FINAL REPORT ON CHEMICAL VAPOR DEPOSITION (CVD) BARREL COATING FOR REFRACTORY FASTENERS

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FOREWORD

This Final Technical Report covers all work under Contract F33615-68-C-1433 from 1 April 1968 through 1 October 1969. The manuscript was released by the author in December 1969 for publication.

This contract with Texas Instruments, Inc., 13500 North Central Expressway, Dallas, Texas, was initiated under Manufacturing Methods Project 474-8, "Chemical Vapor Deposition (CVD) Barrel Coating for Refractory Fasteners." This work was administered under the technical direction of Lt. J.R. Williamson, Fabrication Branch (MATF), Manufacturing Technology Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

This program was directed by Dr. Gene Wakefield, Project Manager and conducted by Dr. Carl L. Yaws, Project Engineer. Contributing to the program were Mr. Charles Epps and Mr. Jim Anderson. Texas Instruments report number is 04-69-09.

This program has been accomplished as 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.

Your comments are solicited on the potential utilization of the information contained herein as applied to your present and/or future production programs. Suggestions concerning additional manufacturing methods development required on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.

JACK R. MARSH
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ABSTRACT

Potential manufacturing-production equipment was established via CVD-barrel coating technology in this program for applying CVD coatings to large quantities of small parts (i.e., refractory fasteners for aerospace structures). In Phase I, the practical equipment was designed, constructed, installed and tested in start-up. In these initial runs, trideposition reaction of hydrogen reduction of gas phase silicon, titanium and chromium chlorides was demonstrated as a CVD chemistry base for depositing chromium-titanium-silicon (Cr-Ti-Si) coating on small parts. In Phase II, optimization, production and evaluation studies were conducted with the designed equipment. Coating improvements including apparent optimum region and key process parameter effects were achieved with statistical runs and analyses (i.e., T- and F-tests at 95% confidence level). Process development was scaled-up to large quantities by uniform coating many small parts: (a) 1/4-in. dia. round rods, 3 per run; (b) 1-in. threaded studs, 6-10 per run; (c) 1 1/2-in. hex head bolts, 10 per run; (d) mixed shapes-bolts, studs, rods and flat panels, 20 per run; (e) refractory fasteners-bolts, studs and nuts, 30 per run; and (f) production demonstration-refractory fastener bolts and nuts, 30-50 per run. More than twenty demonstration runs at the increased capability (i.e., coating 30-50 substrates per run) were conducted with reproducibility to illustrate that the CVD-barrel coating technology is within potential manufacturing production scope. Important coating properties (i.e., oxidation resistance for substrate protection, Cr-Ti-Si concentrations, mechanical strengths, etc.) were evaluated. For 2400°F oxidation environment, more than eighty and twenty hours of protection was achieved for round rod and refractory fastener small parts from production demonstration batches. Uncoated parts experienced severe failure in less than one-half hour. Cursory literature screening revealed favorable state-of-art comparison based on this program and two independent literature sources. In Phase III, fluoride and chloride routes were investigated for tungsten-tungsten silicide ($W-WSi_2$) coating of tantalum. For the fluoride route, tungsten coating of tantalum T222 was demonstrated with uniform coverage of round rod small parts. This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Manufacturing Technology Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

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SECTION I
INTRODUCTION

The objective of the program was continued refinement of CVD refractory coating processes and practical production equipment for applying these coatings to large quantities of small parts (i.e., fasteners for aerospace structures). The equipment which evolved specifically included optimization and production demonstration studies for the chromium-titanium-silicon (Cr-Ti-Si) coating on columbium and coating preparation studies to illustrate process versatility by deposition of the tungsten-tungsten silicide (W-WSi_2) coating on tantalum.

This program represents a unique contribution in the areas of processing equipment and refinement of processing techniques. The equipment and refinement aspect of the program is directed toward the need of a technically oriented manufacturing program to develop processes specifically applicable to this product type with resulting lower costs and increased efficiency.

The specific requirement area is the coating of refractory metal fasteners. The primary need for refractory fasteners is in aerospace applications. The need for a better refractory fastener coating process is a reality at this time, and the need five years from now could be critical. Re-entry body technology at present is based primarily on ablative cooling; however, as refractory hardware is refined, the next generation of re-entry vehicles will depend on radiative cooling utilizing the refractories for structural surfaces. As indication of the immediate order of magnitude, a typical four-vehicle re-entry development program may require as many as 15,000 refractory fasteners, each requiring coating. The total sum represents a

significant cost item. Because previous studies have shown the impractically of coating very large structures, it is apparent that, within the foreseeable future, large refractory bodies will be built up from smaller panels which will necessitate the continued use of fasteners. This need will also become apparent in the areas of hypersonic aircraft, air-breathing missiles, and reusable rocket stages.

