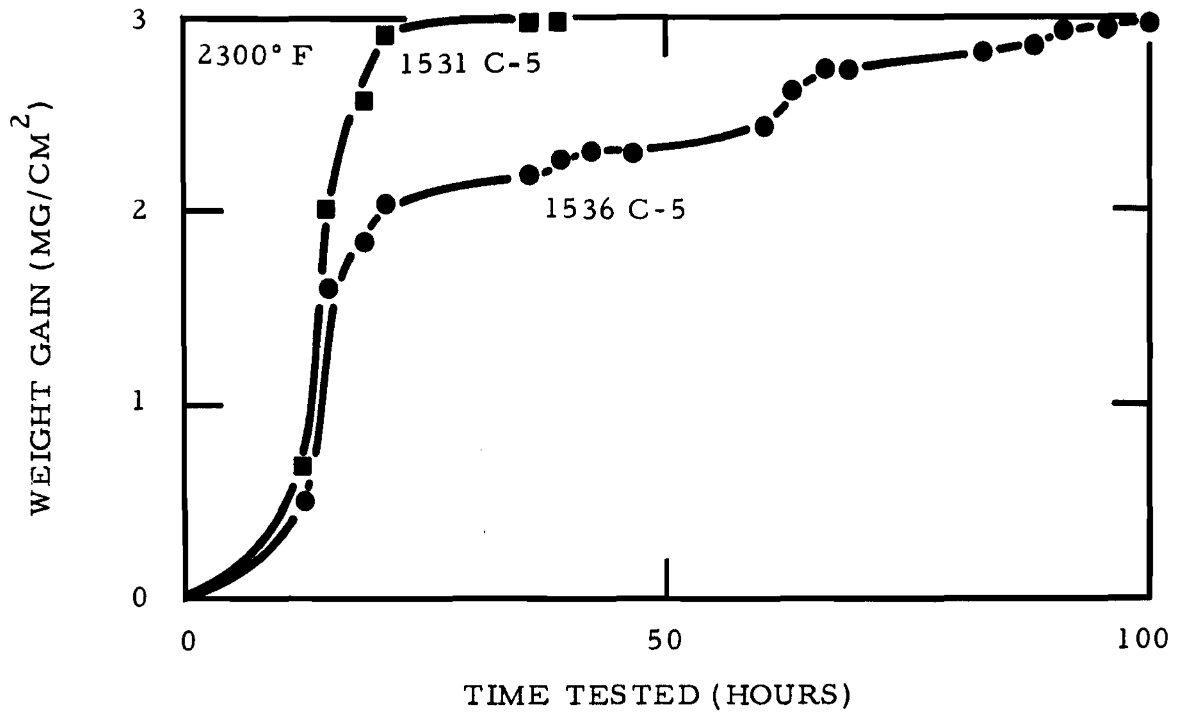
04670-14

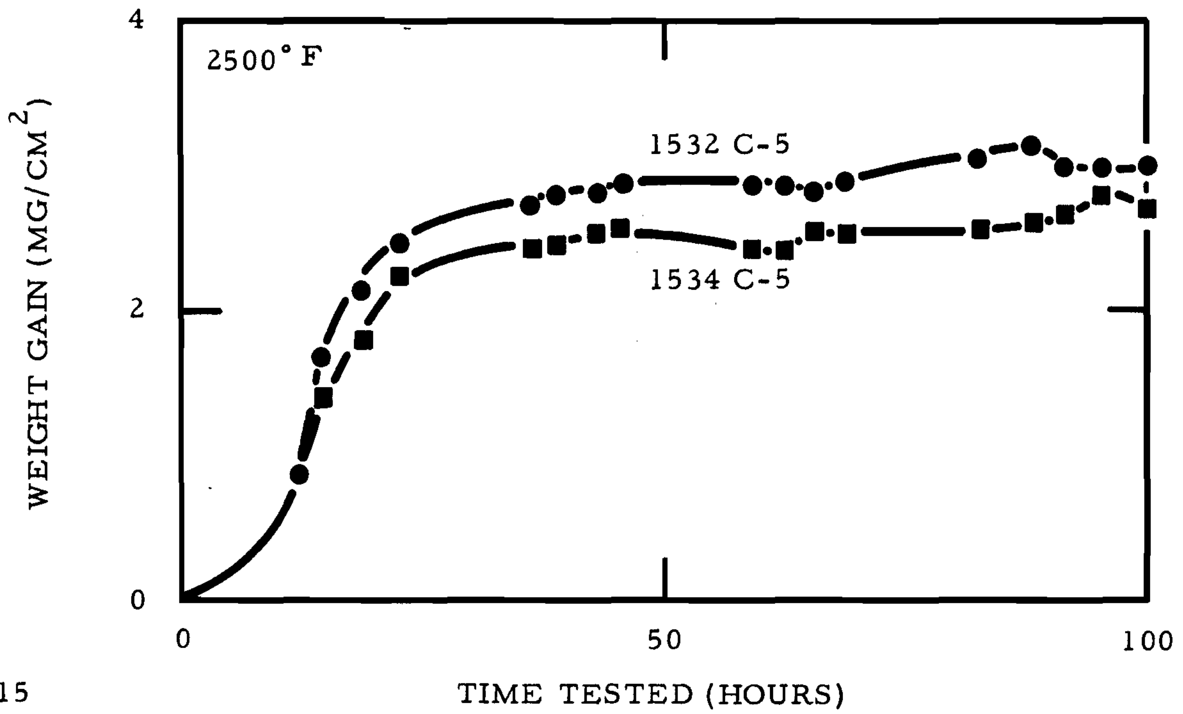
SERIES C-5

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1533	12.2	6.3		
2	1536	13.0	7.7	2300	100
3	1534	12.9	10.9	2500	100
4	1535	13.1	8.4		
5	1531	12.9	10.2	2300	47
6	1532	12.1	7.4	2500	100





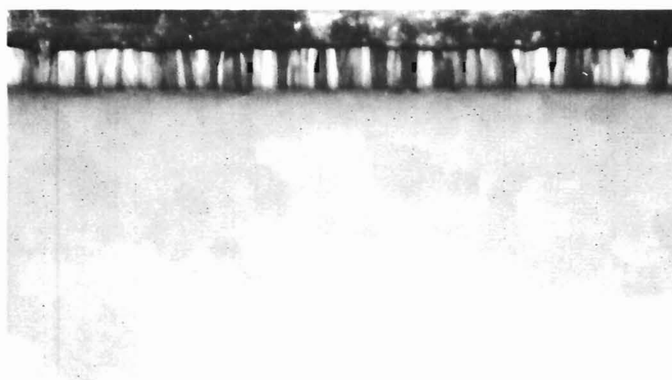


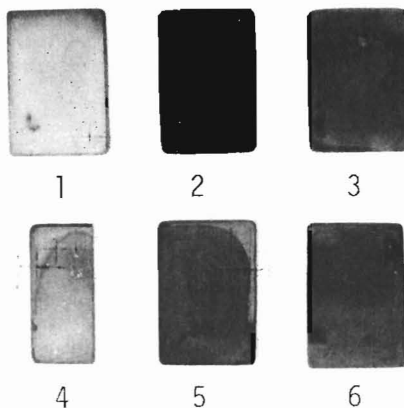


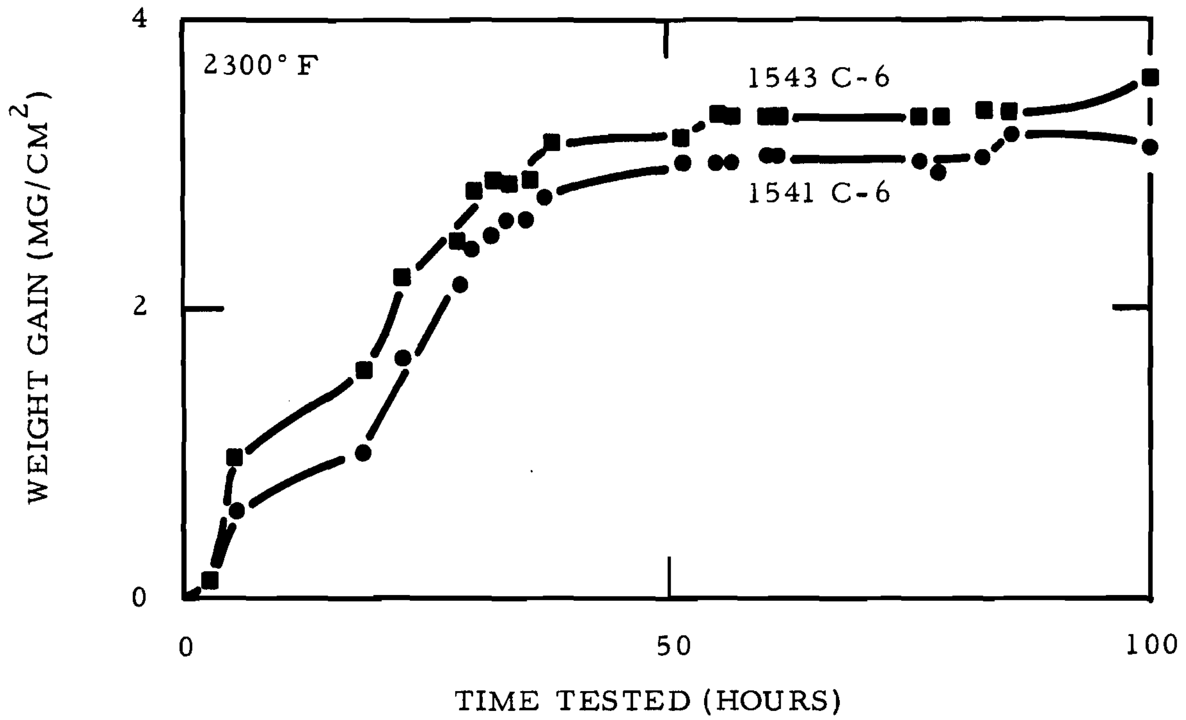
04670-15

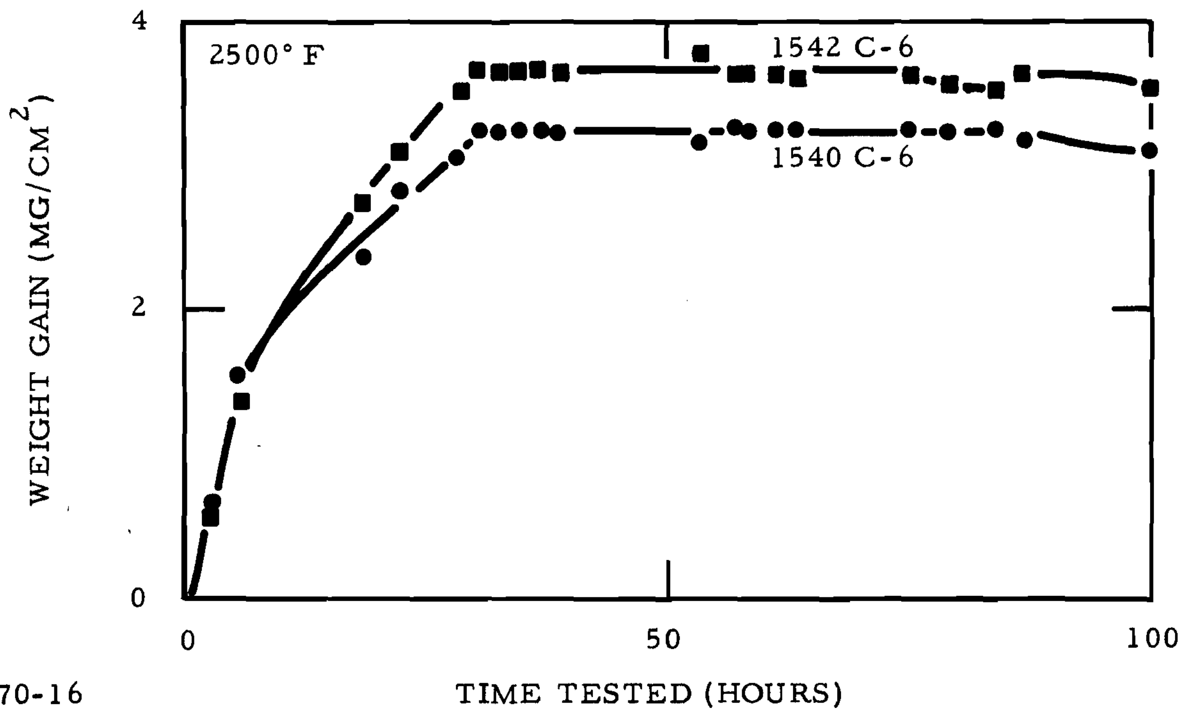
SERIES C-6

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1544	13.4	7.5		
2	1543	12.9	10.8	2300	100
3	1542	13.6	10.4	2500	100
4	1545	13.3	6.7		
5	1541	14.4	9.8	2300	100
6	1540	15.0	8.0	2500	100





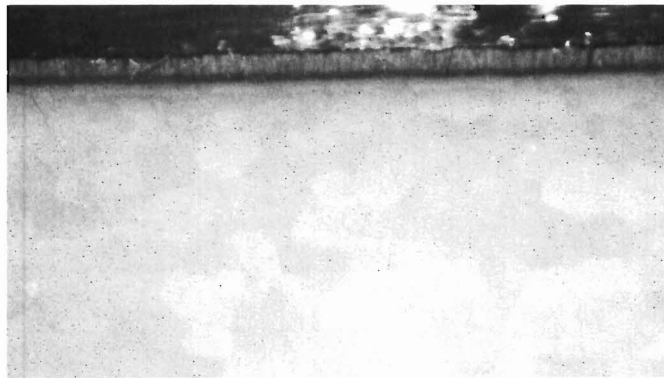


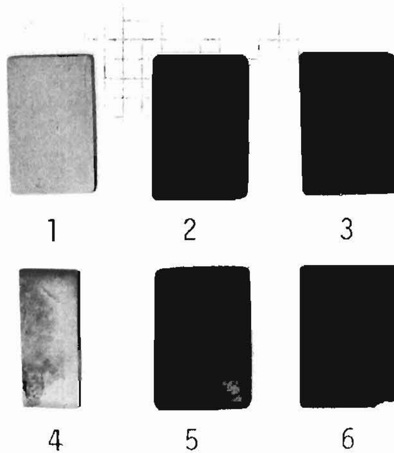


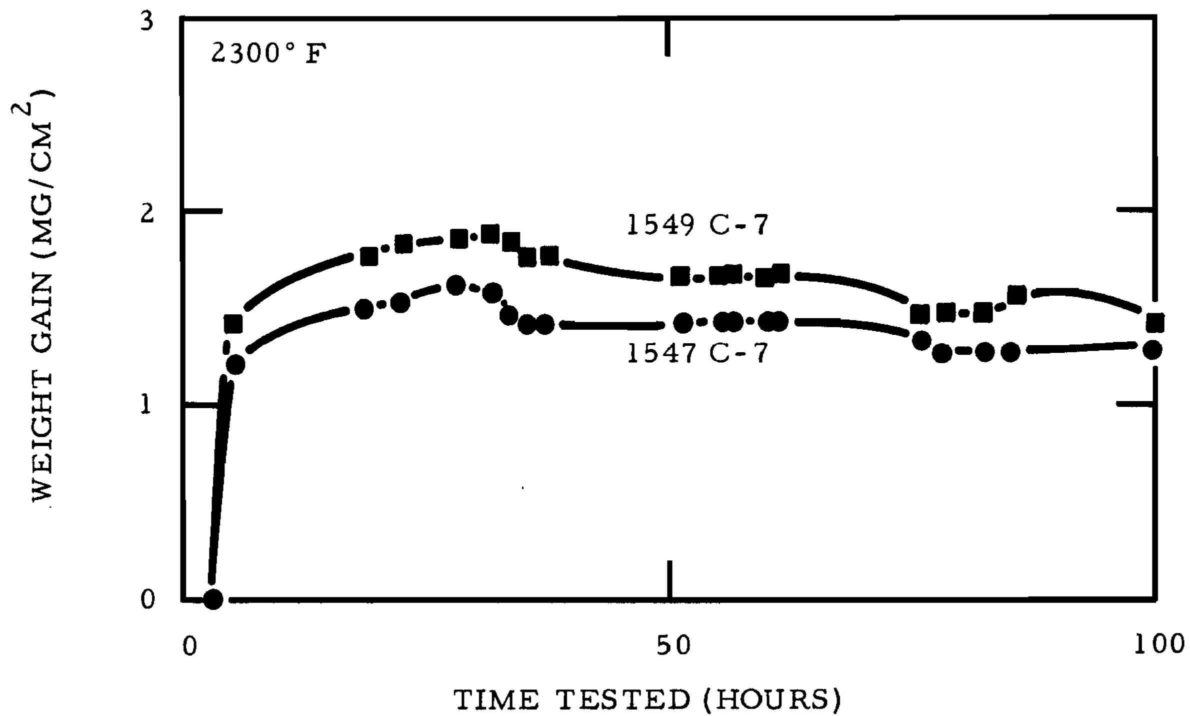
04670-16

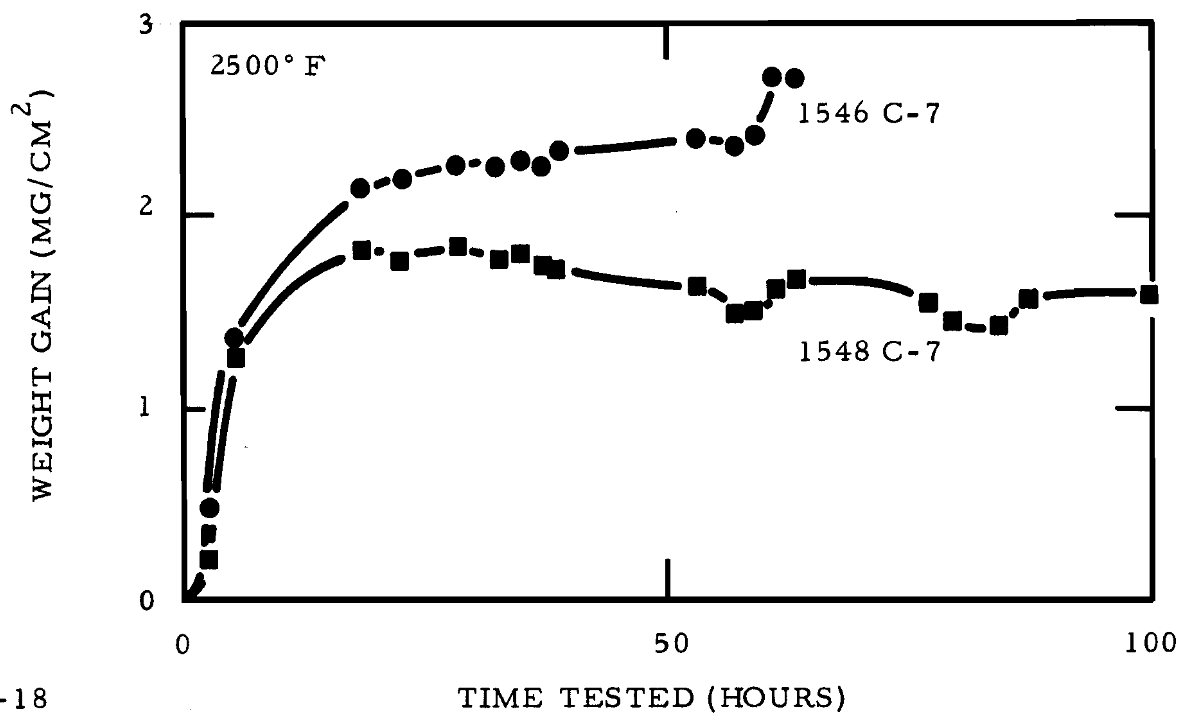
SERIES C-7

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1551	7.9	3.4		
2	1549	8.8	6.9	2300	100
3	1548	9.2	5.9	2500	100
4	1550	8.6	3.5		
5	1547	10.2	5.8	2300	100
6	1546	10.4	5.7	2500	78