Efforts in refractory coatings have primarily used conventional coating techniques on shapes and fasteners. Oxidation protection provided by the coating was generally lost if any deflection or strain of coated parts was attempted. The inherently brittle nature of the common coating compositions, particularly with the silicides, is probably unavoidable. The detrimental effect of fracture, usually of intergranular nature, is increased by the large, normally columnar, grain size. The fracture can propagate rapidly through the coating and then laterally along the substrate-coating interface to produce gross spalling. Thus, either a coating must be maintained in a crack-free condition, or fracture of the coating must be controlled so that the structure continues to provide adequate protection.

The likelihood of maintaining a crack-free coating seems low when the application of the coated hardware is considered. Damage during the assembly process can occur due to mishandling, impact, or being strained to correct misalignments. The structure during actual use will be subjected to shock; thermal stress and strain generated by rapid, non-uniform heating; and a high probability of impact. Designs of flight structures can be developed to minimize and perhaps eliminate flexure, though more optimum utilization might be obtained by permitting some flexing. The coated fasteners used in assembling components will be subject to damage from handling and wrenching and will be torqued to produce some elongation. While the capability to apply patch repair if important, such methods are applicable only to observed and accessible defects, and then primarily during assembly, rather than during service.

The requirement for a coating having ductility or the ability to withstand some strain while remaining protective is critical. Coating processes which can control the nature of the structures must be developed to satisfy this need.

Chemical vapor deposition techniques are especially applicable to this area of fastener coating because of two basic considerations: (1) the close tolerance of threaded fasteners or mechanical fasteners requires a very uniform coating; and (2) since large numbers of fasteners are required in many programs, a technique must be developed for coating large numbers. Other coating techniques are utilized in the area of refractory fasteners, but each has its individual limitations in areas such as coating uniformity and reasonable production cycle. A chemical vapor deposition process provides a high-purity coating which gives oxidation protection of refractory fasteners in high temperature environment while satisfying the basic considerations.

SECTION II
APPROACH

This program was conducted in three phases described in the following paragraphs.

PHASE I. Processing equipment for coating large numbers of refractory fasteners by the chemical vapor deposition process (CVD) was designed, constructed, installed and tested. The design for the equipment was based on equipment presently used for coating by CVD techniques. Because coating uniformity is a critical consideration for fasteners, chemical vapor deposition is especially applicable since it provides a precise control capability. For testing, the process evolvement of the manufacturing processing equipment was centered on start-up coating experiments involving preliminary and parameter variation runs.

PHASE II. The manufacturing equipment and process which evolved during Phase I was used to optimize trideposition of the Cr-Ti-Si coating on columbium. The technology base for this portion of the program was work performed under Contract AF 33(615)-3046, sponsored by the Chemical Processing Branch, Manufacturing Technology Division, Air Force Materials Laboratory. During that contract, Texas Instruments demonstrated the ability to perform the Cr-Ti-Si coating by a one-step, or trideposition process. Subsequent oxidation testing established the good performance levels of this coating. The specific approach of the current program was concentrated on optimization, production demonstration and coating evaluation studies for coated samples produced in the manufacturing processing equipment.

PHASE III. The specific approach for Phase III was based on equipment modification, design, construction, installation and coating preparation studies to illustrate the process versatility for other coatings. The other coating of major interest was the W-WSi_2 system for tantalum alloys.

SECTION III

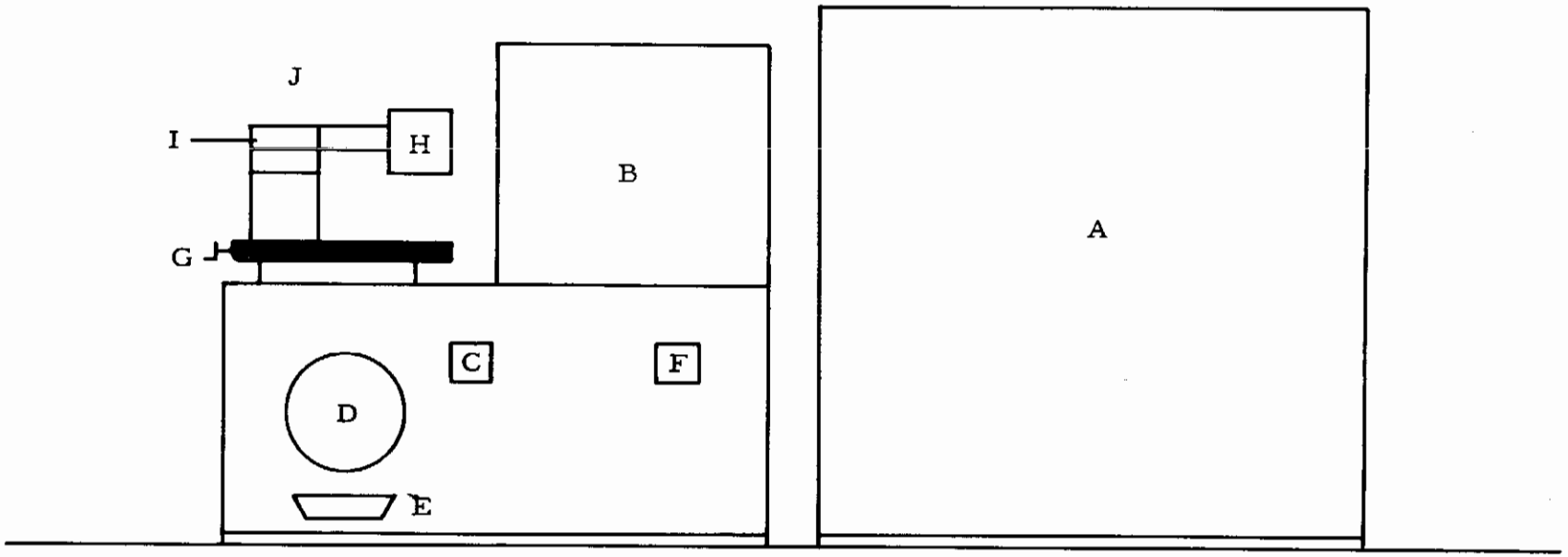
MANUFACTURING PROCESSING EQUIPMENT DESIGN, CONSTRUCTION AND INSTALLATION

Varied and numerous activities were involved in the manufacturing equipment design, construction and installation. The processing equipment, shown schematically in Figure 1, consisted of a reaction chamber (which rotates and tumbles the parts to be coated), a furnace, gas supply cabinet and other equipment. The parts to be coated were loaded into the coating chamber. The coating chamber was then inserted into the furnace and the coating gases were activated to flow through the neck of the chamber.

Several items for the furnace, which contains the rotating reaction chamber during trideposition reaction, were incorporated to provide automatic temperature control. Single phase power supply — using saturable core reactor for controlling power output — was made available in the laboratory since the existing laboratory power supply was not adequate to meet the furnace power requirements. The furnace resistance heating elements were reworked and made amenable to the single phase power supply to provide high reaction temperatures required for trideposition reaction. The electrovolt assembly and magnetic amplifier were then installed.

The temperature controller-recorder was integrated with the system. Initial checking indicated satisfactory automatic temperature control. However, temperature jumps and inaccurate indications were experienced in subsequent use. Instrument repair required to resolve these problems was made and resulted in achieving automatic temperature control.

The rotation-speed control was installed to allow the rotation speed of the reaction chamber to be varied.



LEGEND:

A. Gas supply cabinet
B. Furnace
C. Rotation speed control
D. Temperature recorder controller
E. Electrovolt assembly
F. Magnetic amplifier
G. Track assembly
H. Rotating reaction chamber
I. Gas inlet
J. Gas exhaust

Figure 1. Diagram of Rotating Reaction Chamber Equipment

After initial design, construction and installation, several modifications were made to the track assembly, which is used to transport the rotating reaction chamber into the furnace. The foundation, moving-assembly guide supports and gear drive were reworked and assembled. The track assembly was then center-mounted by using additional supports.

Furnace doors with thiner insulation were fabricated and installed to allow the rotating reaction chamber to enter the high temperature zone inside the furnace.