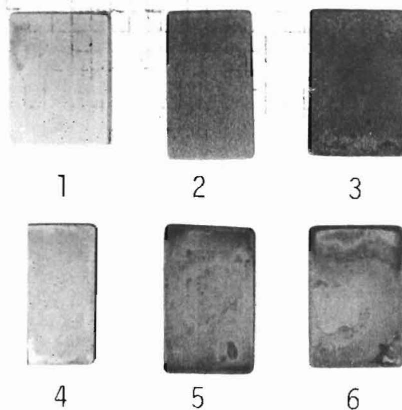


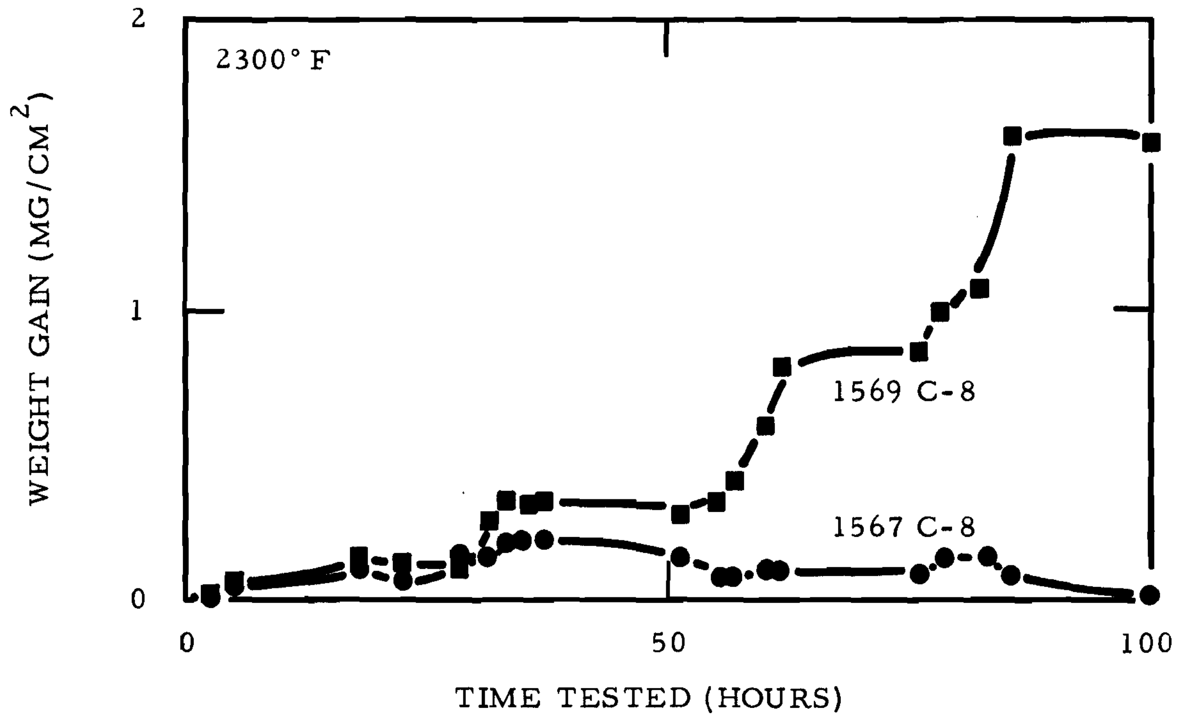


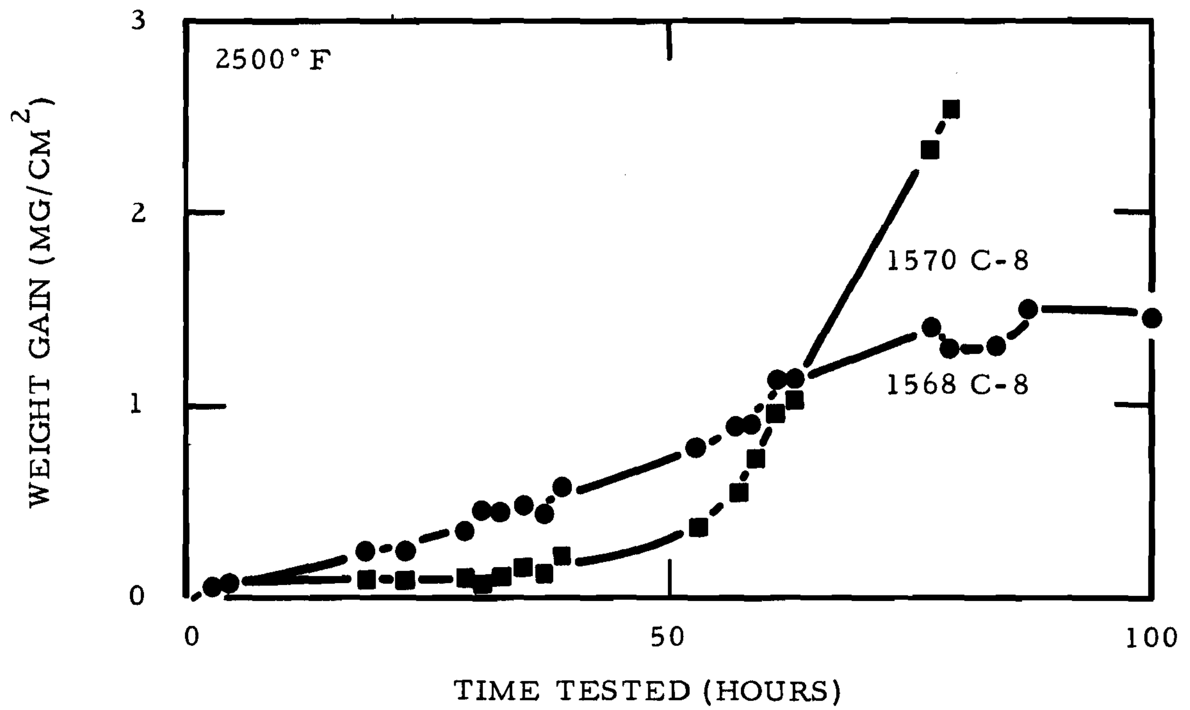
04670-18

SERIES C-8

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1571	8.1	2.4		
2	1569	8.0	4.4	2300	100
3	1570	8.8	4.8	2500	87
4	1566	8.7	3.4		
5	1567	8.5	4.4	2300	100
6	1568	8.1	4.4	2500	100



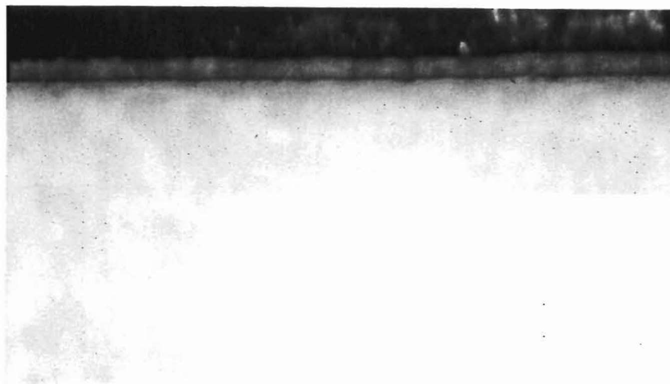


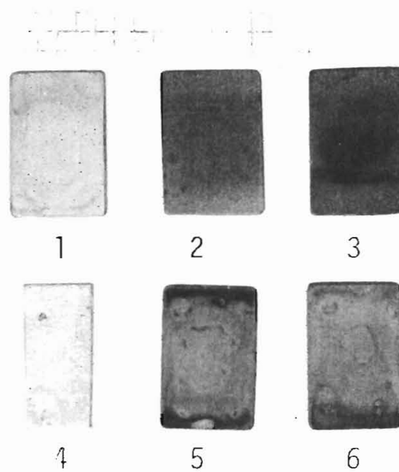


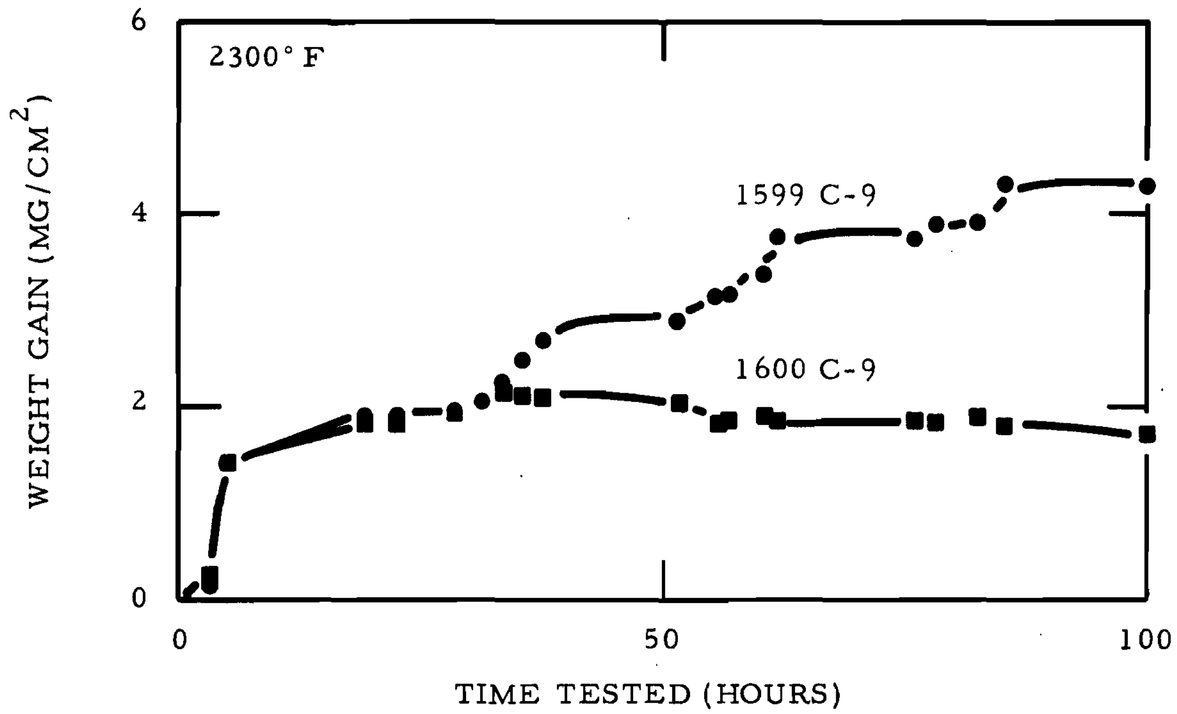
04670-19

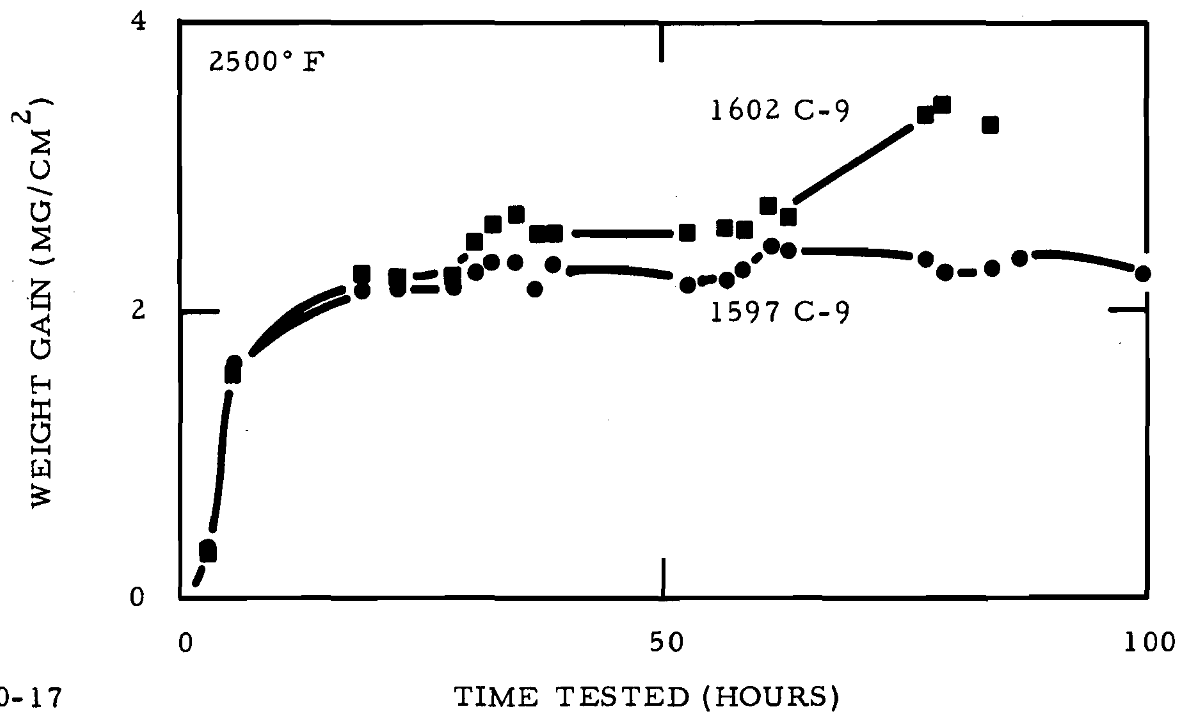
SERIES C-9

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1601	11.4	3.4		
2	1600	10.5	4.7	2300	100
3	1602	11.0	5.7	2500	87
4	1598	10.8	5.6		
5	1599	11.2	5.5	2300	100
6	1597	10.4	5.0	2500	100









04670-17

SECTION V

IRREGULAR SHAPES

Several investigations were carried out in an attempt to establish criteria for scaling-up the process and to assess the applicability of the coating process for samples other than the flat coupon shape. Two different sample shapes were run. One was a flat sample containing a lap-welded joint and the other a curved (bent) sample.

A. Welded Joint (Series D-0)

Samples having a lap joint were made from regular coupons sheared in half and then spot welded together (see the cross section in series D-0, page 154), yielding a faying surface. The mating surfaces received a considerably reduced quantity of the coating gases because the gases were impinged normal to the surface rather than in the more desirable edgewise direction. This is a severe test of ability of the coating process to impart a protective coating. These samples were coated first with titanium-chromium alloy, then with silicon. The photomicrograph of one such sample in series D-0 shows a diminished amount of coating in the faying area. Oxidation tests were carried out at 2300°F and 2500°F to test the amount of protectiveness obtained. As the cyclic testing proceeded, there was no observable failure until a catastrophic, gross oxidation at the point when testing was terminated. The shape of the weight gain curves shows that a truly parabolic rate was not attained, though the total weight gain in these tests was not excessive.

These tests demonstrate that at least a short protective lifetime was imparted even under very nonideal coating conditions and indicated that a potential to provide more useful lifetimes definitely exists.

B. Curved Samples (Series D-1)

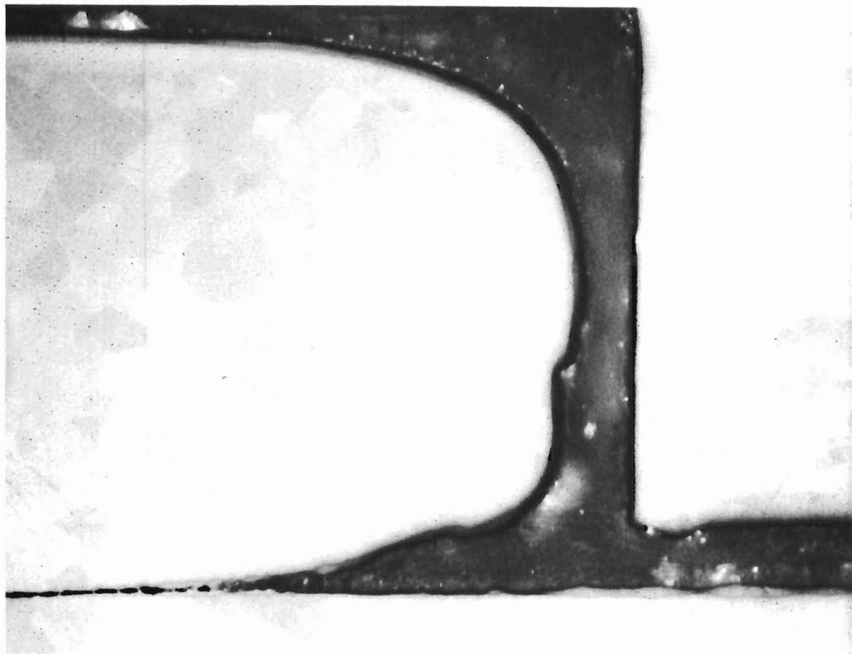
Some of the coupons were bent approximately 90-degrees around on a 3/8-inch diameter radius to form a shape resembling a leading edge. To conserve time, these samples were coated by the trideposition process described in the next section. This process provided an equivalent assessment of the ability to

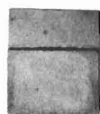
protect curved shapes, since the equipment and conditions utilized were designed and developed specifically for flat coupons. Thus, the flow over the surface and the temperature of the sample could have been nonuniform. Sample 1637-D-1 contained a longitudinal lap-weld joint in addition to the curvature. In tests of these coatings the curves at 2300°F show good protection for the 100-hour tests and a relatively low total weight increase. Appearance of the sample after testing was good. The lap joint sample tested at 2500°F began to fail after about 25 hours at the coating irregularity (caused by poor nozzle design) under the lap joint. Elimination of this irregularity would be expected to improve the useful lifetime.

Though the time to failure at 2500°F was less than desired, the demonstrated ability and the indicated potential of this process to provide protective coatings encourages further investigation.

SERIES D-0

No.	Run No.	Average Weight Cr-Ti (mg/cm^2)	Average Weight Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1617	8.5	1.4		
2	1616	9.7	2.7	2300	80
3	1614	10.2	1.6		
4	1615	9.2	2.4	2500	40

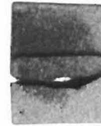




1

2

3



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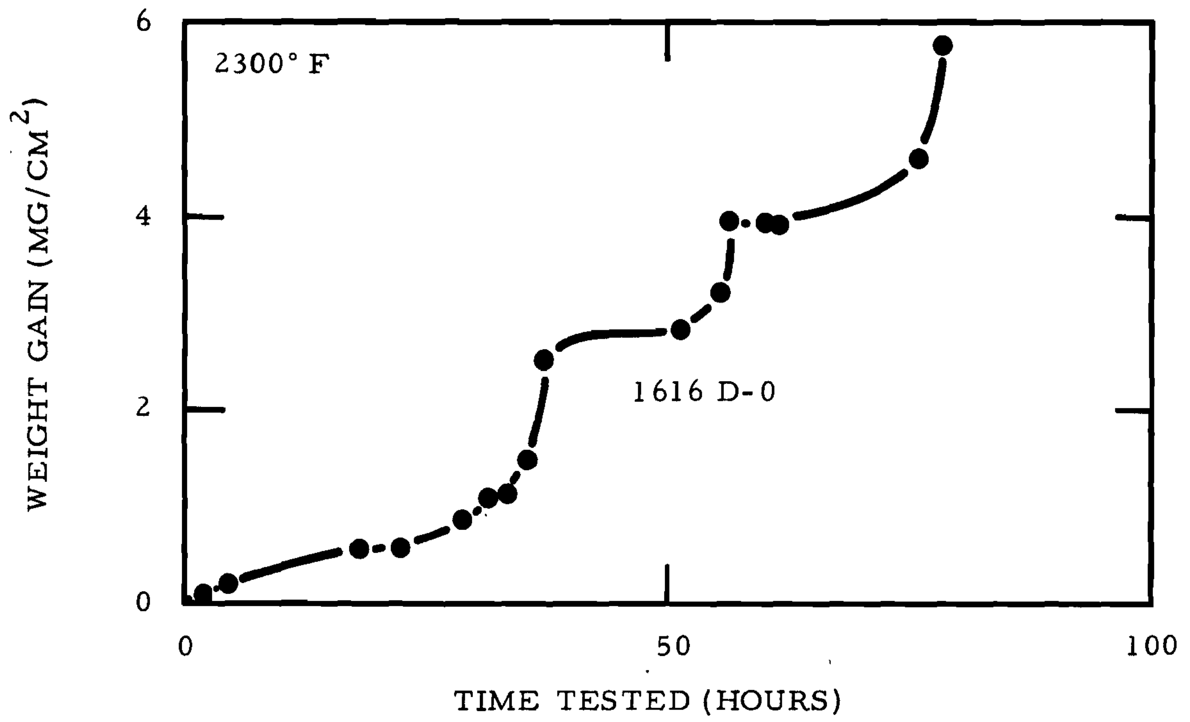
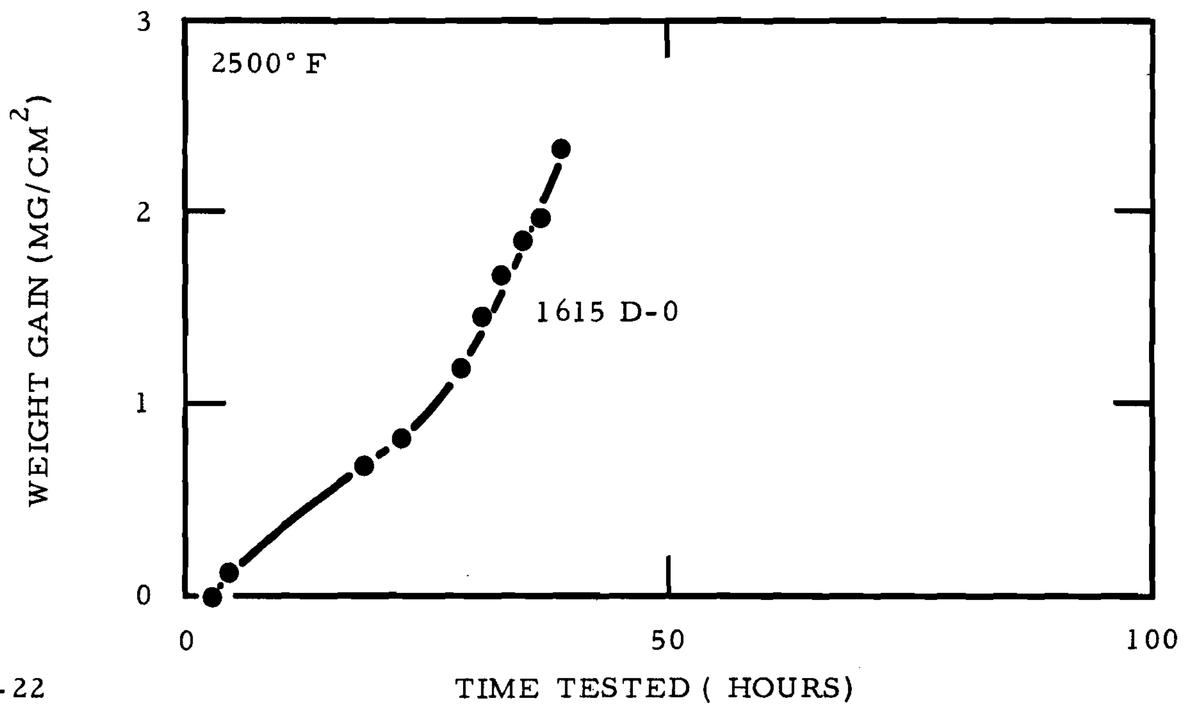
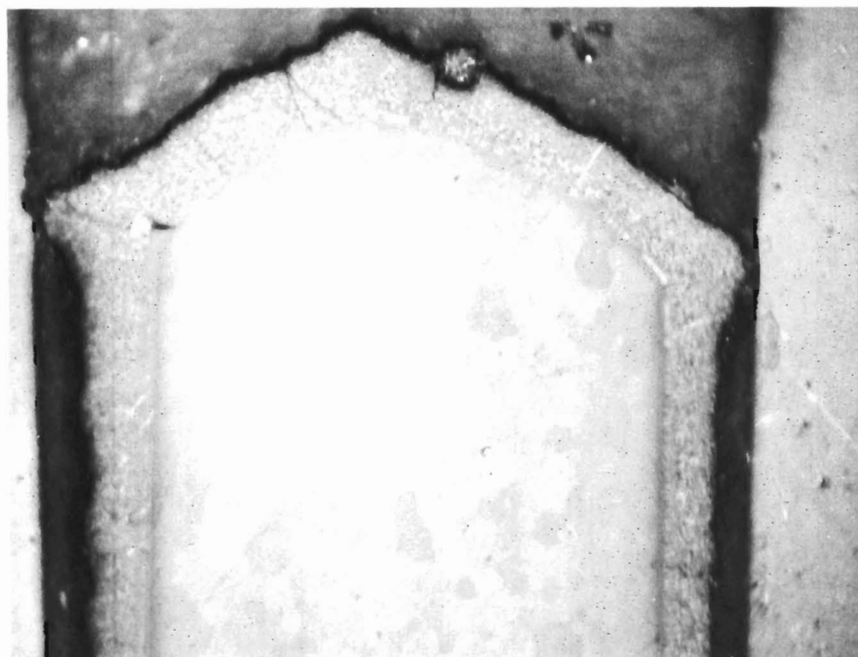