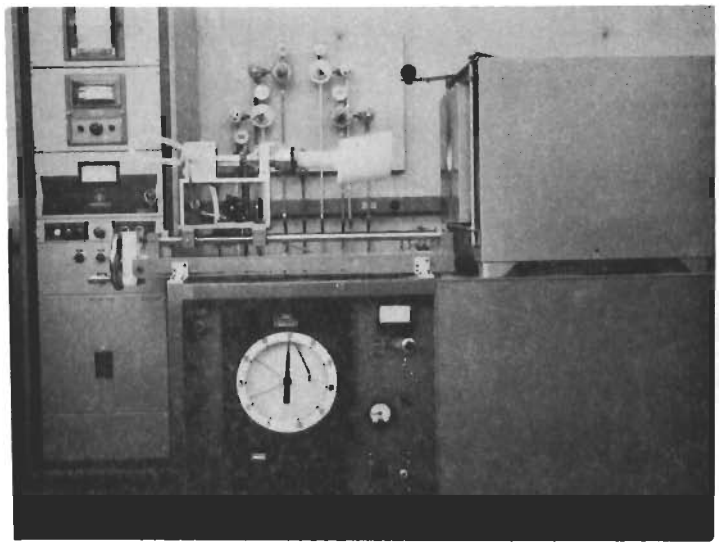
A photograph of the rotating reaction chamber, installed trac assembly, furnace and temperature control system is shown in Figure 2. View a. is with the rotating reaction chamber outside the furnace. View b. is with the rotating reaction chamber inside the furnace.

The gas supply cabinet is shown in Figure 3. Installation of the $TiCl_4$ bubbler, rerouting of plumbing, recharging of the He purifier and integration of SiH_4 into the unit were completed prior to conducting the experiments.

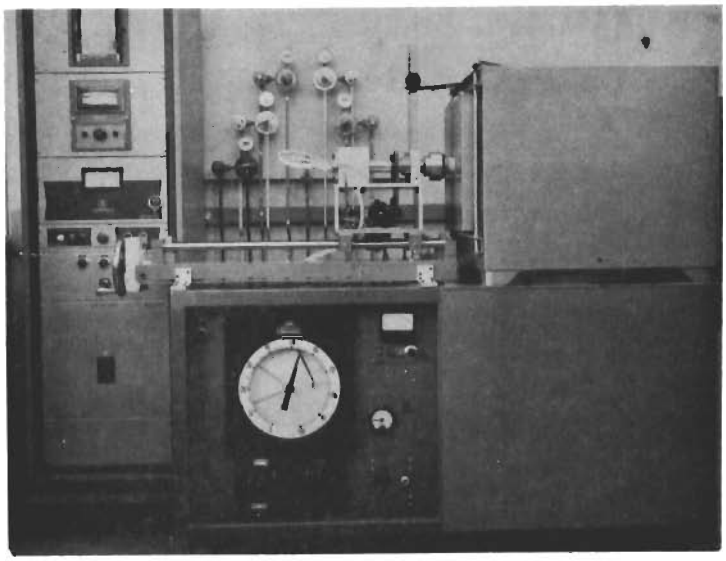
A process flow diagram of the gas supply cabinet is shown in Figure 4. This cabinet was used for the initial preliminary runs using the SiH_4 decomposition reaction.

One of the problems encountered during SiH_4 decomposition reaction was premature decomposition of the SiH_4 in the feed inlet tube. To overcome this problem, the next preliminary runs were conducted with $SiCl_4$ as silicon source using the $SiCl_4$ bubbler, added as shown in Figure 5 for introduction during the trideposition reaction. The flow diagram illustrated in Figure 5 was also used for parameter variation experiments.

A temperature range kit was obtained, installed and calibrate to permit higher temperature variations (i. e., above 1050°C).



a. Rotating Chamber Outside the Furnace



b. Rotating Chamber Inside the Furnace

Figure 2. Composite of Rotating Reaction Chamber, Track Assembly and Furnace

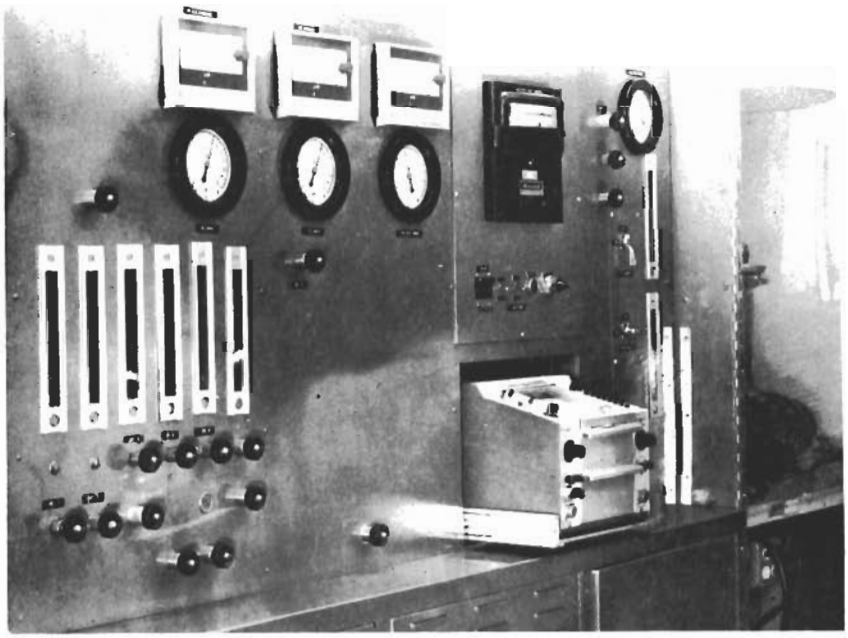


Figure 3. Gas Supply Cabinet for Processing Equipment

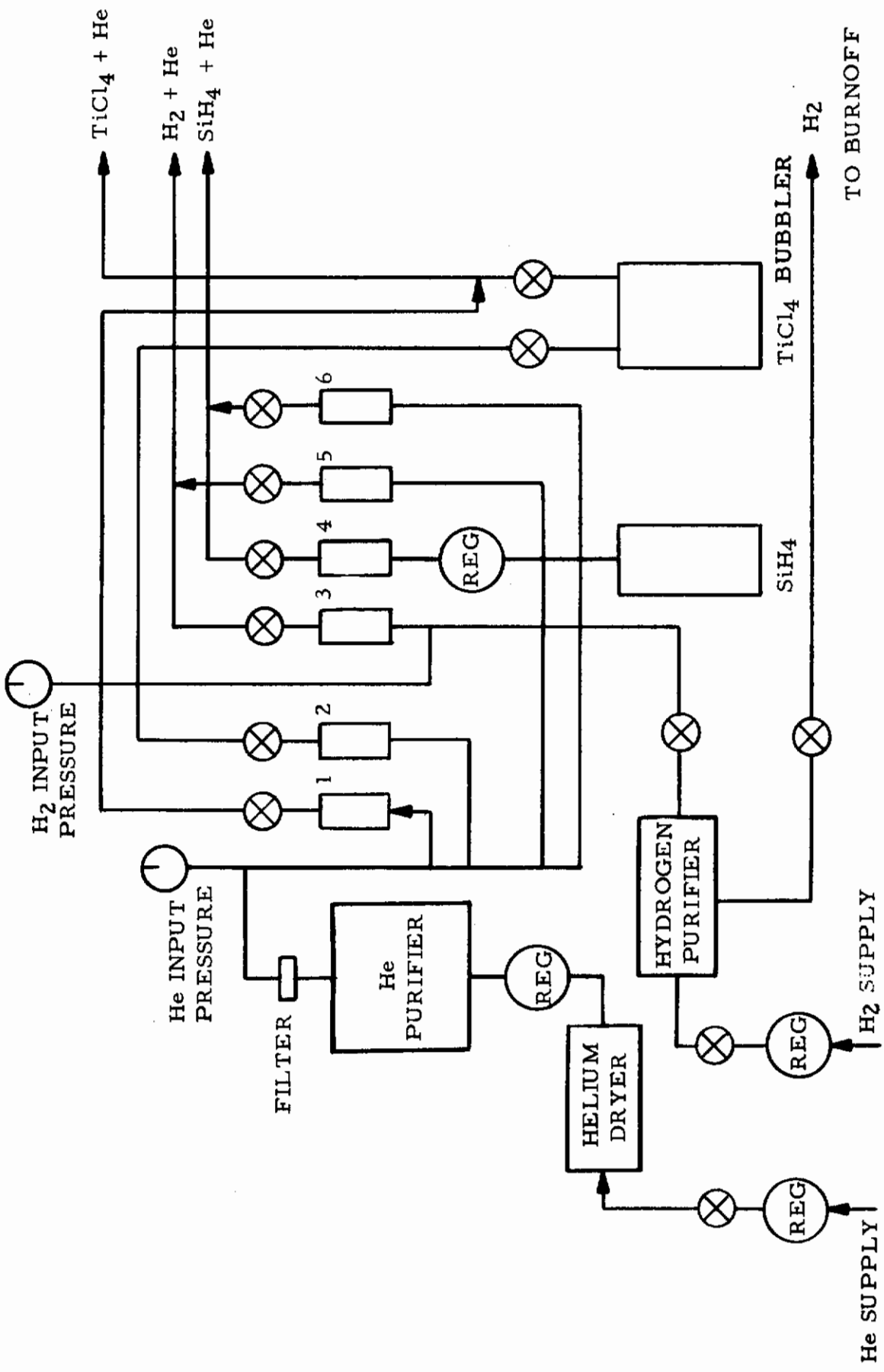