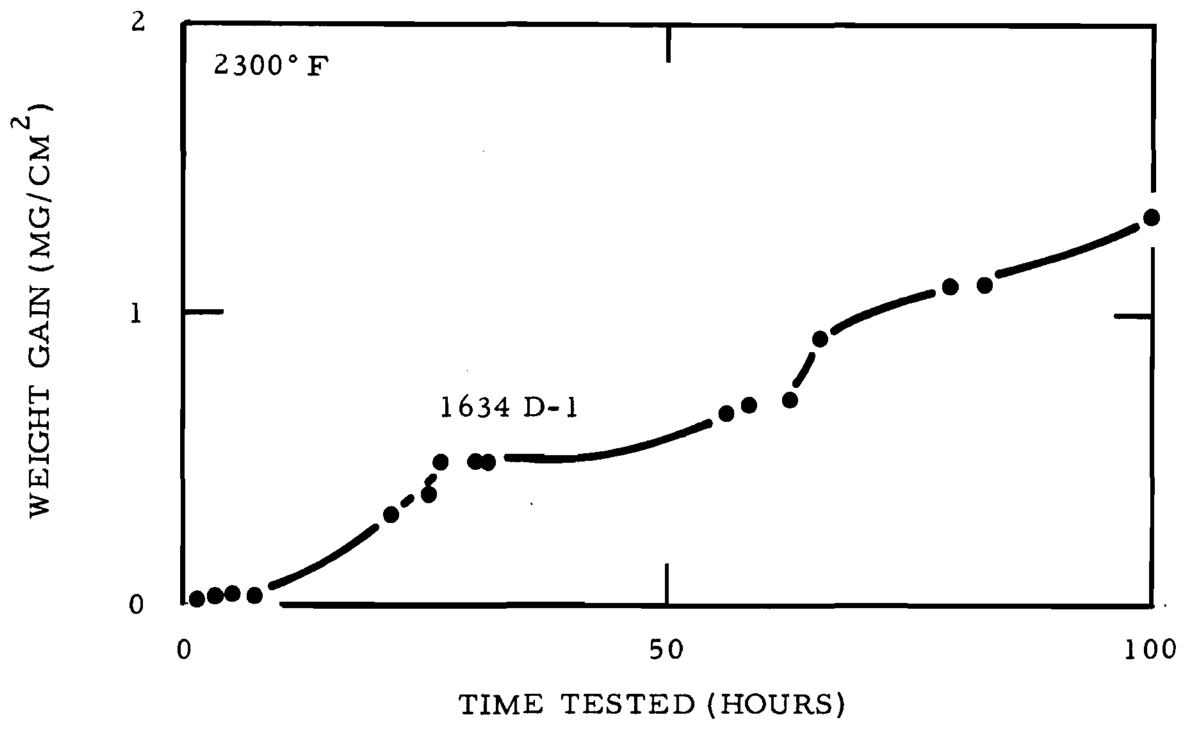
04670-22

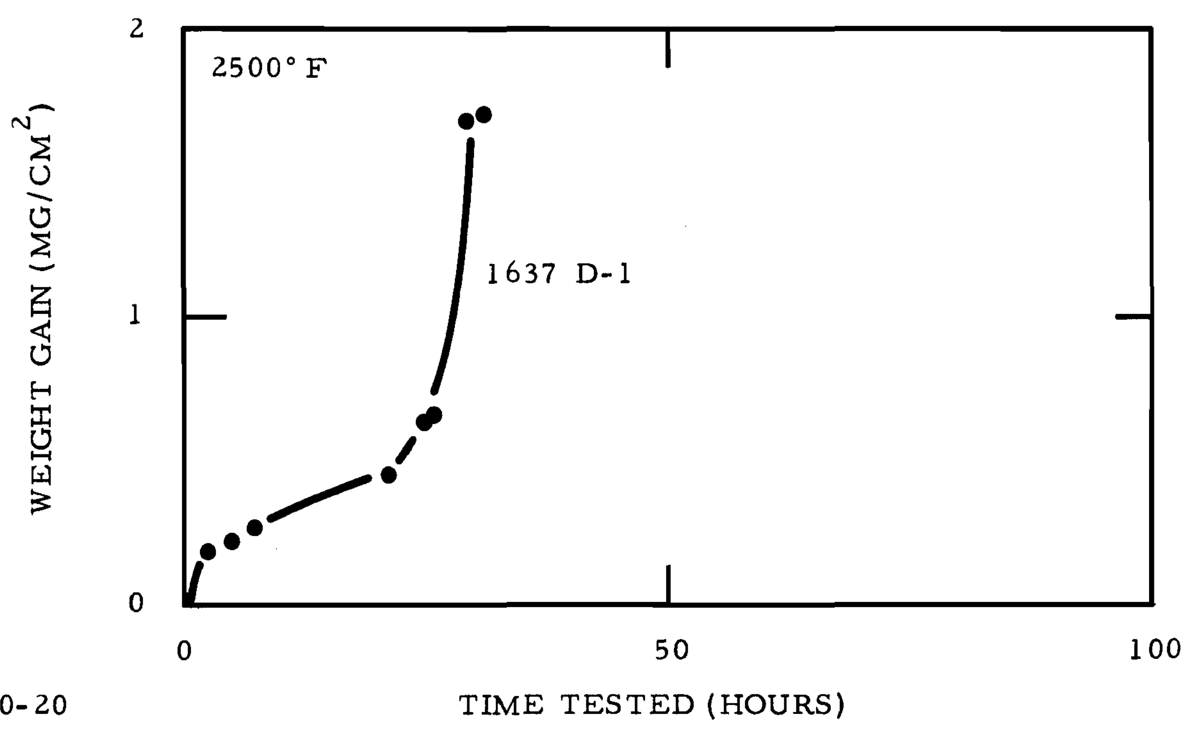
SERIES D-1

No.	Run No.	Average Weight Cr-Ti-Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1636	17.6		
2	1634	21.0	2300	100
3	1635	18.7		
4	1637	17.1	2500	31



* Prepared by the trideposition process





04670-20

SECTION VI

TRIDEPOSITION PROCESS

As discussed in the Introduction, one of the major assets of the CVD process is its versatility in handling different compositions of materials, as well as the sequential combinations which can be deposited. The major work on this process study contract was to produce coatings comparable with vacuum pack coatings. To permit a reasonable comparison of performance results obtained with the two processes, the coatings had to be fabricated in a similar mode. Therefore, the pre-established order for most of the coating preparation was titanium-chromium alloy deposition followed by a siliciding process. In this procedure, the capability to manipulate and control the deposition of metal alloys by simultaneous reactions was demonstrated.

The possibility of codepositing all three elements simultaneously to form a mixed silicide refractory compound could lead to a one-step, rapid coating process. Therefore, in the latter part of the program simultaneous codeposition of the three constituents titanium, chromium, and silicon was given cursory investigation. It was found that the process worked at least as well as expected and demonstrated potential for a number of significant improvements over more common coating processes being utilized or investigated for refractory metal coatings.

Trideposition was accomplished by adapting the alloy deposition equipment by adding an inlet for injection of $SiCl_4$ into the halide stream. These gases then premix with a hydrogen stream in the region just outside the nozzle and are swept on to contact the heated sample. A sketch of the nozzle sample geometry is shown in Figure 45. As expected from this rather elementary arrangement, the sample area immediately under the nozzle was not coated uniformly, though the remainder of the surface was well coated. Inclusion of $SiCl_4$ at a more suitable point in the halide stream would remove this discontinuity.

The experimental parameters of the trideposition coating are given in the Appendix, runs 1618 through 1622' and 1631 through 1638'. Deposition rates observed with the use of this apparatus were more rapid than desired for the

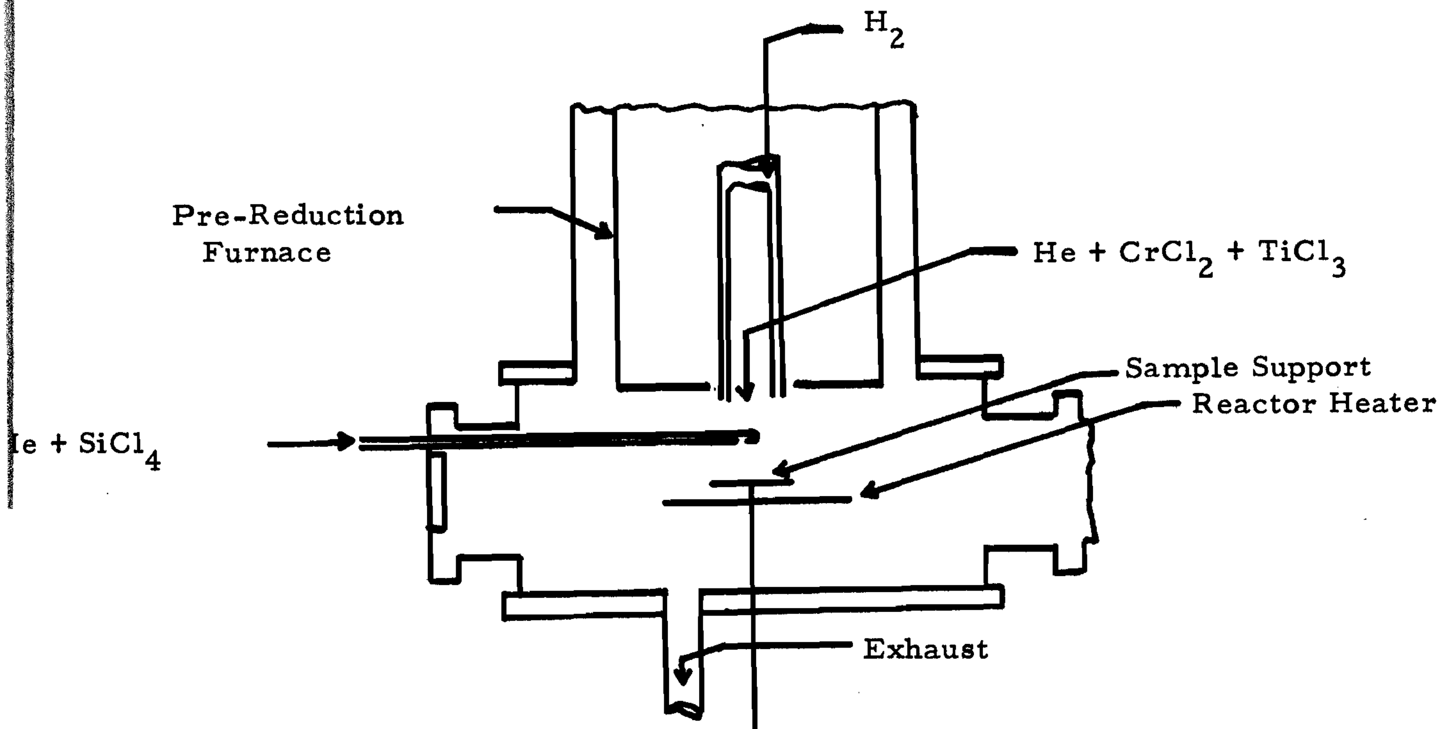
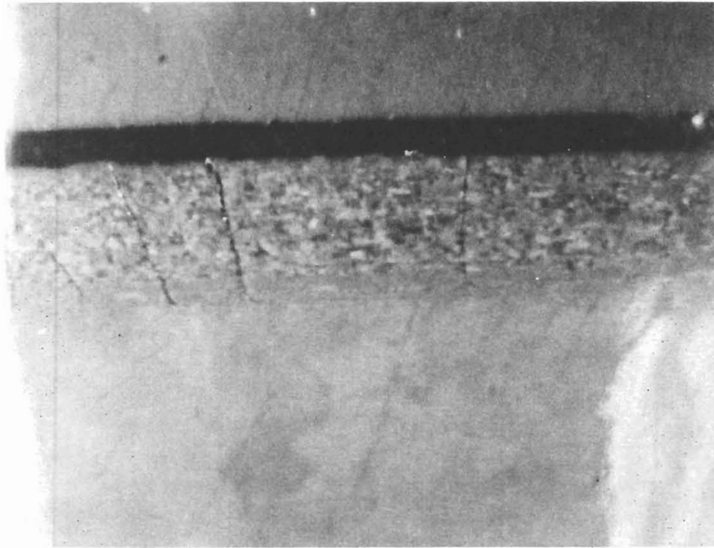


Figure 45 Schematic Diagram of Coating Reactor used to Trideposit Ti-Cr-Si Coating

reaction conditions (which were similar to those used for alloy depositions). Therefore, the coating temperature was lowered by approximately 150 degrees. Except in the nozzle areas, the coatings were uniform in appearance, and edge coverage was good.

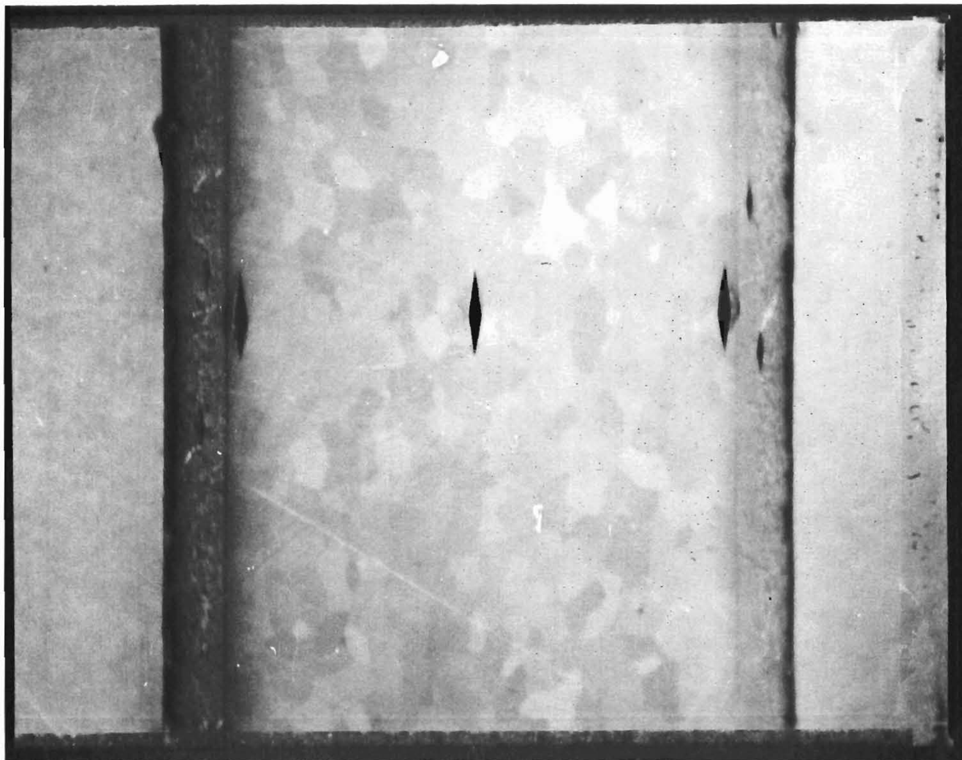
The photomicrographs in Figure 46 illustrate the general appearance of some of the coatings. A very narrow interaction area is observed, which indicates minimum diffusion into the substrate. The hardness indentations also show this. The fine grain ($\sim$ 2 micron diameter) structure is unusual for CVD deposits but is more desirable than the expected columnar grain structure. The thicker coatings near and around the edges of the samples apparently result to some extent from the double coating the edges received when the samples were coated, then turned and coated on the other side. This illustrates that the process has a high degree of "throwing power," since the coating is "lapped under" on areas not directly exposed to the gas stream.

Oxidation tests were performed on a number of the coatings, even though the nonuniformity due to the nozzle could potentially reduce the measured lifetimes. Tests series D-2 and D-3 were trideposition coatings. Two of the samples failed in the nozzle area; the other two samples completed the 100-hour test at 2300°F and 2500°F. No failures occurred at other than the nozzle nonuniformity.



(a)

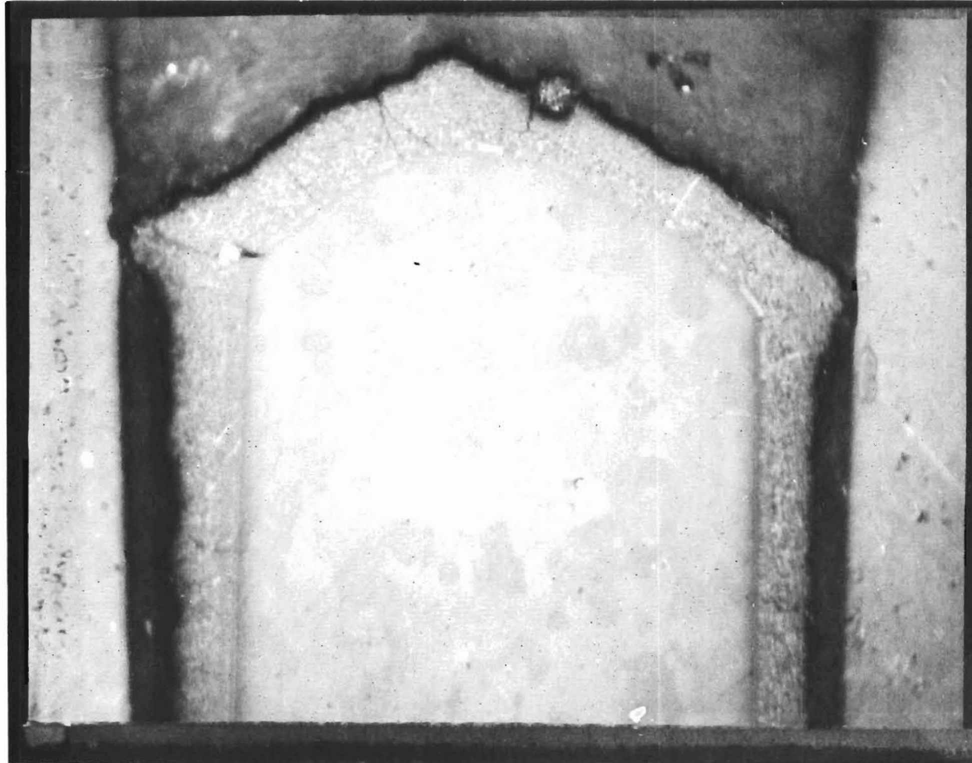
Fine Grain Size ($\sim 5 \times 10^5/mm^2$) and Slight Substrate Interaction Region Typical of this Preparation Method.



(b)

Coating Hardness $\sim$ 900 kHN_{100}, Substrate 210-235 kHN_{100} Unchanged from Uncoated Values (X135)

Figure 46 Cross Sections of Ti-Cr-Si Coatings on Curved Sample No. 1635 Prepared in the Trideposition Process



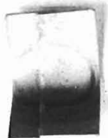
(c)

Excess Coating Buildup Noted on Edges of Curved Samples Due to Lapping Under on This Configuration. Edges well coated (X135)

Figure 46 (Continued) Cross Sections of Ti-Cr-Si Coatings on Curved Sample No. 1635 Prepared in the Trideposition Process

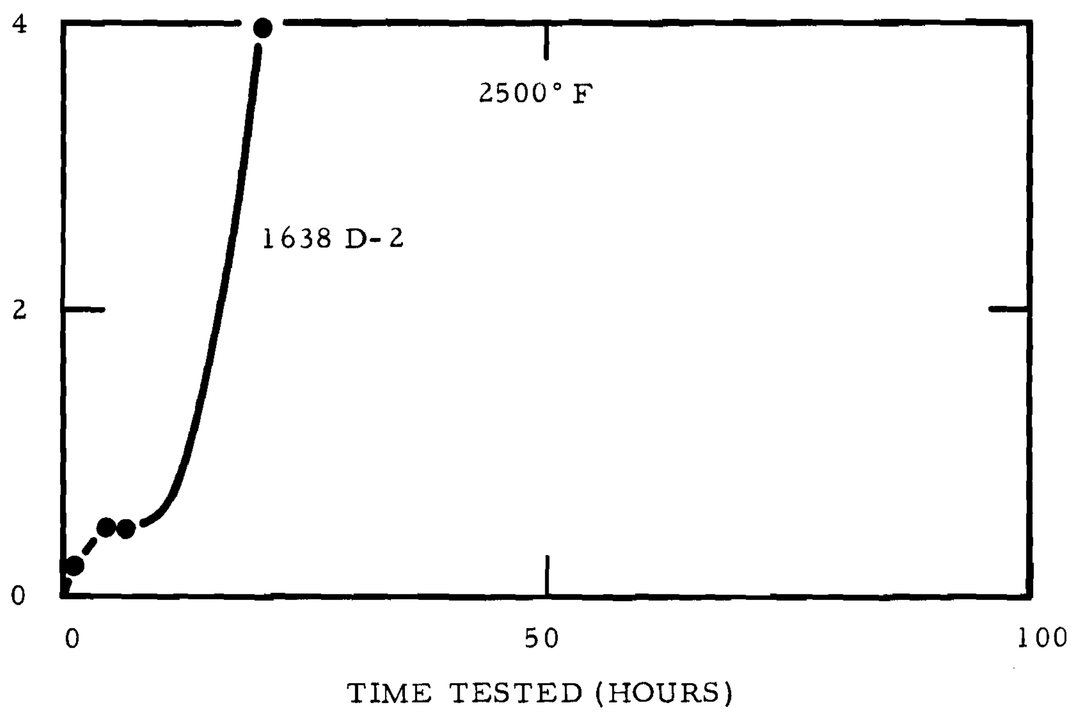
SERIES D-2

No.	Run No.	Average Weight Cr-Ti-Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1639	10.1		
2	1638	13.5	2500	21



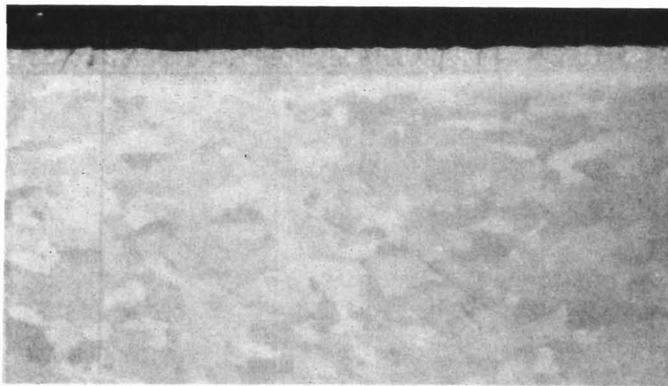
1

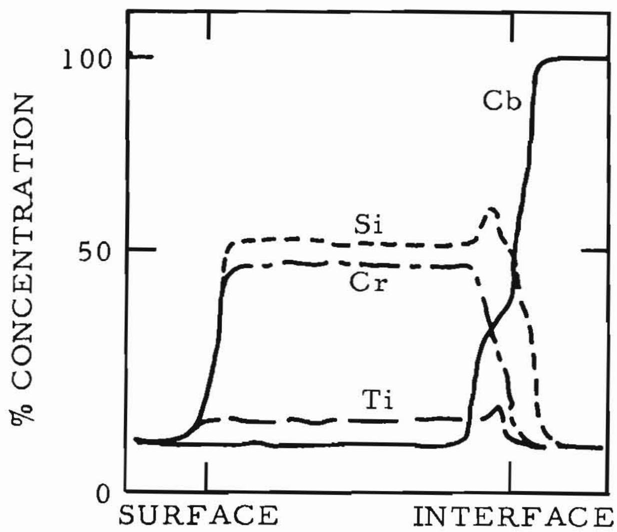
2

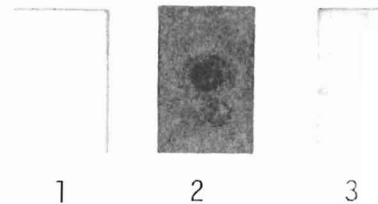

4
2
0
2500° F
1638 D-2
0
50
100
04670-23
TIME TESTED (HOURS)

SERIES D-3

No.	Run No.	Average Weight Cr-Ti-Si (mg/cm^2)	Test Temperature (°C)	Time Tested (hours)
1	1619	21.6		
2	1622	20.3	2500	100
3	1631	12.4		







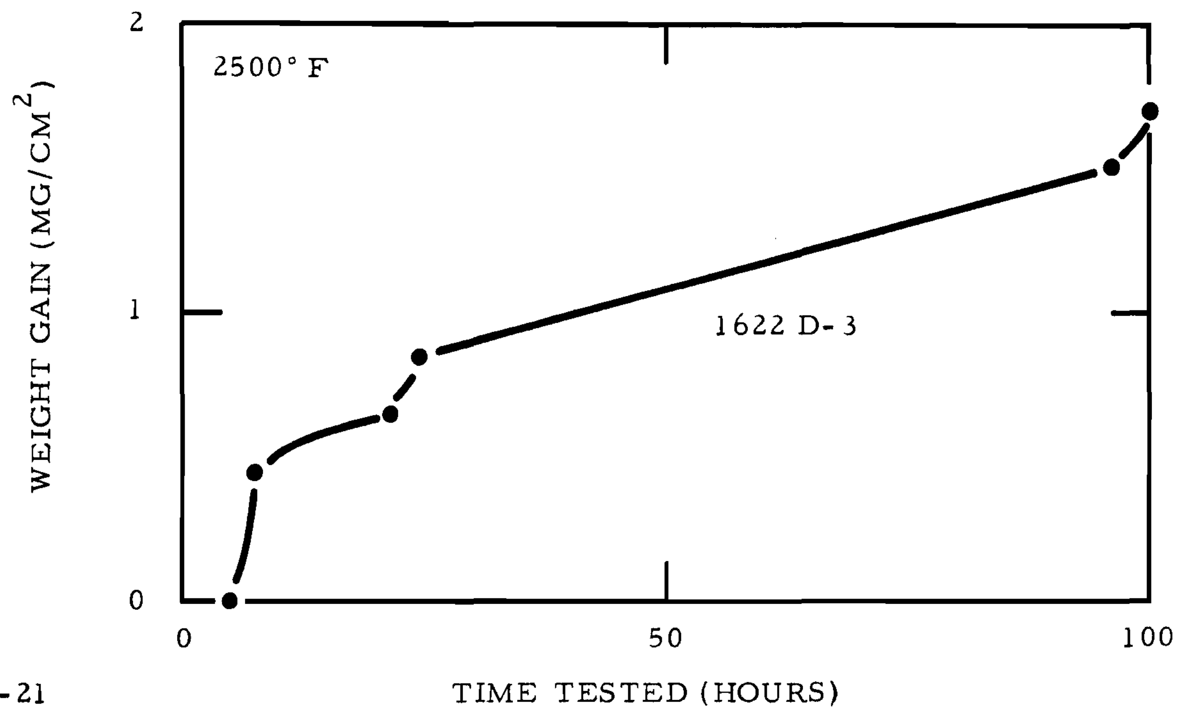

2500° F
1622 D-3
WEIGHT GAIN (MG/CM²)
TIME TESTED (HOURS)
0
1
2
0
50
100
04670-21

TABLE XIII

Results of Oxidation Testing at 2300°F

Sample Number	Time Tested (hrs)	Weight Gain (mg/cm^2)	Location of Failure
1025-A1	74	--	Corner
1026-A1	100	2.7	--
1116-A2	100	--	Edge
1120-A2	100	--	Corner
1133-A3	100	--	Edge Split
1135-A3	70	--	Edge
1196-A4	100	3.7	Protective but Surface Blister
1201-A4	75	--	Corner
1208-A5	76	--	Edge
1209-A5	76	--	Surface
1277-A6	70	--	Edge
1280-A6	100	--	Corner
1290-A7	100	--	Protective but Surface Blister
1291-A7	100	--	Corner
1303-A8	100	--	Edge
1308-A8	100	--	Edge
1325-A9	100	4.1	--
1329-A9	100	4.6	--
1334-A10	100	3.3	--
1335-A10	100	6.2	Protective but Surface Blister
1352-B0	100	3.3	--
1356-B0	100	--	Corner
1378-B1	100	--	Corner
1381-B1	100	4.0	--
1393-B2	68	--	Surface
1394-B2	100	2.7	--
1400-B3	100	6.0	--
1404-B3	100	--	Edge
1409-B4	100	3.2	--
1410-B4	100	3.0	--
1425-B5	40	--	Corner
1428-B5	87	--	Corner
1445-B6	92	--	Surface
1446-B6	86	--	Edge
1451-B7	100	3.2	--
1455-B7	100	1.1	--
1468-B8	100	2.7	--
1469-B8	100	2.7	--
1480-B9	100	2.4	--
1481-B9	100	2.6	--
1486-C0	100	2.9	--
1487-C0	100	2.6	--
1499-C1	100	2.1	--
1503-C1	100	3.1	--
1513-C2	100	4.2	--
1514-C2	51	--	Surface

TABLE XIII
(continued)

Sample Number	Time Tested (hrs)	Weight Gain (mg/cm^2)	Location of Failure
1520-C3	100	1.4	--
1522-C3	100	1.4	--
1526-C4	100	3.0	--
1528-C4	19	--	Surface
1531-C5	47	--	Edge
1536-C5	100	3.0	--
1541-C6	100	3.2	--
1543-C6	100	3.8	--
1547-C7	100	1.4	--
1549-C7	100	2.0	--
1567-C8	100	0.1	--
1569-C8	100	1.0	--
1599-C9	100	4.1	--
1600-C9	100	2.0	--
1616-D0	80	--	Under Lap
1634-D1	100	1.2	--

TABLE XIV

Results of Oxidation Testing at 2500°F

Sample Number	Time Tested (hrs)	Weight Gain (mg/cm^2)	Location of Failure
1024-A1	89	--	Edge
1028-A1	70	--	Corner
1117-A2	100	--	Corner
1118-A2	100	--	Corner
1129-A3	100	3.4	--
1136-A3	100	3.2	--
1197-A4	76	--	Corner
1198-A4	90	--	Edge
1206-A5	44	--	Edge
1207-A5	67	--	Surface
1282-A6	49	--	Edge
1284-A6	15	--	Corner
1288-A7	43	--	Edge
1296-A7	18	--	Edge
1304-A8	67	--	Edge
1307-A8	49	--	Edge
1327-A9	88	--	Surface
1328-A9	63	--	Edge
1336-A10	63	--	Corner
1339-A10	63	--	Corner
1354-B0	100	1.3	--
1355-B0	100	--	Corner
1372-B1	100	3.6	--
1377-B1	100	3.0	--
1389-B2	38	--	Surface
1390-B2	100	3.6	--
1401-B3	100	--	Corner
1402-B3	100	2.2	--
1407-B4	100	2.9	--
1408-B4	100	3.5	--
1426-B5	100	5.4	--
1433-B5	100	2.4	--
1442-B6	63	--	Surface
1448-B6	86	--	Edge
1449-B7	86	--	Edge
1452-B7	86	--	Surface
1466-B8	73	--	Edge
1467-B8	100	3.5	Protective but Surface Blister
1479-B9	100	--	Edge
1482-B9	83	--	Surface
1488-C0	73	--	Surface
1489-C0	100	3.4	--
1500-C1	60	--	Edge
1501-C1	83	--	Edge
1511-C2	100	3.1	--
1515-C2	100	3.1	--
1518-C3	100	1.4	--

TABLE XIV
(continued)

Sample Number	Time Tested (hrs)	Weight Gain (mg/cm^2)	Location of Failure
1523-C3	100	1.4	--
1527-C4	100	3.5	--
1530-C4	100	3.9	--
1532-C5	100	3.0	--
1534-C5	100	2.7	--
1540-C6	100	3.8	--
1542-C6	100	3.6	--
1546-C7	78	--	Corner
1548-C7	100	3.6	--
1568-C8	100	1.4	--
1570-C8	87	--	Protective but Surface Blister
1597-C9	100	2.1	--
1602-C9	87	--	Protective but Surface Blister
1615-D0	40	--	Under Lap
1637-D1	31	--	Under Nozzle Spout
1638-D2	21	--	Under Nozzle Spout
1622-D3	100	1.8	--

SECTION VII

PROTECTIVENESS EVALUATION

A. Process Evaluation

In an attempt to evaluate the reliability of the coating process in its present state of development, the results from the cyclic oxidation testing were plotted in a Weibull analysis method. The latter one-third of the normal series and the complex shape series (i.e., series C-0 through C-9 and D-0 through D-3) were treated as a single, equivalent sample, grouping. Earlier series (A and B) were excluded, since they were prepared mainly for parameter influence investigation and therefore differed more than later samples. Grouping the different series in this manner implies they are similar, which obviously is not entirely true. However, since the criterion of similarity is oxidation performance, the analysis is perhaps somewhat more justified.

Plots of failure occurrence are shown in Figures 47 and 48 for 2300°F and 2500°F oxidation temperature, respectively. The fact that the total percentage of failures was small in the 100-hour test time limit influences the appearance of the plots and makes the determination of the slope less accurate.

For the case of the 2300°F data, only four failures (16%) occurred within the 100-hour test limit. A straight line through the first and last points appears to adequately represent the data in this particular region. The indicated line has a slope, β, corresponding to ~ 0.93, which could be interpreted as indicating that a true "wear-out" type failure was not being observed. Thus, the true potential protection of the coating was probably not being evaluated, but rather experimental variation in the preparation procedure. This is further substantiated by noting that the failures were at visibly distinct areas for series C-2 and C-4 and under a faying surface in series D-0. The expected lifetimes at three confidence levels for this "batch" of coatings (series C-0 through D-1) obtained from the line in Figure 47 is given in Table XV.

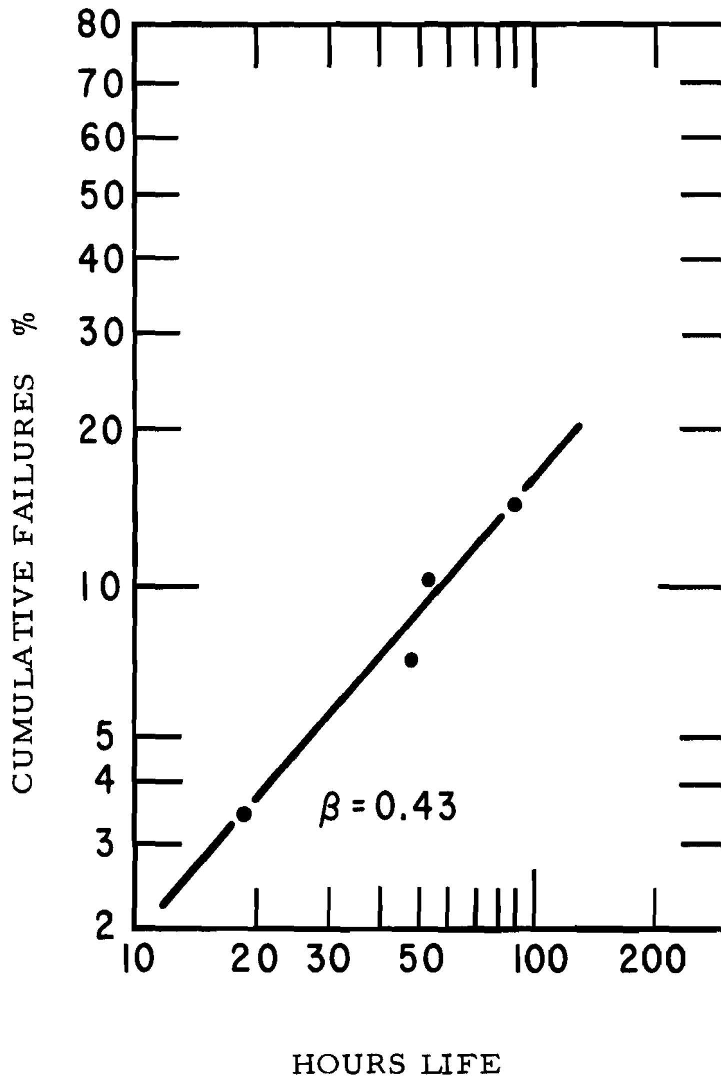


Figure 47 Percent Cumulative Failures vs Cyclic Oxidation Life at 2300°F for all Samples of C- and D- Series

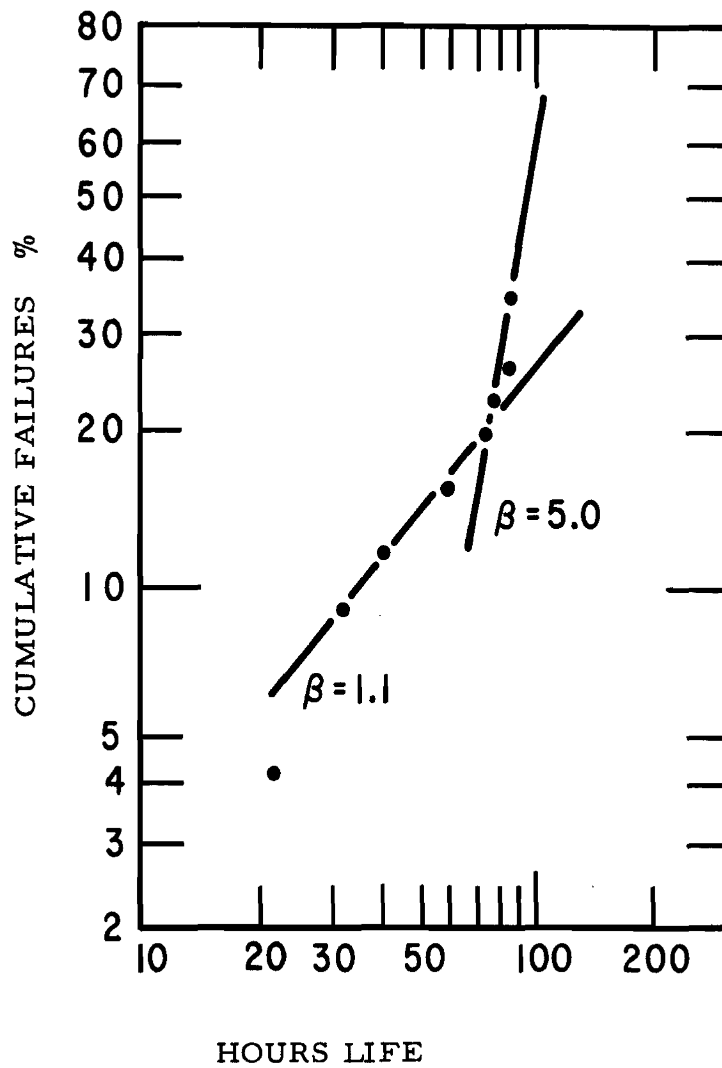


Figure 48 Percent Cumulative Failures vs Cyclic Oxidation Life at 2500°F for all Samples of C- and D- Series

TABLE XV

Coating Life (Hours) at Specified Levels of Reliability*

	70%	90%	95%
2300°F	205	57	28
2500°F $\beta = 1.1$	120	34	19
2500°F $\beta = 5$	82	62	55

* Taken from data of Figures 47 and 48.

For the data on failures at 2500°F, as shown in Figure 48, a single straight line is less representative than the two shown. For the line of lowest slope of β = 1.1 the failure mode is not clearly of a "wear-out" nature. This again would be expected, since the two lowest time failures are due to coating irregularities caused by the nozzle design in the trideposition experiment. The higher slope line (β = 5) indicates a wear-out mode. The expected lifetime at 2500°F for three levels of reliability are given in Table XV for both lines. Thus, removal of the process causing coating irregularities would raise the expected lifetimes at higher confidence levels to those of the higher slope curve.

B. Program Assessment

A comparative analysis of the original purpose and objectives for the program and the results obtained shows that the program goals were achieved.

1. A process was designed and developed to apply high temperature oxidation resistant coatings to refractory metals. This process was demonstrated for application of the TiCrSi coating and would have general applicability for other coating compositions, or the individual steps can be utilized to provide coatings of metals such as chromium, titanium, or alloys, or silicon coatings.

The development of the process to rapid trideposition of the TiCrSi coating is considered a significant contribution, since it allows formation of the entire coating in a few minutes process time. The constant control of the coating process could be further exploited for formation of graded composition coatings or duplex compositions by altering the reactive gases as the coating operation is taking place.

Coatings prepared by either process were capable of controlled variation over wide ranges of composition and were low in impurity content. Both coating processes formed coatings without embrittling the substrate, as shown by the 4T bend tests.

2. The effects of process variables on the coating system were investigated according to statistically designed and analyzed experiments, as reported in the experimental sections of this report. The effects are primarily related to growth rate and composition of the coatings. Composition has one of the major influences on performance. Other variables which are ancillary to the primary process variables, such as uniformity and edge preparation, also influenced performance, as indicated by the shape of the Weibull analysis plots.

3. The potential ability to coat complex shapes and to protect faying surfaces was shown for an airfoil shape and a lapped, spot-weld joint. The trideposition process was utilized for the airfoil shapes, and within the constraints of the coating equipment design, afforded protection to these specimens. This is further significant in view of the fact that the equipment was specifically designed for flat specimens, yet was used without modification for curved specimens. The greater thickness observed at the edges of the samples indicated a "lapping under" effect and shows that surfaces not directly impinged by the gas stream are coated and protected. This potential for coating more complex shapes is shown, particularly where the coating equipment is designed with these shapes in mind. Performance of the lapped, welded samples was not as good as that of flat specimens, though the two-step process gave considerable protection and the only failures observed in the trideposition stemmed from coating nozzle design.

4. Equipment design and process parameters were established for the TiCrSi coating, and parameters for the control of the range of compositions in this system were defined. The methods and process have general applicability to future coating systems for materials of this general category. The specific application to additional materials has been shown in work outside this contract-supported effort.

The trideposition method and techniques for forming coatings have potential capability to form other than diffused or fused coatings as well as to form multilayer coatings in a single process. Alloy coatings are under consideration because of their protective ability, and the present process was shown capable of codepositing alloys over wide ranges of controlled composition.

5. Many of the necessary design and processing criteria were established as a basis for future scale-up operation. Over-all, the size, expense, and complexity of the equipment is comparable to other coating processes. The combination of short process time and moderate temperature requirements would permit higher equipment utilization in a production operation. The temperature for deposition was shown to be ~ 1250°C (2200°F) and could be lower for the trideposition process. The gas introduction nozzles were designed for the metal deposition to yield uniform coatings on flat and curved samples. Nozzle design for the trideposition process was somewhat simpler and resulted in mixing of the reactive gases in the region just exterior to the nozzle rather than closer to the sample. Thus, the nozzle-to-sample distance is not as critical a factor in design and operation of the trideposition system.

We did not investigate the potential size of parts that could be coated by this process. However, it is expected that coatings of this type could be deposited in reactors now used on a commercial, routine basis to deposit refractory coatings on complex shapes 2 feet x 1.5 feet x 2 inches.

SECTION VIII

CONCLUSIONS

1. The basic processes of a manufacturing method for refractory metal coatings for oxidation resistance were developed and demonstrated through fabrication of the typical coating, TiCrSi. The extension of chemical vapor deposition technology to this field represents an advance in the state of the art in refractory metal coatings by permitting continuous control of the coating processes occurring during actual coating by means of reactant and parameter control.

2. The methods and procedures are applicable to processing a variety of materials (as well as for other purposes) and are potentially capable of developing into controlled and efficient manufacturing methods.

3. Reproducibility, reliability, and control of variations through process parameter control were high, particularly for this "first effort" program.

4. One of the most significant developments was the demonstration in cursory experiments of a trideposition process by which the three-component coatings could be rapidly prepared by simultaneous codeposition to result in a fine grained coating. The preliminary oxidation results indicate protection at least comparable to coatings formed in two-stage processes.

5. The overlayer concept of coating formation was demonstrated by the CVD formation of coatings of titanium, chromium, alloys of titanium-chromium, and titanium-chromium-silicon with a minimum of interdiffusion and minimal substrate in the coating.

6. CVD was demonstrated to be usable as a process tool by preparing a relatively large number of samples reproducibly by this method. The rapid coating rate obtained would aid in production.

7. As a laboratory process, CVD showed the capability to deposit varied, controlled compositions of coatings.

8. Hydrogen reduction processes are acceptable for forming coatings for refractory materials without substrate embrittlement. Other impurities (primarily nitrogen and oxygen) can be excluded to produce high-purity materials.

9. The simultaneous codeposition of titanium and chromium alloys was demonstrated to be possible and was controllable over essentially the whole range of binary composition. Since titanium and chromium alloys vary widely in thermodynamic stability, it is expected that many metal combinations more similar in stability could be deposited by a similar process.