Figure 4. Gas Supply Cabinet Process Flow Diagram for Initial Preliminary Runs with SiH_4 Decomposition Reaction

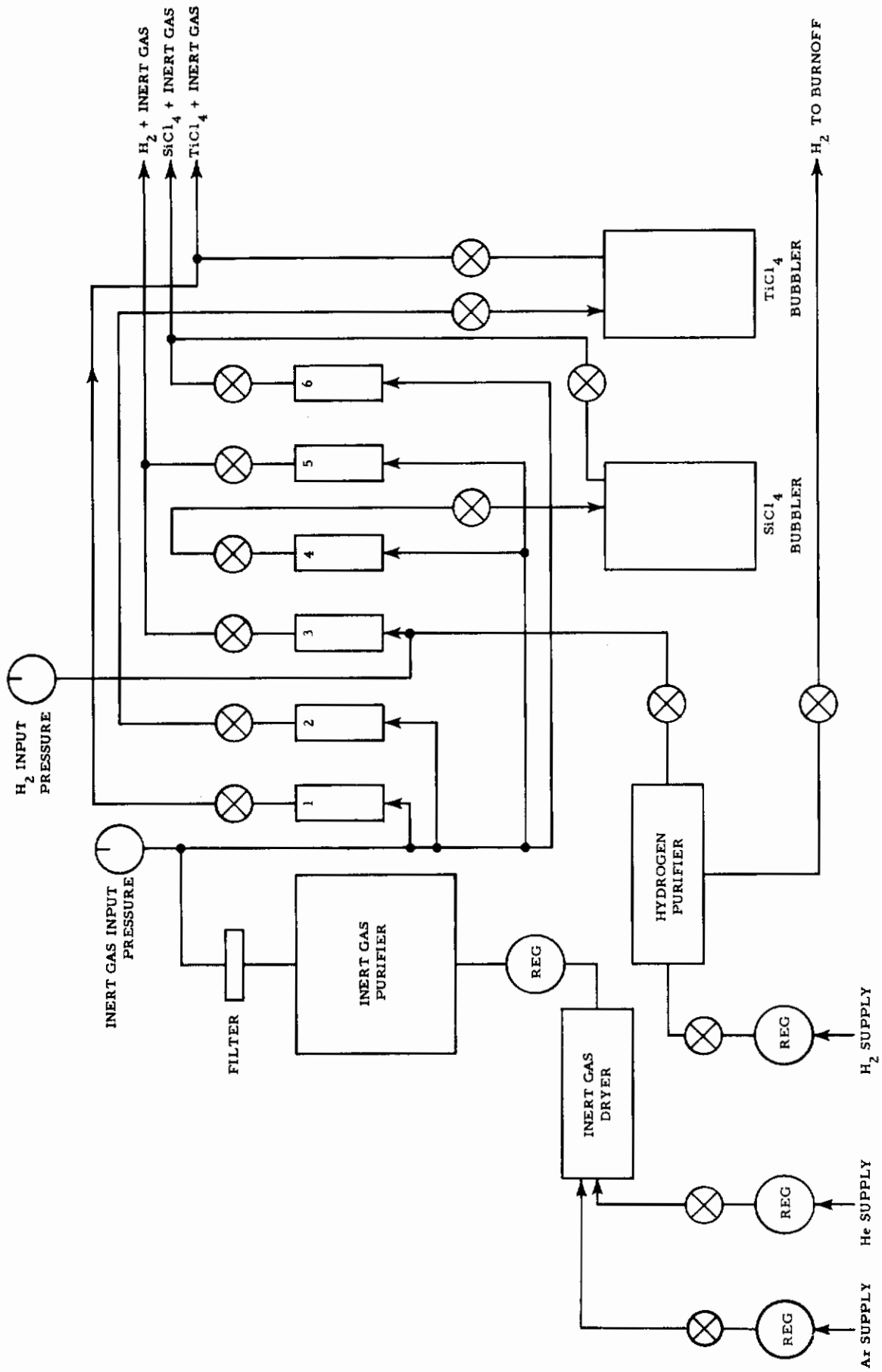


Figure 5. Gas Supply Cabinet Process Flow Diagram for Preliminary Runs and Parameter Variation Experiments