10. Silicon coatings can be deposited by the CVD process to produce unreacted layers, or they can be reacted and diffused to form silicides.

11. Oxidation testing of the coatings has shown performance nearly comparable to that provided by current coating methods. This is considered quite good for the relative amount of effort in the respective methods.

SECTION IX

RECOMMENDATIONS FOR FUTURE DEVELOPMENT

CVD processes have shown a particularly valuable and unique potential for rapid formation of coatings of controlled composition. To continue the process development to practical utilization, the following additional work is needed:

1. Further development of the trideposition process and evaluation of the oxidation performance, substrate interaction, and reliability.

2. Acquiring capability to protect faying surfaces and hidden areas.

3. Development of equipment to permit complete coating of small samples in batches of several samples in a single step.

4. Optimization of the coating procedures and process parameters.

5. Determination of feasibility of continuous coating of small parts.

6. Scale-up to coating of larger prototype parts.

7. Further extension of the coating process to other coatings of similar nature and to different types and new concepts in coatings.

APPENDIX

PARAMETERS AND RESULTS OF ALL COATING DEPOSITION EXPERIMENTS

Parameters and Results of Titanium Depositions

Experiment No.	He Flow Through $CrCl_3$ Tube (ml/min)	H_2 Flow Through $CrCl_3$ Tube (ml/min)	H_2 Flow Through Bubbler (ml/min)	Argon Flow Through Bubbler (ml/min)	$TiCl_4$ Flow (mg/min)	% Conc. $TiCl_4$ at Sample	Preheat Furnace Temp. (°C)	Δ Weight (mg)
(Samples 1 Through 21 Were Used to Check Gas Purity)								
22	800	500	1500	0	120	0.70	200	1.0
24	800	1000	1500	0	120	0.60	200	1.2
26	0	1000	1500	0	120	0.80	200	5.0
28	0	1000	1000	0	80	0.65	200	2.0
30	0	1000	1500	0	120	0.80	200	5.0
32	0	1000	1000	0	80	0.65	200	1.5
33	0	1000	1000	0	80	0.65	200	3.3
37	0	500	500	0	45	0.70	200	1.2
38	0	0	2000	0	160	1.32	200	2.5
40	0	1000	1000	0	80	0.65	200	4.4
42	0	0	1500	0	120	1.33	200	0.6
43	1000	0	1500	0	120	0.80	200	0.5
44	0	0	2500	0	200	1.32	200	1.0
45	1000	0	1000	0	80	0.65	200	0.6
46	0	0	1500	0	120	1.32	200	0.7
47	0	0	1000	0	80	1.30	200	0.3
48	0	0	500	0	45	1.32	200	0.4
49	0	0	2500	0	200	1.32	200	2.5
50	0	0	2500	0	200	1.32	600	3.1
51	0	0	2500	1000	200	0.94	700	1.0
52	0	0	1000	1000	80	0.65	700	4.2

Experiment No.	H_2 Flow (ml/min)	$TiCl_4$ Flow (ml/min)	% Conc. $TiCl_4$	Preheat Furnace (°C)	Δ Weight (mg)
53	500	0.36	10	700	+3.8
54	500	0.71	20	700	+4.4
55	500	1.25	30	600	+7.5
56	500	1.25	30	600	+2.1
57	500	1.25	30	450	+4.4
58	500	0.36	10	400	+1.7
59	2000	0.36	2.5	200	+0.5
60	2000	0.71	5	200	+0.8
61	100	0.26	42	200	-5.7
62	100	0.14	29	200	+1.0
63	100	0.36	50	200	-66.2
64	100	0.50	59	200	-85.6
65	100	0.36	50	200	-55.2
66	500	0.36	10	200	+0.2
67	1000	0.15	3	700	+11.1
68	1000	0.15	3	700	-6.1
69	2500	0.15	1	700	+9.1

All experiments were made at 1350°C and for 10-minute deposition time.

Titanium Depositions (continued)

Experiment No.	He Flow Through $CrCl_3$ Tube (ml/min)	H_2 Flow Through $CrCl_3$ Tube (ml/min)	H_2 Flow Through Bubbler (ml/min)	Argon Flow Through Bubbler (ml/min)	$TiCl_4$ Flow (mg/min)	% Conc. $TiCl_4$ at Sample	Preheat Furnace Temp. (°C)	Δ Weight (mg)
70	0	0	2500	0	200	1.32	700	+18.0
71	0	0	2500	0	200	1.32	700	+17.1
72	0	0	3600	0	285	1.32	700	-
73	0	0	3600	0	285	1.32	700	+24.0
74	0	0	2500	0	200	1.32	800	+16.4
75	0	0	3600	0	285	1.32	800	+21.1
76	0	0	2500	0	200	1.32	900	+14.4
77	0	0	3600	0	285	1.32	860	24.5
78	0	0	3600	1400	525	1.32	800	10.9
79	0	0	3600	1400	525	1.32	800	11.5
80	0	0	3600	1400	525	1.32	750	9.8
81	0	0	2500	0	200	1.32	800	5.0
82	0	0	3600	0	285	1.32	800	25.8
83	0	0	2500	0	200	1.32	800	7.1
84	0	0	2500	0	200	1.32	800	6.0
85	0	0	2500	0	200	1.32	700	6.8
86	0	0	4000	0	320	1.32	700	19.1
87*	0	0	2500	0	200	1.32	700	7.0
88**	0	0	3300	0	260	1.32	750	10.5
89*	0	0	2500	0	200	1.32	800	3.0
90**	0	0	3300	0	260	1.32	750	7.7
91	0	0	2500	0	200	1.32	800	3.7
92	0	0	2500	0	200	1.32	700	10.4
93**	0	0	3300	0	260	1.32	750	8.8
94	0	0	4000	0	320	1.32	800	19.2
95*	0	0	4000	0	320	1.32	800	7.8
96	0	0	2500	0	200	1.32	800	11.6
97*	0	0	4000	0	320	1.32	700	8.3
98**	0	0	3300	0	260	1.32	750	12.8

All experiments 10 minute deposition time and 1350°C except * 1200°C reactor temperature and ** 1275°C reactor temperature.

Parameters and Results of Chromium Depositions

Run No.	Ar Flow Through $CrCl_3$ Tube (mℓ/min)	H_2 Flow Through $CrCl_3$ Tube (mℓ/min)	H_2 Flow Through Bubbler (mℓ/min)	Ar Flow Through Bubbler (mℓ/min)	Preheat Furnace Temperature (°C)	Δ Wt. (mg)
99	1800	0	2000	0	500	11.6
100					500	2.1
101					500	- -
102					775	2.0
103					775	3.6
104					840	1.8
105					900	2.7
106					850	58.0
107	1800				850	5.2
108	3600				800	9.2
109	3600		2000		800	6.8
110	900		1800		775	102.2
111	900		1800		775	-31.5
112	900		1800		775	147.0
113	500		2000		725	108.8
114	1800				690	14.3
115	2500					5.5
116	2500		2000			8.0
117	2500		500		690	- -
118	1800		2000		675	4.4
119	2500		2500		675	5.0
120	2500		2500		675	4.7
121	2700		2700		690	7.5
122			4700			7.7
123			4300			9.2
124	2700		2000			5.7
125	1800		2000			106.6
126	500		1000			137.0
127			1000			169.8
128			1000			54.5
129			4600			91.9
130	500		4600		690	82.8
131	100		2000		850	16.2
132	100				890	7.2
133	500				875	37.5
134	500				900	68.2
135	200		2000			110.7
136	200		4700			15.2
137	200		4700		900	108.1
138	100		4700		830	53.5
139	500		6500		850	39.8
140	125		500		820	68.0
141	75	0	500	0	840	18.8

Argon Bubbled Through Hot $CrCl_2$

Run No.	H_2 Flow (ℓ/min)	Ar Flow (ℓ/min)	$CrCl_2$ Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
142	0.5	1.15	800	1200	31.3
143		1.15	800	1200	36.9
144		1.4 to 0.0	800	1100	36.0
145		1.5 to 0.8	775	800	34.3
146	0.5	0.7 to 0.3	800	925	-12.8

Argon + HCl Passed Over Hot Chromium Using Laval Orifice for $CrCl_2$

Run No.	HCl Flow (ml/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
147	5	3.5	0.0	1.5	800	1050	62.5
148	2			0.5			Dropped
149	2			0.5			3.1
150	5			1.0			2.7
151	10			1.0	800		2.6
152	10	3.5	0.0	1.0	900	1050	3.7

Chromium Depositions (continued)

Run No.	HCl Flow (mℓ/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
153	10	3.5	0.0	2.0	900	1050	2.8
154	20						2.7
155	30						2.8
156	75	3.5					3.7
157		2.0		2.0			12.0
158				3.0			48.8
159				3.0			14.9
160	75		0.0	0.5	900		4.7
161	25	2.0	2.0	1.0	800	1050	7.7
162	25	2.0	2.0	1.0	800	1050	4.1
163	25			2.0	800	1050	3.8
164	50			2.0	900	800	20.9
165	50	2.0	2.0	0.5			10.9
166	30	3.0	1.5	3.0			5.8
167		1.0	2.0	4.7		800	18.3
168		1.0	2.0	4.7		920	23.8
169		0.5	2.0	4.7			8.8
170		1.0	1.0	4.0			Dropped
171							26.5
172					900		37.5
173		1.0			850		39.0
174		1.5			850		31.2
175		2.0			850	920	6.9
176		1.0			900	1050	37.4
177		2.0			900	1050	20.1
178	30	0.5	1.0	4.0	850	1050	32.9
179	20	1.0	0.8	3.2		1265	6.9
180	60		1.2	4.8		1200	25.8
181	4		0.4	1.6		1200	18.1
182	4		0.4	1.6		1325	9.2
183	20		0.8	3.2		1265	31.9
184	12		1.2	4.8		1200	8.3
185	20		0.4	1.6		1200	13.2
186	20		0.4	1.6		1325	13.7
187	20		0.8	3.2		1265	8.3
188	12		1.2	4.8		1325	5.6
189	60		1.2	4.8		1325	10.3
190	20	1.0	0.8	3.2	850	1265	Dropped
191	20	1.0	0.8	3.2		1265	24.4
192	60		1.2	4.8		1200	7.0
193	4		0.4	1.6		1200	18.0
194	4		0.4	1.6		1325	10.2
195	20		0.8	3.2		1265	25.5
196	12		1.2	4.8		1200	13.9
197	60	1.0	1.2	4.8		1325	7.2
198	20	1.0	0.4	1.6		1325	53.7
199	20		0.8	3.2		1265	16.1
200	12		1.2	4.8		1325	13.0
201	20		0.4	1.6		1200	13.2
202	20		0.8	3.2		1265	14.5
203	60	1.0	1.2	4.8	850	1325	9.3

Adapter Plate Used to Reduce Size of H_2 + Argon Outlet

Run No.	HCl Flow (mℓ/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
204	30	1.0	1.0	4.5	850	1325	101.9
205	5	2.0	1.0	4.5			38.3
206		3.0	1.0	2.0			16.8
207			1.6	2.0			13.2
208				1.0			9.5
209				1.0			19.7
210			1.6	0.5		1325	8.7
211			1.0	4.5		1200	9.1
212			1.0	2.0			8.9
213			1.6	2.0			10.5
214			1.6	1.0			8.2
215			1.6	0.5			6.1
216			0.0	1.0			5.7
217				4.5			5.8
218	5			0.5			21.9
219	20			0.5		1200	41.2
220	5	3.0		4.5		1325	7.7
221	10	2.5	0.0	4.5	850	1325	22.3

Chromium Depositions (continued)

Run No.	HCl Flow (ml/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
Adapter Plate Removed, Allowing H_2 + Argon to Exit Through 1/2" Opening							
222	5	2.0	1.0	4.5	850	1325	28.2
223		3.0	1.6	2.0			15.3
224			1.6	0.5			11.9
225			0.0	1.0			16.1
226		3.0		5.0			8.1
227		3.75					5.9
228		3.75				1325	14.4
229	5	3.35				1200	5.9
230	15	3.0		5.0			20.0
231	5	2.6		7.0			13.2
232		2.5				1200	9.1
233		2.0				1325	7.8
234		2.0				1200	Dropped
235		3.3				1325	3.6
236						1200	9.7
237						1200	12.2
238		3.3				1325	12.6
239		0.3				1325	4.5
240		0.3				1325	6.6
241	5	0.5				1200	7.2
242	20	0.4				1200	10.5
243	60	0.5	0.0	7.0	850	1200	31.8
Nozzle Used That Forces Gas Streams to Converge, Diverge, and Rotate							
244	5	2.0	0.0	3.0	800	1325	5.7
245		2.0	0.0	3.0	800	1325	5.1
246		1.0	3.0	2.0	800	1325	4.3
247			3.0	4.0	850	1250	5.7
248	5		0.0	4.7			12.1
249	10		3.0	4.0			14.6
250	5	1.0	3.0				8.8
251	5	0.2	3.0		850		9.4
252	10	3.7	1.9		800		19.4
253	5	1.0	4.0	4.0	800		6.6
254	10	1.0	4.0	4.0	800		8.8
255	5		0.0	6.5	850		9.2
256	30	1.0	4.0	4.0	800		41.5
257	5	0.5	4.0				14.9
258	5	1.0	3.4				9.5
259	15	1.0	3.4				14.8
260	10	1.0	3.4	4.0	800	1250	13.6
261	15	1.0	3.0	4.0	800	1250	16.7
262	15		0.0	6.5	800	1250	21.6
263	20		0.8	3.2	850	1275	28.7
264	4		0.4	1.6		1200	7.4
265	4		0.4	1.6		1350	28.9
266	20		0.8	3.2		1275	31.8
267	4		0.4	1.6		1200	6.3
268	4		0.4	1.6		1350	33.8
269	15		4.0	4.0		1275	15.9
270			1.0				18.0
271			1.0				12.5
272			1.0				10.5
273			4.0				6.4
274			1.0				40.0
275			4.0	4.0			10.0
276			0.0	1.0	850		19.2
277				6.5	800		6.6
278		1.0		4.0	800		15.2
279		2.0		4.0			23.2
280		2.0		4.0			16.5
281		1.0		6.5			8.0
282		2.0		4.0			11.3
283	15			4.0	800		10.2
284	20			3.5	850		---
285	20			3.5		1275	10.1
286	7.5			1.0		1200	4.0
287	40			6.0		1200	5.8
288	20			3.5		1275	22.2
289	7.5			1.0		1350	10.9
290	20	2.0	0.0	6.0	850	1200	29.4

Chromium Depositions (continued)

Run No.	HCl Flow (cm^3/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
291	40	2.0	0.0	6.0	850	1350	28.1
292	Purity Check - All Gasses						
293	20	2.0	0.0	3.5	850	1275	10.2
294	15	2.0	0.0	1.0	850	1350	11.7
295	20			6.0		1350	5.4
296	15			1.0		1350	12.9
297	15			1.0		1200	14.4
298	20			3.5		1275	2.7
299	7.5			1.0		1350	3.5
300	40			6.0		1350	3.0
301	40			6.0		1200	3.9
302	20			6.0		1200	1.0
303				3.5		1275	0.5
304							15.6
305							15.0
306	20	2.0	0.0	3.5	850	1275	12.5
307	Purity Check - All Gasses						
308	Purity Check - Ar + H_2						
309	Purity Check - Ar						
310	Purity Check - No Gases						
311	Purity Check - H_2						
312	Purity Check of HCl + Ar - Discolored						
313	20	2.0	0.0	3.5	850	1275	8.0
314	15			1.0		1275	7.7
315	15			1.0		1200	8.2
316	40	2.0		6.0		1200	28.1
317	20	1.0		3.5		1275	13.9
318	20	2.0		3.5		1275	16.9
319	15			1.0		1275	15.6
320	15			1.0		1200	15.5
321	15			1.0		1350	12.3
322	20			3.5		1275	15.8
323	7.5			1.0		1200	4.8
324	7.5	2.0	0.0	1.0	850	1350	5.3
325	7.5	2.0	0.0	1.0	850	1350	5.3
326	20			3.5		1275	4.5
327	20			3.5		1275	6.0
328	15			1.0		1200	2.2
329						1200	2.5
330						1050	2.6
331						1350	3.4
332	15					1200	2.2
333	40			1.0	850	1200	2.8
334	20			3.5	750	1275	19.0
335						1275	19.5
336						1275	15.4
337				3.5	750	1350	17.9
338				0.5	800		15.3
339					800		13.3
340	20				900		16.3
341	5			0.5	900		5.2
342	20			3.5	850	1350	11.9
343	20			3.5	850	1275	11.0
344	40			3.5	900	1275	21.2
345	15			1.0		1200	7.4
346	15			1.0		1125	3.8
347	15			1.0		1275	6.0
348	40			3.5	900		19.5
349	15			1.0	850		6.5
350	15	2.0		1.0			8.3
351	40	3.0		3.5			16.7
352	20	2.0		1.0			9.4
353	15	2.0		1.0			14.0
354	40	3.0	0.0	3.5	850	1275	21.9

Chromium Depositions (continued)

Run No.	HCl Flow (cm^3/min)	Ar Flow Through Cr (ℓ/min)	Ar Flow Through Ti (ℓ/min)	H_2 Flow (ℓ/min)	Cr Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
355	15	2.0	0.0	1.0	850	1275	4.8
356	40	3.0	0.0	3.5			17.4
357	40	3.0	1.5	2.0			26.2
358	18	2.0	0.0	2.0		1275	9.8
359	15			0.5		1200	8.1
360	33			3.5		1200	25.0
361	18			2.0		1275	18.2
362	7.5			0.5		1350	6.8
363	16.5			3.5		1200	14.3
364	33			3.5		1350	34.3
365	18			2.0		1275	18.7
366	15			0.5		1350	12.3
367	16.5			3.5		1350	19.1
368	7.5			0.5		1200	11.0
369	7.5			0.5		1200	8.4
370	18			2.0		1275	15.4
371	7.5			0.5		1200	5.2
372	7.5	2.0	0.0	0.5	850	1200	4.2

Run No.	H_2 Flow Through Bubbler & Ti (ℓ/min)	H_2 Flow Through Ti Only (ℓ/min)	Ar Flow Through Cr (ℓ/min)	HCl Flow (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
373	3.5	0.0	0.0	0.0	800	1275	4.3
374	2.0		2.0				3.7
375	3.5		1.0				2.0
376	3.5		0.0			1275	2.5
377	3.5					1200	2.8
378	3.5					1200	0.2
379	2.0					1200	1.1
380	3.5					1350	3.2
381	3.5		0.0		800	1075	0.7
382	2.0		2.0		850	1275	4.2
383	2.0		0.0			1275	6.8
384	4.0					1350	3.1
385	2.0					1350	1.8
386	2.0		0.0	0.0		1200	0.4
387	2.0		2.0	20.0	850	1275	8.2
388	6.0		0.0	0.0	850	1275	1.1
389	0.5				850	1275	0.3
390	2.0				850	1275	0.6
391	4.0				700	1350	6.3
392	4.0	0.0				1350	Dropped
393	2.0	1.0	0.0	0.0	700	1350	5.7
394	2.0	0.0			700		2.3
395	1.5				850		0.8
396	4.0		0.0		850		1.1
397	4.0	0.0	1.0		800		1.9
398	1.0	2.5	1.0		800		22.2
399	4.0	0.0	0.0		850		39.7
400	4.0				850	1350	20.1
401	2.0				850	1200	1.5
402	4.0				900	1350	10.2
403	2.0						4.8
404	4.0						7.3
405			0.0				5.1
406			1.0		900		7.1
407			0.0			1350	12.3
408					900	1275	3.0
409	4.0				750	1200	0.6
410	6.0					1200	1.9
411						1350	8.5
412					750	1275	16.4
413					850		6.9
414					850		7.3
415					775		3.8
416					725	1275	1.6
417					800	1240	6.0
418					825	1350	9.1
419					800	1225	4.5
420	6.0	0.0	0.0	0.0	800	1275	3.8

Chromium Depositions (continued)

Run No.	H_2 Flow Through Bubbler & Ti (ℓ/min)	H_2 Flow Through Ti Only (ℓ/min)	Ar Flow Through Cr (ℓ/min)	HCl Flow (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
421	6.0	0.0	0.0	0.0	700	1275	2.7
422	8.0				750	1275	1.6
423	6.0				775	1270	2.3
424					800		1.1
425					800		0.3
426	6.0				750		1.0
427	4.0				750		1.1
428					875		5.2
429					825		6.6
430					800		10.2
431					700		10.2
432					825		8.1
433	4.0				750		13.5
434	2.5				675		7.0
435	2.5				800		5.0
436	4.0	0.0			750		5.6
437	2.0	2.0			750		22.5
438	3.0	3.0			775		21.0
439	3.0	1.0			750		21.1
440	1.0	3.0			775		Dropped
441	2.0	2.0			775		3.2
442	2.0	2.0			750		2.2
443	2.0	2.0			725		1.3
444	4.0	0.0			700		1.2
445	4.0	0.0			800		4.2
446	2.0	2.0	0.0	0.0	700		3.6
447			2.0	20.0	725		13.9
448			2.0	10.0	750		17.9
449			0.0	0.0	750		12.9
450	2.0	2.0	0.0	0.0	725	1270	12.6
451			1.0	0.0	725		19.4
452			1.0	20.0	750		15.0
453			2.0	10.0	725		13.6
454			2.0	0.0	750		2.0
455			2.0				2.1
456			1.0				3.1
457			1.0				5.6
458			1.0				3.3
459			0.0				2.2
460							3.4
461						1270	4.2
462						1275	5.4
463			0.0	0.0		1300	7.2
464	2.0	2.0	1.0	5.0		1300	6.2
465	2.0	2.0	2.0	0.0	750	1275	11.6
466	2.0	2.0	2.0				8.1
467	0.0	6.0	0.0				3.6
468		6.0	0.0				2.4
469		6.0	1.0				2.0
470	0.0	4.0	0.0				4.2
471	2.0	2.0	2.0				5.6
472	2.0	2.0	2.0				3.9
473	2.0	2.0	0.0				9.7
474	0.0	4.0	0.0	0.0	750		5.5
475	4.0	0.0	1.0	5.0	775		0.5
476	4.0		2.0	20.0	775		12.7
477	2.0			10.0	775		9.7
478	2.0	0.0		10.0	800		2.1
479	0.0	2.0	2.0	0.0	800		1.2
480	0.0	2.0	1.0	0.0	800	1275	1.4
481	2.0	2.0	1.0	0.0	800	1275	4.0
482		2.0	1.0				8.8
483		2.0	2.0				9.0
484	2.0	3.0		0.0			8.9
485	4.0	0.0		10.0			1.6
486	4.0	0.0		10.0			6.2
487	4.0	0.0		20.0	800		9.8
488	2.0	2.0		0.0	700		3.9
489		2.0			750		8.2
490		2.0	2.0				10.4
491		5.5	0.0			1275	7.1
492	2.0	2.0	2.0	0.0	750	1300	11.4

Chromium Depositions (continued)

Run No.	H_2 Flow Through Bubbler & Ti (ℓ/min)	H_2 Flow Through Ti Only (ℓ/min)	Ar Flow Through Cr (ℓ/min)	HCl Flow (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
493	2.0	0.0	2.0	0.0	750	1300	8.6
494	0.0	3.0	0.0			1300	4.7
495			0.0			1250	4.0
496			2.0				3.9
497			0.0				3.1
498			0.0				5.9
499			1.0		750		4.7
500		3.0	0.0		600		6.9
501	0.0	4.5	0.0		700	1250	-
502	2.0	2.0	1.0			1275	5.6
503	2.0	2.0	0.0			1275	2.7
504	0.0	4.0	0.0		700	1275	2.6
505			1.0		750	1300	28.7
506					750	1300	9.2
507		4.0			650	1300	5.7
508	0.0	2.0		0.0		1250	1.4
509	3.0	0.0		10.0			4.9
510	0.0	0.0		20.0			17.5
511		3.0		0.0			0.9
512			1.0				0.7
513			0.0		650		1.0
514	0.0	3.0	1.0		750	1250	1.0
515	3.0	0.0			750	1300	3.1
516	3.0	0.0		0.0	700		1.5
517	0.0	3.0		20.0	750		25.8
518	1.5	1.5		0.0	800	1300	3.6
519	3.0	0.0				1275	7.0
520							5.4
521					800		2.8
522					750		1.7
523							1.2
524	3.0	0.0		0.0			0.9
525	0.0	3.0		20.0			30.8
526	3.3	3.3	1.0	0.0	750		5.9
527	2.0	2.0	0.0		700		6.2
528	3.0	0.0	1.0		800		1.2
529	6.0	0.0		0.0	800		2.2
530	0.0	3.0		30.0	750		2.2
531			1.0	75.0	750	1275	5.7
532			0.0		750	1200	2.6
533		3.0		75.0	825	1350	3.9
534		4.0		90.0	825	1350	8.8
535				90.0	825	1350	3.0
536			0.0	75.0	775	1250	
537			1.0				8.0
538			1.0				5.6
539			0.0				5.6
540	0.0	4.0	1.0	75.0	775	1250	7.0
541	Purity Check						
542	Purity Check						
543	Purity Check						
544	0.0	3.0	1.0	75.0	750	1275	2.3
545			0.0	75.0	800		1.2
546			0.0	30.0	750		1.4
547	0.0	3.0	1.0	20.0			3.0
548	3.0	0.0		0.0			0.5
549					750		0.2
550					800		10.9
551			1.0				4.8
552	3.0		0.0				3.2
553	5.0	0.0	0.0	0.0	800	1275	4.4

Run No.	H_2 Flow Through Ti & Bubbler (ℓ/min)	H_2 Flow Through Ti Only (ℓ/min)	Ar Flow Through Cr (ℓ/min)	HCl Flow (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
554	5.0	0.0	0.0	0.0	0.0	1275	4.0
555	3.0		1.0			1150	0.5
556	3.0					1275	3.0
557	5.0						5.3
558							6.7
559							8.6
560			1.0				10.0
561	5.0		0.0				8.8
562	4.0					1275	3.2
563						1200	2.6
564			0.0			1350	7.1
565			1.0		800		12.9
566		0.0			700		10.9
567		1.5			800		19.6
568		2.5					23.8
569							22.5
570							22.7
568							16.2
569							14.3
571	4.0	2.5		0.0			22.2
572	0.0	5.0	1.0	20.0			7.7
573		5.0	1.0				7.4
574		5.0	1.0				8.2
575		3.0	1.0				10.7
576		3.0	2.0	20.0			10.0
577		3.0	3.0	30.0			21.8
578		4.0	2.0	20.0			13.7
579	0.0	4.0	2.0	20.0			21.0
580	2.0	2.0	2.0	0.0			3.6
581	2.0	2.0	2.0	0.0	800	1350	2.4
582	4.0	2.0	1.0	0.0	800	1350	7.2
583		2.0					5.7
584		2.5					7.1
585		2.5					1.1
586	4.0	2.5		0.0			0.9
587	0.0	5.0		20.0			9.6
588	0.0	4.0		20.0			19.3
589	0.0	4.0		70.0			65.4
590	3.0	1.0		0.0			34.0
591	3.0	1.0					5.5
592	4.0	2.5					11.1
593	4.0						10.8
594	3.0				800		13.6
595	4.0				750		15.3
596	4.0	2.5					10.4
597	6.0	4.0					17.0
598	4.0	2.5					16.3
599		0.0					9.0
600		2.5	1.0				13.2
601			2.0				8.9
602			0.0				6.7
603			1.0				21.8
604			1.0				23.6
605	4.0	2.5	2.0	0.0			21.5
606	0.0	5.0	1.0	20.0			15.7
607	3.0	1.0		20.0			35.8
608	0.0	4.0		20.0			37.0
609	4.0	2.5		0.0			13.8
610							16.4
611							12.6
612							13.8
613	4.0	2.5	1.0	0.0	750	1350	11.7

Chromium Depositions (continued)

Run No.	H_2 Flow Through Ti & Bubbler (ℓ/min)	H_2 Flow Through Ti Only (ℓ/min)	Ar Flow Through Cr (ℓ/min)	HCl Flow (mℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
614	4.0	2.5	1.0	20.0	750	1350	12.9
615	0.0	5.0		20.0			6.8
616	0.0	3.0		20.0			7.9
617	0.0	3.0		50.0			12.4
618	4.0	2.5		0.0			16.2
619	4.0	2.5		0.0			23.9
620	0.0	3.0		20.0			12.2
621	3.0	0.0		0.0	750	1350	11.2
622	3.0				700	1250	8.5
623	3.0				750		11.7
624	4.0						10.4
625							---
626		0.0					7.5
627		2.5		0.0	750		6.3
628				20.0	800		6.4
629	4.0		1.0	0.0	800		6.4
630	5.0		2.0	30.0	750		26.2
631	4.0	2.5	1.0	20.0	750	1250	12.1

Parameters and Results of Titanium-Chromium Alloy Deposition

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Bubbler & Cr (ℓ/min)	Ar Flow Through Cr Only (ℓ/min)	Argon With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt (mg)
632	4.0	2.5	0.0	0.0	800	1275	42.7
633	6.5	4.0		0.0	800		87.8
634	6.5	1.0		0.0	750		28.0
635	3.0			2.0	775		25.7
636	6.1			0.0	800		39.9
637	4.0			1.0			46.8
638	4.0			1.0			46.1
639	4.0	1.0	0.0	1.0	800	1275	41.1
640	4.0	1.0	0.0	0.0	600	1250	4.3
641			1.0	1.0	700	1250	16.7
642			0.0	1.0	700	1325	21.7
643				1.5	700	1325	16.6
644		1.0		1.5	800	1325	42.8
645	4.0	1.5		1.5		1300	53.8
646	3.0	1.0		2.0			52.1
647	2.0	0.6		2.5			36.8
648	1.0	0.6		2.5			40.0
649	2.0	0.3		2.5	800		23.6
650	5.8	0.6		0.0	750		54.9
651	5.8	1.0		0.0	700		44.3
652	5.8			0.0	700		36.2
653	4.0		0.0	1.0	800		40.5
654	4.0	1.0	1.0	1.0			42.3
655	2.0	0.5	0.0	2.5			16.0
656		0.6		2.5			20.0
657		0.6		2.0			28.7
658		0.5		2.0			24.9
659		0.0		2.0			(Purity Check)
660		0.5		2.2	800		21.6
661		0.5		2.4	740		12.8
662		0.5	0.0	2.4			10.3
663	2.0	0.7	2.0	2.4			16.9
664	0.5	0.7	2.5	0.0			16.3
665	2.0	0.7	0.0	2.0			11.2
666	2.0	1.0	0.0	2.0	740		19.8
667	2.0	1.0	0.0	2.0	700	1300	19.3

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Bubbler & Cr-Ti (ℓ/min)	Ar Flow Through Ti-Cr Only (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
668	2.0	1.0	0.0	2.0	800	1250	4.4
669		1.5				1250	4.7
670		2.0				1325	10.0
671		2.0				1325	10.9
672		2.5				1325	11.3
673		2.5				1250	5.8
674	2.0	2.0	0.0	2.0			8.9
675	4.5		1.0	0.0			12.1
676	2.0			2.0			11.8
677	1.5			2.2		1250	10.4
678	1.0			2.2		1350	11.0
679	1.0	2.0		2.2			10.0
680	2.0	1.0		2.0			8.2
681					800		4.6
682					840		7.8
683	2.0	1.0		2.0			4.7
684	4.5	2.5		1.0		1350	23.4
685	4.0	2.5	1.0	1.5		1250	14.3
686	4.8	2.5	0.0	0.0	840	1250	29.9

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
687	2.0	0.0	2.5	2.0	840	1250	24.9
688	2.0		1.0	2.0			12.0
689	2.0		1.0	3.0			8.3
690	5.0	0.0	2.0	3.0			18.9
691	5.0	1.0	2.0	3.0			20.2
692	2.0	0.0	1.0	2.0		1250	10.3
693				2.0	840	1350	17.7
694				2.0	910	1300	14.5
695				1.0	910	1300	22.7
696				2.0	840	1300	---
697				2.0	860	1275	4.2
698				1.0			9.4
699			1.0	2.0			2.9
700			2.0	2.0			7.1
701			2.0	3.0	860		7.0
702			2.5	3.0	800		8.8
703			2.0	2.0			4.8
704			2.0	1.8		1275	6.4
705			2.0	2.0		1325	10.0
706			4.0	0.0			30.3
707	2.0		4.0	1.6			25.5
708	5.0		5.0	0.0			47.8
709	5.0		4.0	6.0			18.5
710	2.0		4.0	0.0			32.2
711			2.0	2.0			13.2
712							10.3
713							6.9
714			2.0				7.3
715			4.0	2.0			5.7
716			3.0	4.0			3.7
717			2.0	2.0			6.1
718			1.0				4.2
719			1.0		800		18.0
720	2.0		1.0		725		3.6
721	4.0		4.0	2.0	550		1.3
722	2.0		2.0	0.0	800		3.3
723	1.0		1.0	1.0			6.9
724	2.0		2.0	2.0			3.0
725	4.0	0.0	2.0	2.0	800	1325	5.0

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
726	4.0	0.0	4.0	2.0	800	1325	5.0
727			4.0	0.0			16.5
728			5.5				14.2
729		0.0	4.0			1325	18.9
730	4.0	2.0				1300	10.7
731	5.0	2.8				1300	11.3
732	5.0	0.0				1300	15.4
733	4.0		4.0			1250	11.1
734	3.0		5.0			1300	16.3
735	3.0		3.0			1200	10.3
736	5.0		3.0			1200	12.7
737	4.0		4.0			1250	8.5
738	3.0		3.0			1300	31.2
739	4.0		4.0			1250	8.6
740	4.0		4.0			1250	14.0
741	3.0		3.0			1300	14.0
742	5.0		5.0			1300	20.4
743	4.0		4.0			1250	15.8
744	5.0		5.0			1200	15.7
745	5.0		3.0			1300	---
746	5.0		3.0			1300	22.5
747	3.0		5.0			1200	15.1
748	4.0		4.0			1250	17.0
749	3.0		5.0			1300	18.7
750	3.0		5.0			1200	11.9
751	4.0		4.0			1250	9.8
752	5.0		3.0			1300	22.6
753	4.0		4.0			1250	18.8
754	5.0		5.0			1300	17.0
755	5.0		3.0			1300	16.3
756	4.0	0.0	4.0			1250	17.3
757	3.0	2.4	0.6			1300	8.2
758	3.0	2.4	0.6			1200	5.7
759	5.0	0.0	3.0	0.0	800	1300	18.4

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
760	4.0	0.0	4.0	0.0	730	1250	11.4
761					650		4.0
762					650		4.2
763					800		1.4
764							---
760'							29.5
765							26.1
766							23.7
766'					800		16.8
767					750		16.6
768							20.0
769							22.3
770							20.7
769'							21.1
770'							22.2
771							15.0
772							22.9
773							23.6
772'							23.6
774							25.3
773'							24.9
775							15.9
776							26.9
774'							26.5
775'							28.2
777							27.6
776'							27.1
777'							26.7
778	4.0	0.0	4.0	0.0	750	1250	3.9

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow with H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
779	5.0	0.0	4.0	0.0	750	1250	6.9
780	5.0		5.0			1300	10.5
781	5.0		6.0				8.9
782	4.0		4.0				6.7
783	5.0		4.0				7.6
784	5.0		5.0			1300	9.1
785	4.0		4.0			1250	8.5
786	5.0		4.0			1250	8.6
787	5.0		6.0			1300	10.3
788	4.0		4.0			1200	13.3
789						1230	11.2
790						1230	10.9
791						1300	8.8
792						1250	8.0
793						1250	8.2
794						1240	9.1
795						1240	9.2
796						1265	4.9
797						1265	7.3
798						1270	6.8
799	4.0	0.0	4.0	0.0	750	1260	---

Parameters and Results of Silicon Depositions

Run No.	Substrate	H_2 Flow	Ar Flow To Reactor	Ar Flow Through Bubbler	Reactor Temperature (°C)	Δ Wt. (mg)
800 F	Mo	7.0	7.0	1.0	1000	11.4
800 C					1000	11.8
800 B					1000	8.8
801			7.0		1050	6.9
802			15.0	1.0		6.4
803			15.0	0.5		5.2
804		7.0	7.0	0.5	1050	4.5
805		4.5		1.0	1250	16.9
806	Mo	7.0		0.2		8.2
807	Ta			0.2		8.3
808	Ta					12.0
809	Ta					7.6
810 F	Ti on B66 #437					19.8
810 C	Cr on B66 #667					---
810 B	Cr-Ti on B66 #773					35.6
811	Ta					2.4
812	Ta					9.6
813 F	Cr-Ti on B66 #770					33.5
813 C	Cr-Ti on B66 #773'					21.5
813 B	Cr on B66 #362	7.0	7.0	0.2	1250	9.6

Parameters and Results of Titanium-Chromium Alloy Depositions

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
814	4.0	0.0	4.0	0.0	750	1300	---
815	4.0				750		4.9
816	4.0				750		4.4
817	5.0				650		1.2
818	4.0		4.0		750	1300	1.7
819	5.0		5.0			1200	1.3
820		0.0	5.0			1350	3.0
821		3.0	2.0				6.0
822		3.0	2.0				4.5
823		3.5	4.0	0.0			3.2
824		3.0	2.0	4.0		1350	3.1
825				0.0		1400	7.0
826							8.7
827							5.8
828							5.9
829			2.0				5.1
830			4.0				8.7
831		3.0	2.0				12.5
832		0.0	2.0			1400	11.8
833			2.0			1250	4.4
834			5.0			1400	5.5
835	5.0		1.0			1400	18.2
836	2.0		1.0			1400	12.1
837	2.0		1.0			1450	12.1
838	5.0		2.5		750	1250	3.9
839					840	1250	---
840					750	1300	4.7
841					750	1300	6.0
842					800	1350	16.1
843			2.5		750	1350	7.7
844			4.0		750	1350	4.8
845			2.5		800	1220	9.3
846			2.5		700	1350	3.5
847			2.5		760	1300	5.9
848			4.0		700	1350	3.0
849			1.0		700	1220	7.1
850			1.0		825	1220	9.1
851			2.5		760	1300	7.7
852			1.0		700	1350	12.9
853			4.0		825	1350	10.3
854			2.5		760	1300	8.0
855			4.0		825	1220	6.5
856			1.0		825	1350	16.5
857			2.5		720	1250	3.4
858			2.5		720	1300	5.5
859			2.5		820		16.5
860			1.0				15.7
861			0.5			1300	8.4
862			1.0			1350	13.1
863			2.5				12.0
864			4.0				21.2
865						1350	12.4
866						1300	---
867			4.0				15.0
868			5.0				18.0
869			5.0				17.2
870			6.0				20.6
871			1.0				10.7
872			2.0				8.7
873			3.0				16.2
874			6.0				7.3
875	5.0		1.0		820		9.0
876	5.0		1.0		900		11.0
877	5.5	0.0	5.0	0.0			28.1

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
878	5.5	0.0	5.0	0.0	900	1300	92.4
879	5.0					1000	28.2
880						900	27.5
881					900	1100	31.5
882					840	1000	12.9
883					900	1000	29.0
884					900	1200	36.2
885					900	1300	37.5
886					875	825	22.1
887					850	1000	31.4
888					950	1000	42.6
889					850	1000	22.4
890					900	1000	34.8
891					850	1000	75.3
892					850	850	84.7
893			5.0		850	1250	---
894			4.0		800	1300	33.1
895			4.0				33.1
896			5.0				38.0
897			3.0		800		12.5
898		0.0	1.0		750		28.5
899		4.0			800		14.2
900		0.0			750		15.0
901			1.0		800		15.5
902			1.5			1300	12.6
903			1.5			1200	4.8
904			1.0		800	1270	7.6
905					900		10.1
906					950		11.7
907					1000	1270	8.6
908					900	1325	16.0
909						1375	17.3
910			1.0			1300	19.0
911			4.0		900		12.9
912					1000		16.9
913							18.1
14							11.6
915			4.0				14.1
916			1.0				14.1
917			5.5				11.1
918			5.0				11.4
919			5.0				9.7
920			3.0				13.1
921			4.0				16.2
922			4.0			1300	16.2
923			4.0			1200	15.4
924			3.0				11.6
925			1.0		1000		8.6
926			1.0		1100		9.7
927			4.0		1100		13.5
928			1.0		1100		11.2
929			4.0		1000	1200	7.7
930	5.0		5.5			1250	7.3
931	1.0		4.0				9.8
932	1.0		3.0		1000		9.2
933	5.0		1.0		900		9.7
934	5.0		3.0		900		8.6
935	4.0		4.0		800		5.0
936	5.0		1.0				8.4
937			2.0				9.0
938	5.0	0.0	3.0	0.0	800	1250	6.5

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
939	5.0	0.0	2.0	0.0	850	1200	8.5
940			5.5		850	1250	6.3
941			4.0		900	1275	10.7
942			1.0		900	1300	12.5
943			4.0		1000	1300	17.0
944			4.0		1000	1200	12.2
945			2.0		1000	1200	11.8
946			1.0		900	1350	16.9
947			4.0		900	1350	18.2
948					900	1000	3.8
949					1000	1000	3.8
950						1300	19.9
951			4.0				22.7
952	5.0		1.0				16.3
953	2.0		1.0				15.4
954	1.0	0.0	1.0				13.6
955	5.0	1.0	3.0				----
956	5.0	2.0				1300	14.6
957	4.0					1275	----
958						1275	17.1
959					1000	1300	17.6
960					900	1250	10.5
961	4.0	2.0	3.0		1000	1250	13.5
962		2.0	4.0			1250	16.0
963	4.0	1.0	4.0			1275	18.0
964	3.0	1.0	4.0			1275	17.8
965	5.5	1.0	4.0		1000	1275	18.1
966	5.0	0.0	1.0		800	1300	----
967					900	1300	19.9
968					900	1250	15.4
969					1000	1200	17.7
970			1.0			1000	7.3
971			4.0			1200	25.4
972			4.0			1200	25.5
973	5.0	0.0	4.0	0.0	1000	1300	30.7
974	5.0	0.0	1.0	4.0	900	1000	20.7
975			1.0				20.1
976			4.0				19.6
977	5.0		1.0		900	1300	19.0
978	3.0		2.0		1000	1250	15.5
979	3.0					1250	22.6
980	3.0					1250	14.2
981	2.0					1200	13.6
982	3.0					1300	20.9
983	3.0		2.0			1250	17.2
984	5.0		1.0			1250	11.3
985	3.0		2.0			1300	26.4
986	5.0						11.5
987							8.7
988							6.9
989							8.4
990	5.0						7.3
991	3.0						13.2
992	3.0				1000		21.5
993	3.0		2.0		900		15.6
994	5.0		1.0				9.2
995	5.0		1.0				9.1
996	3.0		2.0		900		10.3
997	3.0		2.0		1000		18.6
998	5.0		1.0				12.6
999	4.0					1300	11.0
1000	3.0					1350	12.3
1001	3.0						13.6
1002	5.0						13.8
1003	1.0		1.0				12.8
1004	2.0		2.0				18.0
1005	3.0		3.0				20.9
1006	3.0		3.0				19.2
1007	4.0	0.0	3.0	0.0	1000	1350	22.1

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1008	4.0	0.0	3.0	0.0	1000	1350	20.0
1009	5.0		5.0				25.2
1010	7.0						26.0
1011	3.0						25.8
1012	1.0				1000		24.3
1013	1.0				950		19.3
1014	1.0		5.0				17.4
1015	5.0		1.0				12.2
1016	4.0		5.0				21.6
1017	7.0				950		23.3
1018	4.0				1000		28.2
1019							28.1
1020							27.5
1018'							30.0
1019'					1000		29.5
1021			5.0		900		25.2
1022			2.0		900		22.1
1023			5.0		1000		44.0
1024							47.6
1025							50.4
1023'							47.8
1024'							48.2
1025'							44.7
1026							42.4
1027							47.3
1028							47.4
1026'							45.3
1027'							45.8
1029							47.6
1028'							45.4
1029'	4.0		5.0		1000		47.0
1030	5.0		4.0		900		7.5
1031	2.0		5.0		900	1350	3.3
1032	7.0				900	1350	12.0
1033	7.0			0.0	1000		12.3
1034	3.0			3.0			7.8
1035	2.0			0.0		1350	2.7
1036	2.0		5.0	2.5		1450	7.3
1037	5.0		4.0	0.0		1350	12.1
1038	2.0		4.0				14.0
1039	5.0		2.0				10.4
1040	2.0	0.0	5.0				13.7
1041	2.0	2.0	3.0				11.8
1042	2.0	2.0	1.0				7.8
1043	4.0	2.0	3.0				14.7
1044	5.0	3.0					13.8
1045	7.0	2.0					12.2
1046	4.0	2.0					12.9
1047		1.0					15.0
1048		1.0					16.9
1049	4.0	2.0					13.1
1050	2.0	2.0					11.2
1051	7.0	0.0					17.2
1052	1.0	2.0					8.8
1053	4.0						10.8
1054	4.0						8.0
1055	4.0	2.0					7.4
1056	7.0	0.0					12.6
1057	5.0	2.0					5.4
1058	10.0	2.0					5.2
1059		0.0	3.0				9.5
1060			5.0				9.6
1061	10.0		5.0				6.9
1062	4.0		4.0				3.0
1063	2.0		5.0	0.0			1.4
1064	7.0		4.0	2.5	1000		6.9
1065	4.0	0.0	4.0	0.0	1100	1350	2.3

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1066	4.0	0.0	4.0	0.0	1000	1350	33.2
1067	5.0		2.0			1300	26.2
1068	5.0					1300	22.3
1069	5.0					1250	21.2
1070	7.0					1300	27.3
1071	7.0					1300	23.9
1072	7.0	0.0	2.0			1325	30.8
1073	5.0	3.0	0.0			1325	0.4
1074	7.0	0.0	2.0			1300	37.6
1075			1.0			1250	35.5
1076						1275	34.9
1077							27.0
1078							28.8
1079							26.8
1078'							18.0
1079'							1.5
1080			1.0			1275	16.9
1081			3.0			1350	39.5
1082						1300	35.6
1083						1275	32.7
1084	7.0		3.0			1275	28.7
1085-1	5.0		5.0			1300	26.8
1085-2							24.9
1085-3							8.1
1085-4	5.0	0.0	5.0	0.0	1000	1300	18.4

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1086	5.0	0.0	3.0	0.0	1000	1300	25.6
1087						1325	25.8
1088						1300	21.5
1089					1000	1350	21.7
1090			3.0		940		16.8
1091			5.0		950		19.2
1092			3.0				17.3
1093							18.0
1090'							18.2
1092'							18.0
1093'	5.0						20.3
1094	4.0						8.5
1095	4.0						8.3
1096	10.0		3.0				88.1
1097	3.0		2.0				7.6
1098	5.0		1.0				6.4
1099			3.0			1350	7.4
1100			3.0		950	1400	8.8
1101	5.0		5.0		1000	1450	9.5
1102	3.0		5.0			1450	8.5
1103	4.0		4.0			1450	11.7
1104	5.0		5.0			1480	13.3
1105	5.0		4.0			1510	11.2
1106	5.0		5.0			1540	11.8
1107	2.0						13.2
1108							25.4
1109							37.9
1110						1540	7.2
1111						1480	16.2
1112	2.0	0.0	5.0	0.0	1000	1400	15.9

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	Ar Flow Through Cr & Ti Only (ℓ/min)	Ar Flow Through Bubbler (ℓ/min)	Ar Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1113	7.0	0.0	5.0	0.0	1000	1400	15.3
1114	2.0					1400	15.2
1115						1250	14.0
1116							13.7
1117							14.3
1115'							15.4
1116'							16.4
1118							14.6
1117'							16.9
1119							16.9
1118'							15.3
1120							15.2
1119'							16.9
1121							15.8
1120'							16.3
1121'					1000	1250	17.4
1122	2.0		5.0		800	1400	4.2
1123	5.0		1.0		800		5.1
1124	5.0		1.0		900		7.0
1125	5.0		5.0		900		9.9
1126	2.0		5.0		900		8.7
1127	5.0		5.0		1000		9.7
1128	5.0	0.0	1.0	0.0	1000	1400	7.2

Run No.	H_2 Flow (ℓ/min)	He Flow Through Cr & Ti Only (ℓ/min)	He Flow Through Bubbler (ℓ/min)	He Flow With H_2 (ℓ/min)	Cr & Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1129	5.0	5.0	5.0	0.0	950	1400	24.5
1130	5.0	10.0					14.9
1131	7.0	5.0					26.7
1132	5.0	0.0					27.8
1133	7.0	5.0					25.8
1134							27.9
1135							28.7
1129'							27.0
1131'							28.1
1133'							27.9
1134'							28.5
1136							26.1
1137							29.5
1135'							30.2
1136'							27.4
1137'	7.0						27.0
1138	3.0		5.0				36.2
1139	5.0	5.0	1.0				14.8
1140	5.0	9.0	1.0	0.0	950	1400	11.7

Parameters and Results of Silicon Depositions

Run No.	Substrate No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)	H_2 Through Bubbler (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1141-1	B-66	7.0	7.0	0.2	1250	17.9
1141-2						21.9
1142-1						16.0
1142-2						15.5
1142-3	B-66					16.9
1143-1	889					19.5
1143-2	887					20.8
1143-3	882	7.0	7.0	0.2	1250	24.1

Silicon Depositions (continued)

Run No.	Substrate No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)	H_2 Through Bubbler (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1144-1	1115	7.0	7.0	0.2	1250	31.9
1144-2	1116					31.2
1144-3	1117					34.3
1144-4	1118					33.1
1144-5	1119					34.7
1144-6	1120					32.9
1145-1	1121					36.1
1145-2	1129					40.1
1145-3	1131					41.5
1145-4	1133					40.4
1145-5	1134					45.0
1145-6	1135					41.6
1146-1	1115					14.6
1146-2	1116					14.5
1146-3	1117					17.9
1146-4	1118					15.7
1146-5	1119					16.9
1146-6	1120					14.3
1147-1	1121					20.8
1147-2	1129					19.7
1147-3	1131					22.5
1147-4	1133					23.8
1147-5	1134					33.1
1147-6	1135			0.2		27.3
1148-1	1024			0.1		17.6
1148-2	1025					21.2
1148-3	1029					23.7
1148-4	1028					21.2
1148-5	1027					22.8
1148-6	1026			0.1		19.6
1149-1	1137			0.2		37.8
1149-2	1023			0.2		37.2
1149-3	1136			0.2		37.1
1150-1	1024			0.1		17.7
1150-2	1025					22.0
1150-3	1029					23.6
1150-4	1028					18.6
1150-5	1027					21.8
1150-6	1026			0.1		20.9
1151-1	1137			0.2		30.0
1151-2	1023			0.2		27.4
1151-3	1136			0.2		30.1
1152-1	766			0.1		29.0
1152-2	769					31.1
1152-3	774					35.3
1152'-1	766					20.8
1152'-2	769					16.5
1152'-3	774	7.0	7.0	0.1	1250	10.0

Parameters and Results of Titanium-Chromium Alloy Depositions

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Cr and Ti Only	Through Bubbler	With H2			
1153	5.0	5.0	5.0	0.0	1000	1400	12.1
1154	5.0	5.0	10.0				12.1
1155	5.0	7.0	7.0				19.9
1156	7.0	4.0	7.0				-
1157	7.0	3.0	3.0			1400	27.4
1158	5.0	5.0	5.0			1300	32.8
1159	5.0	5.0	5.0			1450	29.7
1160	7.0	3.0	3.0			1400	30.0
1161		5.0	1.0				17.3
1162		3.0	3.0				29.4
1163	7.0	3.0	3.0	0.0	1000	1400	33.7

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Cr and Ti Only	Through Bubbler	With H_2			
1157'	7.0	3.0	3.0	0.0	1000	1400	30.9
1160'							31.6
1164							35.0
1165							38.7
1162'							37.2
1163'							37.6
1164'							37.7
1165'					1000		38.9
1166					930		23.2
1167							21.2
1168							20.7
1166'							16.4
1169							16.3
1167'					930		12.0
1170					950		14.3
1168'					960	1400	7.7
1169'			3.0		980	1370	9.6
1171			6.0				28.6
1172			6.0				39.4
1173			6.0				47.4
1174			5.0				42.0
1175			4.0		980		35.4
1176					960		29.4
1177		3.0					24.5
1171'		3.5					19.7
1178		5.0					21.3
1177'							19.0
1176'							22.0
1178'							21.1
1179							23.2
1180							26.4
1179'							25.2
1180'		5.0	4.0				26.1
1181		3.0	6.0				38.9
1182		3.0	4.0				35.4
1183		0.0	6.0				42.1
1184		0.0	4.0				35.3
1185		0.0	2.0				17.8
1186		3.0	4.0				30.6
1187			4.0				-
1188			4.0				29.6
1191			6.0				7.9
1192			6.0				15.7
1193		3.0	8.0				9.7
1194		0.0	8.0		960	1370	11.0
1195		3.0	6.0		1000	1400	9.6
1196							16.0
1197							16.0
1198							20.1
1199							12.9
1196'							14.5
1200							16.8
1201							14.8
1192'							8.5
1197'							23.1
1198'							22.2
1199'							32.9
1200'							23.5
1201'	7.0	3.0	6.0	0.0	1000	1400	18.2

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Cr and Ti Only	Through Bubbler	With H_2			
1202	7.0	3.0	6.0	0.0	1000	1400	23.0
1202-1	7.0	3.0	6.0		900	1380	16.7
1202-2	7.0	3.0	9.5			1400	16.3
1203	4.0	0.0	6.0				18.7
1204			4.0				30.4
1205							32.1
1206							32.1
1207							31.6
1205'							38.9
1204'							32.6
1208							34.8
1206'							37.7
1209							35.4
1207'							26.6
1208'							16.7
1209'	4.0	0.0	4.0			1400	18.1
1210	7.0	3.0	6.0			1380	12.4
1211	4.0	0.0	4.0			1420	16.6
1212						1380	24.8
1213							-
1214							25.3
1215		0.0					19.6
1216		3.0					15.8
1212'		0.0					20.0
1217							15.3
1218							29.0
1219		0.0	4.0				28.0
1220		3.0	6.0				39.0
1221			4.0				31.0
1222	4.0				900	1380	20.4
1228	5.0	3.0			800	1400	7.2
1229	5.0	0.0	4.0		820		4.9
1230	7.0		7.0		850		6.5
1231	5.0		4.0				8.1
1232	9.0		10.0				17.3
1233	9.0		10.0				17.3
1234	3.0	0.0	10.0			1400	11.2
1235	4.0	3.0	4.0			1380	9.9
1236	4.0	0.0	6.0			1400	17.0
1237	4.0		10.0				15.6
1238	7.0		10.0				9.2
1239	4.0		6.0				19.1
1240			10.0				23.7
1241			10.0		850		25.0
1245			6.0		875		29.2
1246							42.6
1247							29.1
1248							23.3
1249							30.1
1245'							26.0
1250							37.0
1247'							32.2
1249'							37.7
1250'					875	1400	23.1
1260					825	1300	10.4
1261					800		6.8
1262							-
1263	4.0	0.0					5.0
1264	5.0	3.0					5.9
1265	4.0	0.0				1300	5.2
1266	4.0				800	1350	4.7
1267	4.0				850	1350	7.1
1268	7.0	0.0	6.0	0.0	850	1400	6.9

Parameters and Results of Silicon Depositions

Run No.	Substrate No.	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (Minutes)
1189-1	1171	7.0	7.0	0.1	1225	-	10
1189-2	1177					-	
1189-3	1178					-	
1189-4	1179					-	
1189-5	1180					-	
1189-6	1176					-	10
1190-1	1165					-	12
1190-2	1157					-	
1190-3	1163					-	
1190-4	1164					-	
1190-5	1162					-	
1190-6	1160				1225	-	12
1189'-1	1171				1200	-	15
1189'-2	1177					-	
1189' 3	1178					-	
1189'-4	1179					-	
1189'-5	1180					-	
1189'-6	1176				1200	-	
1190'-1	1165				1180	-	
1190'-2	1157					-	
1190'-3	1163					-	
1190'-4	1164					-	
1190'-5	1162					-	
1190'-6	1160				1180	-	
1223-1	B-66				1200	5.8	
1223-2						7.3	
1223-3						3.5	15
1223'-1						8.2	20
1223'-2						7.2	
1223'-3						5.5	
1224-1						6.0	
1224-2						5.3	
1224-3						5.0	
1224'-1						8.4	
1224'-2						8.1	
1224'-3					1200	7.6	20
1225-1					1215	15.7	25
1225-2					1215	11.3	25
1225-3	B-66					9.7	25
1226-1	1138					15.0	20
1226-2	1132					10.8	
1227-1	1139					17.1	
1227-2	1140				1215	15.8	
1242-1	B-66				1120	12.4	
1242-2					1120	7.9	
1242-3					1120	5.5	
1243-1					1205	7.9	
1243-2					1205	9.5	
1243-3					1205	8.7	
1244-1					1250	7.2	
1244-2					1250	15.8	
1244-3					1250	12.1	
1251-1					1210	17.3	
1251-2					1210	16.4	
1251-3				0.1	1210	13.2	
1252-1				0.15	1225	12.5	
1252-2					1225	14.1	
1252-3					1225	10.7	
1253-1					1215	17.9	
1253-2					1215	17.0	
1253-3					1215	10.1	
1254-1					1200	12.7	
1254-2					1200	13.6	
1254-3					1200	12.1	
1255-1					1220	11.2	
1255-2					1220	15.5	
1255-3	B-66	7.0	7.0	0.15	1220	15.9	20

Silicon Depositions (continued)

Run No.	Substrate No.	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (Minutes)
1256-1	B-66	7.0	7.0	0.15	1240	25.1	20
1256-2						30.3	
1256-3						20.4	
1257-1						15.8	
1257-2						14.2	
1257-3	B-66				1240	20.0	
1258-1	1199				1250	21.4	
1258-2	1200					16.4	
1258-3	1198					26.2	
1258-4	1197					22.9	
1258-5	1196					27.1	
1258-6	1201					21.9	
1259-1	1207					52.2	
1259-2	1209					42.1	
1259-3	1205					50.5	
1259-4	1206					55.5	
1259-5	1208					33.5	
1259-6	1204					37.2	
1258'-1	1199					16.2	
1258'-2	1200					24.7	
1258'-3	1198					28.4	
1258'-4	1197					24.4	
1258'-5	1196					18.2	
1258'-6	1201					23.5	
1259'-1	1207					10.5	
1259'-2	1209					10.0	
1259'-3	1205					15.9	
1259'-4	1206					19.6	
1259'-5	1208					10.5	
1259'-6	1204					-	
1269-1	1240					20.3	
1269-2	1241					21.0	
1269-3	1236					19.0	
1269-4	1222					18.6	
1269-5	1239					15.2	
1269-6	1221					18.3	
1269-7	1200					19.6	
1269'-1	1240					19.7	
1269'-2	1241					37.5	
1269'-3	1236					25.7	
1269'-4	1222					32.7	
1269'-5	1239					12.4	
1269'-6	1221					18.7	
1269'-7	1220					13.7	
1270-1	1215					34.9	
1270-3	1214				1250	31.4	
1285-1	1271				1235	39.2	
3	1274					30.8	
4	1273					22.0	
6	1272				1235	22.6	
1285'-1	1271				1200	28.0	
3	1274					22.2	
4	1273					17.1	
6	1272				1200	10.0	
1292-1	1212				1210	16.8	
3	1211					14.2	
4	1210					18.4	
6	1203					21.5	
1292'-1	1212					15.4	
3	1211					14.4	
4	1210					8.3	
6	1203					6.7	
1293-1	1001					20.0	
3	1002					18.3	
4	1006					35.6	
6	1000	7.0	7.0	0.15	1210	15.6	20

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (min)
1293'-1	1001	7.0	7.0	0.15	1210	7.8	20
3	1002					6.7	
4	1006					6.0	
6	1000				1210	5.0	
1297-1	1232				1200	27.0	
3	1237					20.0	
5	1233					11.0	
1297'-1	1232					9.3	
3	1237					11.1	
5	1233	7.0				8.3	
1298-1	1238	6.0				16.2	
3	1235					14.0	
5	1234					11.2	
1298'-1	1238					10.6	
3	1235					8.6	
5	1234					8.3	
1299-1	1294					15.2	
3	1295					11.7	
5	1287	6.0				12.0	
1305-1	1106	5.0				10.1	
3	1107					9.9	
5	1110					10.7	
1306-1	1114					11.8	
3	1113					12.8	
5	1111	5.0				7.2	
1314-1	860	4.0				9.1	
3	859					6.9	
5	871					7.0	
1315-1	909					16.3	
3	910					-	
5	908	4.0			1200	6.7	
1322-1	958	7.0			1210	26.9	
3	962				1210	25.8	
5	959				1210	15.3	
1323-1	965				1200	21.0	
3	964					30.5	
5	963					17.5	
1323'-1	965					15.9	
3	964					11.1	
5	963				1200	7.1	
1330-1	961				1215	20.6	
3	954					17.3	
5	956					13.6	
1330'-1	961					15.0	
3	954					12.6	
5	956					10.1	
1331-1	953					15.1	
3	946					6.9	
5	952				1215	15.0	
1332-1	944				1205	-	
2	942					-	
3	941					23.1	
4	920					19.5	
5	915					20.9	
6	916					18.6	
7	921					21.0	
1332'-1	920					7.1	
3	941					6.0	
5	915					4.7	
6	916					3.6	
7	921	7.0	7.0	0.15	1205	3.5	20

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (min)
1333-1	862	7.0	7.0	0.15	1215	22.4	20
2	867					27.3	
3	968					21.7	
4	901					21.1	
5	978					18.6	
6	983					20.2	
7	969					16.2	
1333'-1	862					7.0	
2	867					12.0	
3	968					7.6	
4	901					9.1	
5	978					8.3	
6	983					11.3	
7	969				1215	8.1	
1342	-				1200	-	
3	1278				1200	7.9	
	-				1200	-	
1343-1	1192				1215	14.0	
2	1166					18.4	
3	1090					16.4	
4	1092					17.5	
5	1250					12.3	
6	1247					11.8	
7	1249					11.4	
1343'-1	1192					10.0	
2	1166					6.5	
3	1090					11.0	
4	1092					11.2	
5	1250					7.2	
6	1247					5.8	
7	1249					6.4	
1344-1	1167					10.5	
2	1217					15.4	
3	1093					19.5	
4	1216					9.6	
5	1078					12.3	
6	1219					7.9	
7	1245					12.9	
1344'-1	1167					6.9	
2	1217					11.3	
3	1093					17.7	
4	1216					10.3	
5	1078					12.4	
6	1219					12.5	
7	1245				1215	9.6	
1345-1	1089				1200	11.6	
3	1087				1200	15.4	
5	1088				1200	16.5	
1346-1	1296				1210	36.9	
2	1284					22.7	
3	1288					20.6	
4	1283				1210	24.9	
1347-1	1277				1200	26.5	
2	1282					25.1	
3	1281					15.0	
4	1280				1200	17.4	
1346'-1	1296				1210	20.9	
2	1284					9.2	
3	1288					13.4	
4	1283	7.0	7.0	0.15	1210	6.8	20

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (min)
1347'-1	1281	7.0	7.0	0.15	1200	12.8	20
2	1282					12.7	
4	1277					10.6	
6	1280					11.5	
1348-1	1328					16.8	
2	1327					17.3	
4	1329					17.1	
5	1325					16.4	
6	1326					16.4	
7	1324					17.7	20
1349-1	1304					24.2	40
2	1303					26.2	
4	1307					20.9	
5	1308					18.1	
6	1301					19.9	
7	1309					22.1	40
1348'-1	1328					27.1	20
2	1327					28.0	
4	1329					25.5	
5	1325					25.4	
6	1326					25.3	
7	1324					25.5	20
1349'-1	1304					21.7	40
2	1303					23.4	
4	1307					21.2	
5	1308					20.1	
6	1301					17.2	
7	1309					15.1	
1350-1	1336					53.6	
2	1339					51.8	
4	1335					28.2	
5	1334					25.4	
6	1340					28.1	
7	1337					19.5	
1350'-1	1336					28.4	
2	1339					30.0	
1350'-4	1335					31.3	
5	1334					26.9	
6	1340					28.2	
7	1337					20.1	40
1351-1	1291					26.8	30
2	1290					25.1	
4	1289					18.7	
6	1286					13.5	
1351'-1	1291					24.2	
2	1290					23.1	
4	1289					8.3	
6	1286				1200	14.1	
1373-1	1191				1215	5.4	
3	1193					5.1	
6	1194					5.2	
1374-1	1080					13.1	
2	1079					10.1	
3	1077					12.2	
4	1084					13.7	
5	1081					9.6	
6	1109					18.2	
7	1112				1215	4.1	
1374'-2	1079				1200	33.3	
3	1077					33.0	
4	1084					37.3	
5	1081					29.5	
6	1109					51.1	
7	1112				1200	42.2	30
1375-1	1099				1175	-	10
2	1102					-	
3	1100					-	
4	1101					-	
5	1103					-	
6	1104	7.0	7.0	0.15	1175	-	10

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)	Time (min)
1376-1	1098	7.0	7.0	0.15	1125	16.7	10
2	1097					7.6	
3	1096					17.0	
4	1095					14.7	
5	1094					10.2	
6	1074				1125	10.6	
1382-1	1069				1100	13.5	
2	1068					28.3	
3	1067					12.2	
4	1070					12.9	
5	1075					12.7	
6	1076					11.7	
1383-1	1365					12.1	
2	1363					22.5	
3	1364					11.0	
1383'-1	1365					11.4	
2	1363					16.3	
3	1364					10.0	
1384-1	1354					18.2	
2	1356					22.0	
3	1357					35.0	
4	1352					21.0	
5	1355					16.9	
6	1353				1100	11.8	10
1384'-1	1354				1080	19.1	15
2	1356					22.5	
3	1357					16.5	
4	1352					12.6	
5	1355					16.7	
6	1353				1080	17.7	15
1385-1	1380				1090	17.1	10
2	1379					15.6	
3	1381					17.4	
4	1378					16.9	
5	1372					18.2	
6	1377				1090	17.9	10
1385'-1	1380				1080	25.0	15
2	1379					24.3	
3	1381					22.2	
4	1378					24.8	
5	1372					20.8	
6	1377	7.0	7.0	0.15	1080	16.9	15

Parameters and Results of Titanium-Chromium Alloy Depositions

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Cr and Ti Only	Through Bubbler	With H_2			
1271	4.0	0.0	6.0	0.0	850	1350	17.8
1272					850	1350	16.3
1273					850	1350	38.1
1274					800	1375	36.5
1275					800		32.2
1276	4.0				750		25.5
1277	7.0		6.0		750		28.8
1278			4.0		800		29.7
1279			6.0		750		21.8
1280							27.0
1281	7.0	0.0	6.0	0.0	750	1375	25.7

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min) Cr and Ti Only	He Flow (ℓ/min) Through Bubbler	He Flow (ℓ/min) With H_2	Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1282	7.0	0.0	6.0	0.0	750	1375	24.6
1277'							21.1
1279'							-
1280'							23.4
1281'							19.3
1283							25.9
1284							23.9
1282'							22.2
1283'							33.8
1284'			6.0				26.7
1286'			3.5		750		27.5
1287					700		19.7
1288					750		23.2
1289							22.2
1290							25.7
1291							26.7
1286'							26.5
1288'							26.4
1289'			3.5				29.6
1294			3.5				14.1
1295							13.8
1296							22.0
1290'							19.1
1291'							17.4
1296'			3.5			1375	27.1
1300			3.0			1400	14.5
1301			6.0			1400	22.5
1302			8.0			1415	24.0
1303			6.0			1400	23.3
1304							22.7
1307							23.7
1308							24.8
1301'							17.3
1303'							19.6
1304'							20.1
1307'							22.7
1309							26.1
1308'							18.2
1309'						1400	17.8
1310						1425	17.4
1311							15.9
1312							18.6
1313						1425	17.3
1316						1400	25.4
1317							26.4
1318							22.5
1319							24.8
1316'							22.5
1317'							23.3
1320							28.3
1318'							21.2
1321							27.4
1319'							20.8
1320'							24.6
1321'	7.0					1400	15.4
1324	4.0					1375	29.7
1325							29.5
1326							24.6
1327							25.1
1328							26.2
1325'							27.4
1329							28.1
1327'							27.4
1324'							27.8
1326'	4.0	0.0	6.0	0.0	750	1375	26.0

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Cr and Ti Only	Through Bubbler	With H_2			
1328'	4.0	0.0	6.0	0.0	750	1375	27.2
1329'	4.0					1375	26.3
1334	5.0					1400	42.9
1335							41.6
1336							30.3
1337							35.8
1338							33.3
1339							35.0
1334'							26.7
1335'							30.0
1337'							31.0
1336'							33.2
1339'							26.1
1340							30.9
·1340'						1400	27.7
1341						1350	19.9
1352							34.8
1353							28.6
1352'							30.0
1355							33.1
1353'							21.3
1354'							23.1
1356							27.5
1355'							25.9
1357							31.4
1356'							28.2
1357'	5.0		6.0		750	1350	27.0
1358	7.0		11.5		800	1250	23.7
1359	6.0		6.0		800	1250	28.2
1360	5.0		6.0		800	1350	32.5
1361	5.0		6.0		750		21.3
1362	7.0		10.0		750		-
1363	5.0		6.0		800		27.0
1363'						1350	21.0
1364						1400	33.9
1365							21.9
1366							19.8
1367						1400	15.2
1368						1450	21.3
1369						1350	16.8
1370					800		18.6
1371	5.0		6.0		850		28.6
1372	7.0		10.0				36.1
1377							31.9
1378							34.5
1379							33.8
1380							38.2
1372'							32.0
1377'							30.0
1381							35.0
1378'							28.8
1379'							30.0
1380'							30.0
1381'							30.2
1386			10.0				32.1
1387			6.0				44.0
1388			3.0		850	1350	39.7
1389			6.0		860	1375	21.7
1390							39.9
1391							30.4
1392							24.4
1393							23.2
1394							36.3
1395							39.3
1389'							22.1
1390'							26.9
1392'							16.3
1394'							26.8
1395'							35.6
1391'							29.7
1393'	7.0	0.0	6.0	0.0	860	1375	27.6

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min) Through Bubbler	Cr and Ti Only	With H_2	Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1396	7.0	6.0	0.0	0.0	880	1325	45.9
1397							45.8
1398							22.2
1399			0.0		880		18.9
1400			3.0		860		20.7
1401							23.4
1402							24.1
1403							26.3
1398'							22.8
1400'							21.3
1401'							33.6
1404							23.5
1402'							18.0
1403'							21.6
1404'	7.0		3.0		860	1325	27.3
1407	5.0		0.0		850	1400	28.0
1408							23.7
1409							25.1
1410							26.5
1411							27.1
1407'							23.6
1408'							20.2
1412							26.8
1409'							22.2
1410'							23.5
1411'							25.3
1412'		6.0				1400	26.3
1415		2.5				1375	30.6
1416		6.0					27.7
1417		4.0					---
1418		6.0				1375	---
1423	5.0	4.0				1350	16.1
1424	7.0	4.0				1400	---
1425		4.5					26.5
1426							27.1
1427							29.8
1425'							24.8
1426'							20.0
1428							23.7
1429							13.5
1430							13.5
1431						1400	16.0
1432						1300	15.0
1433						1400	25.4
1434							23.6
1427'							16.4
1428'							24.7
1433'							28.4
1434'	7.0	4.5			850	1400	18.2
1435	5.0	6.0			875	1375	6.1
1436	7.0	6.0					13.4
1437	7.0	2.5					13.9
1438	3.0	6.0			875	1375	3.7
1439	5.0	5.0			850	1350	6.8
1440	5.0	5.0				1400	14.2
1441	7.0	6.0					18.2
1442							27.7
1443							26.0
1444							24.1
1445							21.0
1446							21.1
1442'							21.7
1443'							26.2
1444'		6.0				1400	26.5
1441'		5.0				1300	6.0
1447'	7.0	5.0	0.0	0.0	850	1400	12.2

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min)			Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
		Through Bubbler	Cr and Ti Only	With H_2			
1448	7.0	5.0	0.0	0.0	850	1300	20.2
1449	5.0				900	1300	19.9
1445'	7.0				850	1400	20.6
1446'	7.0				850	1400	20.0
1448'	7.0				850	1400	21.1
1450	5.0				900	1300	11.3
1451							25.6
1452							22.2
1453							23.9
1454							23.4
1449'							20.4
1455							21.5
1451'							19.0
1464							29.1
1452'							29.2
1453'							23.4
1454'							21.7
1455'							23.1
1465							23.4
1466							19.6
1467							22.8
1468							24.6
1469							22.4
1464'							20.2
1465'							26.7
1466'							24.6
1467'							17.6
1468'							21.7
1469'		5.0				1300	17.0
1476		7.0				1350	23.7
1477							21.2
1478							23.0
1479							21.9
1480							22.9
1481							21.0
1476'							15.2
1478'							24.8
1479'							20.0
1482							22.9
1480'							20.9
1481'							19.4
1482'	5.0	7.0				1350	18.0
1483	4.0	5.0				1300	40.7
1484							27.2
1485							23.5
1486							26.5
1487							24.3
1488							24.9
1489							22.3
1484'							26.6
1485'	4.0	5.0					24.9
1490	6.0	3.0					19.6
1486'	4.0	5.0					20.2
1487'							20.3
1488'							20.0
1489'	4.0	5.0				1300	---
1498	5.0	4.0				1350	26.8
1499			0.0				23.1
1500			2.5				22.5
1501							22.7
1502							17.1
1503							20.8
1498'							22.3
1499'							24.8
1500'							24.9
1501'							20.7
1502'	5.0	4.0	2.5	0.0	900	1350	20.6

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min) Through Bubbler	Cr and Ti Only	With H_2	Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1503'	5.0	4.0	2.5	0.0	900	1350	12.0
1509	4.0	5.0	0.0		880		19.2
1510	5.0						18.5
1511							26.7
1512							30.6
1513							31.5
1514							29.4
1515							30.3
1510'							32.9
1511'							35.5
1512'							32.5
1513'							34.5
1514'							35.8
1515'		5.0	0.0		880		35.9
1518		4.0	2.5		900		25.5
1519							23.7
1520							23.7
1521							23.6
1522							23.8
1518'							21.9
1519'							27.5
1520'							28.9
1521'							23.0
1522'							20.7
1523							23.4
1523'						1350	23.0
1524						1300	38.9
1525							42.3
1526							40.0
1527							37.2
1528							35.4
1529							27.7
1524'		4.0				1300	27.9
1530		5.0				1350	36.6
1531		3.0				1375	34.0
1532							29.8
1533							30.4
1534							30.3
1535							31.3
1536							32.2
1531'							30.8
1532'							30.5
1533'							30.7
1535'							34.2
1534'							34.0
1536'		3.0				1375	32.5
1525'		4.0				1350	35.8
1526'							35.8
1527'							37.4
1528'							38.4
1530'					900		42.5
1540					880		36.7
1541							38.5
1542							34.4
1543							34.5
1544							36.5
1545							35.4
1540'							38.1
1541'							33.7
1542'							33.5
1543'							30.1
1544'							30.7
1545'		4.0			880	1350	31.0
1546		3.0			890	1375	29.8
1547							29.0
1548							26.0
1549	5.0	3.0	2.5	0.0	890	1375	23.4

Titanium-Chromium Alloy Depositions (continued)

Run No.	H_2 Flow (ℓ/min)	He Flow (ℓ/min) Through Bubbler	Cr and Ti Only	With H_2	Cr and Ti Temperature (°C)	Reactor Temperature (°C)	Δ Wt. (mg)
1550	5.0	3.0	2.5	0.0	890	1375	22.4
1546'							22.1
1547'							21.9
1548'							20.2
1549'							20.7
1550'							20.4
1551							21.0
1551'		3.0			890	1375	18.3
1565		4.0			870	1350	14.6
1566		3.5			880	1325	22.8
1567							21.8
1568							20.3
1569							20.1
1570							22.4
1571							20.1
1566'							20.8
1567'							20.7
1568'							20.2
1569'							20.0
1570'							21.4
1571'		3.5				1325	20.4
1585	5.0	5.0			880	1350	11.8
1586	4.0	4.0			910		10.8
1587	4.0	6.0					9.7
1588	4.0	6.0					10.7
1589	5.0	4.5			910		13.3
1590		4.5			900	1350	40.2
1591		3.5	2.5		880	1325	31.7
1592	5.0	3.0	6.0				28.4
1593	4.0	2.0	2.5				21.9
1594							19.0
1595							22.9
1596						1325	21.5
1597						1350	28.5
1598							29.0
1599							26.2
1600							26.9
1601							29.9
1602							28.0
1598'							25.0
1597'							23.3
1599'							29.8
1600'							25.6
1601'							27.1
1602'							27.2
1610	4.0		2.5			1350	23.4
1611	6.0	2.0	2.0			1375	26.8
1612	7.0	1.25	1.5				28.1
1613	6.0	1.5	1.5				28.0
1614	7.0	1.25	1.25				26.8
1615							24.5
1616							26.6
1617							24.3
1615'							21.5
1616'							21.7
1617'							18.4
1614'	7.0	1.25	1.25	0.0	880	1375	24.2

Parameters and Results of Silicon Depositions

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1405-1	1202-1	7.0	7.0	0.15	1090	22.1
2	1202				1090	40.6
3	1188				1090	18.6
1406-1	1399				1080	8.1
2	1392				1080	9.2
3	1071				1080	6.0
1405'-1	1202-1				1090	11.5
2	1202				1090	---
3	1188				1090	4.7
1406'-1	1399				1080	6.9
2	1392				1080	12.4
3	1071				1080	5.7
1413-1	1311				1090	18.7
2	1310					24.6
3	1302					13.1
1413'-1	1311					9.5
2	1310					11.9
3	1302					10.4
1414-1	1185					26.4
2	1186					30.9
3	1184				1090	54.3
1418-1	1391				1085	28.4
2	1393					21.0
3	1394					27.3
4	1390					23.2
5	1395					39.7
6	1389					23.5
1418'-1	1391					10.6
2	1393					12.5
3	1394					16.4
4	1390					13.3
5	1395					12.1
6	1389				1085	13.5
1419-1	1400				1080	32.4
2	1404					40.5
3	1398					37.3
4	1403					37.3
5	1402					35.9
6	1401					29.8
1419'-1	1400					13.1
2	1404					17.0
3	1398					16.1
4	1403					15.2
5	1402					4.4
6	1401					5.2
1420-1	1408					32.7
2	1410					33.7
3	1407					29.9
1421-1	1409					40.1
2	1412					31.1
3	1411					28.9
1420'-1	1408					17.7
2	1410					16.6
3	1407					13.2
1421'-1	1409					17.9
2	1412					19.5
3	1411					19.3
1422-1	1105					29.1
2	1072					27.3
3	1066				1080	22.0
1456-1	1130				1090	27.0
2	1142					10.0
3	1141					6.7
1456'1	1130	7.0	7.0	0.15	1090	12.6

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1456'-2	1142	7.0	7.0	0.15	1090	2.2
3	1141					2.1
1457-1	1182					24.8
2	1175					18.2
3	1181					15.1
1458-1	1431					14.4
2	1418					16.7
3	1416					12.9
1459-1	1370					18.0
2	1368					16.6
3	1371					17.3
1460-1	1434					13.5
2	1428					16.5
3	1433					16.1
1461-1	1427					20.7
2	1425					18.2
3	1426					14.9
1460'-1	1433					18.1
2	1428					9.4
3	1434					2.4
1461'-1	1427					2.3
2	1425					10.6
3	1426				1090	22.1
1462-1	1172				1085	24.9
2	1174				1085	---
3	1173				1085	29.1
1463-1	1437				1090	20.9
2	1440					17.9
3	1463					19.0
1470-1	1153					23.7
2	1154					17.8
3	1155					13.6
1471-1	1450					22.4
2	1108					22.3
3	1447					17.7
1472-1	1448					27.9
2	1442					22.8
3	1444					15.3
1473-1	1445					27.9
2	1446					19.0
3	1443					13.2
1472'-1	1448					15.0
2	1442					11.5
3	1444					7.5
1473'-1	1445					14.2
2	1446					12.4
3	1443					5.8
1474-1	1449					29.2
2	1453					26.4
3	1454					21.4
1475-1	1451					32.7
2	1452					25.4
3	1455					20.7
1474'-1	1449					7.7
2	1453					7.8
3	1454					4.6
1475'-1	1451					22.5
2	1452					20.2
3	1455					12.6
1491-1	1046					---
2	1047					18.2
3	1048					10.7
1492-2	982					---
3	976				1090	11.9
1493-1	1128				1080	20.0
2	1142				1080	3.8
3	1142	7.0	7.0	0.15	1080	2.4

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1494-1	1231	7.0	7.0	0.15	1090	---
2	1230					---
3	1202					12.0
1495-1	1266					16.5
2	1265					15.6
3	1267				1090	13.5
1496-1	1467				1095	29.8
2	1466				1095	33.6
3	1465				1095	33.3
1497-1	1469				1080	27.8
2	1468				1080	27.8
3	1464				1080	11.3
1496'-1	1467				1095	11.5
2	1466				1095	11.8
3	1465				1095	10.4
1497'-1	1469				1080	11.6
2	1468				1080	12.7
3	1464				1080	14.1
1504-1	1479				1090	24.2
2	1480					25.8
3	1476					13.7
1505-1	1481					29.1
2	1482					32.9
3	1478					19.0
1504'-1	1479					8.6
2	1480					8.9
3	1476					2.8
1506-1	1229					15.0
2	1268					17.4
3	1246					15.5
1505'-1	1481					9.2
2	1482					6.0
3	1478					4.2
1507-1	1489					32.0
2	1488					30.2
3	1485					33.0
1508-1	1487					29.5
2	1486					29.4
3	1484					38.0
1507'-1	1489					26.5
2	1488					18.8
3	1485					13.3
1508'-1	1487					20.1
2	1486					19.4
3	1484					18.6
1516-1	1386					7.8
2	1388					6.8
3	1387					4.7
1517-1	1490					9.5
2	1005					20.0
3	1483					---
1537-1	822					17.0
2	832					16.7
3	831					10.1
1538-1	849					11.6
2	851					11.2
3	850					7.7
1552-1	846					3.8
2	844					5.4
3	847					2.4
1553-1	1439					16.5
2	1436					16.6
3	1509					15.0
1554-1	1367					18.6
2	1369					16.9
3	1366	7.0	7.0	0.15	1090	9.5

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1555-1	1503	7.0	7.0	0.15	1090	9.5
2	1499					16.1
3	1498					15.2
1556-1	1501					19.9
2	1500					18.1
3	1502					12.4
1555'-1	1503					3.1
2	1499					4.9
3	1498					6.2
1556'-1	1501					6.8
2	1500					7.7
3	1502					5.3
1557-1	1300					---
2	1361					19.5
3	1360					16.7
1558-1	1514					24.4
2	1513					30.1
3	1510					18.7
1559-1	1511					25.5
2	1515					24.3
3	1512					22.0
1558'-1	1514					7.2
2	1513					8.7
3	1510					9.3
1559'-1	1511					7.7
2	1515					16.2
3	1512					12.5
1560-1	1523					19.0
2	1518					16.0
3	1519					5.3
1561-1	1522					17.2
2	1520					3.6
3	1521					11.3
1560'-1	1523					10.9
2	1518					3.0
3	1519					3.9
1561'-1	1522					11.5
2	1520					7.2
3	1521					6.3
1562-1	841					---
2	781					14.4
3	771					19.7
1563-1	1530					36.2
2	1527					29.4
3	1524					7.1
1564-1	1528					21.7
2	1526					21.8
3	1525					17.1
1563'-1	1530					18.3
2	1527					25.5
3	1524					20.6
1564'-1	1528					24.2
2	1526					13.0
3	1525					18.4
1572-1	787					17.0
2	733					15.6
3	734					11.5
1573-1	1536					30.8
2	1531					18.1
3	1533					18.2
1574-1	1532					17.4
2	1534					26.0
3	1535					24.2
1573'-1	1536					20.3
2	1531					20.3
3	1533					13.5
1574'-1	1532	7.0	7.0	0.15	1090	19.7

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	Δ Wt. (mg)
1574'-2	1534	7.0	7.0	0.15	1090	28.5
3	1535					17.6
1575-1	1429					13.8
2	1430					14.1
3	1313					17.8
1576-1	1441					16.0
2	1517					11.0
3	1397					12.2
1577-1	1124					16.0
2	1126					16.9
3	1125					9.5
1578-1	1543					27.7
2	1541					31.5
3	1545					23.9
1579-1	1542					28.8
2	1540					32.5
3	1544					32.8
1578'-1	1543					26.3
2	1541					17.3
3	1545					14.6
1579'-1	1542					23.0
2	1540					7.2
3	1544					4.7
1580-1	722					6.9
2	720					14.6
3	729					10.8
1581-1	1548					14.8
2	1546					14.9
3	1550					8.8
1582-1	1549					19.6
2	1547					16.1
3	1551					9.6
1581'-1	1548					14.8
2	1546					13.6
3	1550					8.7
1582'-1	1549					14.8
2	1547					13.1
3	1551					7.2
1583-1	1569					12.9
2	1567					15.7
3	1571					4.6
1584-1	1568					14.6
2	1570					14.5
3	1566					10.8
1583'-1	1569					9.0
2	1567					6.3
3	1571					7.6
1584'-1	1568					7.2
2	1570					9.4
3	1566					6.2
1603-1	755					15.8
2	756					18.7
3	749					13.0
1604-1	704					6.4
2	728					14.2
3	727					16.5
1605-1	792					16.9
2	793					16.9
3	786					12.0
1606-1	782					12.2
2	783					12.2
3	785					9.8
1607-1	761					14.5
2	758					14.9
3	779					9.6
1608-1	824					16.3
2	827	7.0	7.0	0.15	1090	17.3

Silicon Depositions (continued)

Run No.	Substrate	H_2 Flow (ℓ/min)	Dilution Flow (ℓ/min)	Bubbler Flow (ℓ/min)	Reactor Temperature (°C)	∆ Wt. (mg)
3	825	7.0	7.0	0.15	1090	11.6
1609-1	823					13.4
2	829					13.4
3	828					8.8
1624-1	1593					15.6
2	1592					12.0
3	1591					11.4
1625-1	1594					18.7
2	1596					15.3
3	1612					23.6
1626-1	1590					10.6
2	1584					7.2
3	1580					---
1627-1	1599					20.0
2	1600					17.0
3	1601					6.0
1628-1	1602					20.8
2	1597					18.9
3	1598					17.8
1627'-1	1599					7.6
2	1600					6.3
3	1601					11.0
1628'-1	1602					7.9
2	1597					6.0
3	1598					10.2
1629-1	1613					8.2
2	1611					2.3
1630-1	1615					8.3
2	1616					8.8
3	1614					6.1
4	1617					5.2
1630'-1	1615					3.9
2	1616					4.6
3	1614					2.0
4	1617	7.0	7.0	0.15	1090	1.5

Parameters and Results of Chromium-Titanium-Silicon Depositions

Run No.	H_2 Flow (ℓ/min)	He Flows (ℓ/min)				Cr & Ti Temperature (°C)	Reactor Temperature (°C)	∆ Wt. (mg)
		$TiCl_4$ Bubbler	$TiCl_4$ Dilutant	$SiCl_4$ Bubbler	$SiCl_4$ Dilutant			
1618	7.0	1.25	1.25	0.10	1.25	910	1350	52.8
1619		4.0	2.5	0.05				54.0
1620								52.8
1621								53.2
1622								51.1
1623								43.2
1622'		4.0	2.5	0.05		910	1350	50.2
1631		1.5	4.0	0.03		880	1250	31.0
1632		0.0	5.0					14.4
1633		1.5	4.0					27.5
1634								47.5
1635								44.3
1634'								57.4
1636								40.9
1635'								49.0
1637								37.2
1636'								47.1
1637'								48.5
1638								31.8
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1638'	7.0	1.5	4.0	0.03	1.25	880	1250	35.5

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The basic processes necessary to manufacture refractory metal coatings using chemical vapor deposition technology were investigated. The processes developed were demonstrated on a typical oxidation resistant coating of titanium-chromium-silicon but would have general applicability to other similar coatings. The processes utilized both two-stage deposition (metal alloy coating followed by silicon deposition) and a new method developed for the rapid (10 minute) deposition of all three elements in a single step. The processes were used for deposition of metallic coatings and for controlled variation of the composition of titanium and chromium alloys. Substrate property degradation and interaction were minimal for all types of coatings.

Performance of the coatings was evaluated by oxidation testing in air and was found to be nominally comparable to coatings by other processes. Reliability and reproducibility, indicated by statistical analysis of results, were high for this initial effort program.

The processes have potentials for utilization in rapid and economical manufacturing of a variety of coatings on parts with complex shapes.

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