Additional manufacturing processing equipment design, construction and installation activities were completed prior to testing. These activities involved: installation of "Limitrol" for overheat protection, replacement of electrovolt assembly, adjustment of magnetic amplifier, installation of new temperature sensing device, modifications of gas inlet and exhaust, modifications and fillings of $SiCl_4$ and $TiCl_4$ bubblers, fabrication of reaction chambers, fabrication and installation of several gas feed geometries for introducing reactants into the reaction chamber, repair of the rotation speed control unit (including replacement of fine speed control assembly), reworking furnace doors, replacing furnace heating elements and installation of heavier duty electrical power supply. Completion of the manufacturing equipment design, construction and installation permitted start-up of coating experiments involving preliminary and parameter variation runs in the process optimization.

SECTION IV

PROCESS OPTIMIZATION START-UP COATING EVALUATION

A. PRELIMINARY RUNS

The trideposition reaction coating chemistry involved hydrogen reduction of gas phase silicon, titanium and chromium species. In the preliminary runs, several reactions (i.e., $SiCl_4$-Cr; $TiCl_4$-Cr; SiH_4 decomposition; $TiCl_4$-Ti; HCl-Cr and trideposition with Si, Ti and Cr chloride feeds) were studied as routes for introducing the respective gas phase species inside the rotating reaction chamber for coating deposition. From this study, the trideposition reaction with silicon, titanium and chromium chloride feeds was selected as the chemistry base for next program activity involving parameter variations. The demonstrated $TiCl_4$-Cr and $TiCl_4$-Ti reactions provided the respective titanium and chromium species for the chemistry base.

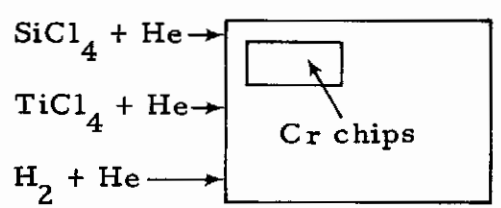
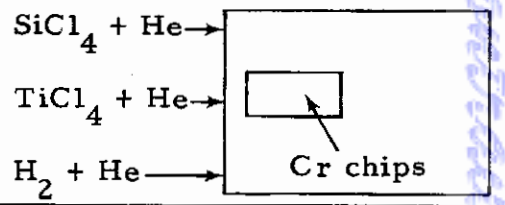
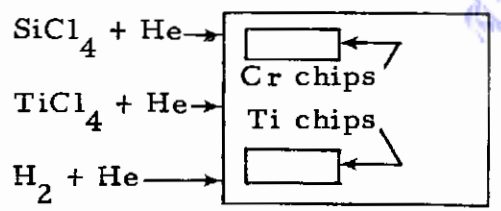
1. $SiCl_4$-Cr and $TiCl_4$-Cr Reactions

The reaction chemistry for the trideposition coating was based on hydrogen reduction of gas phase silicon, titanium and chromium species inside the rotating reaction chamber. For the chloride species (i.e., $SiCl_x$, $TiCl_y$ and $CrCl_z$), introduction of the $SiCl_4$ and $TiCl_4$ feeds (tetrachlorides) may be achieved by conventional means of bubbling an inert gas through the respective liquids and achieving saturation. Introduction of $CrCl_z$ presents a feed entry problem since both chromium chlorides (di and tri) are solids and have negligible vapor pressure at room temperatures.

Several routes for introducing the chemical feeds into the rotating reaction chamber are detailed in Table I. Two routes, from among several, to overcome this feed entry problem are to react $SiCl_4$ or $TiCl_4$ with solid Cr chips to generate the $CrCl_z$. Further, the $CrCl_z$ product should be generated at sufficiently high temperature so that the $CrCl_z$ component is furnished in the vapor phase and available for subsequent hydrogen reduction.

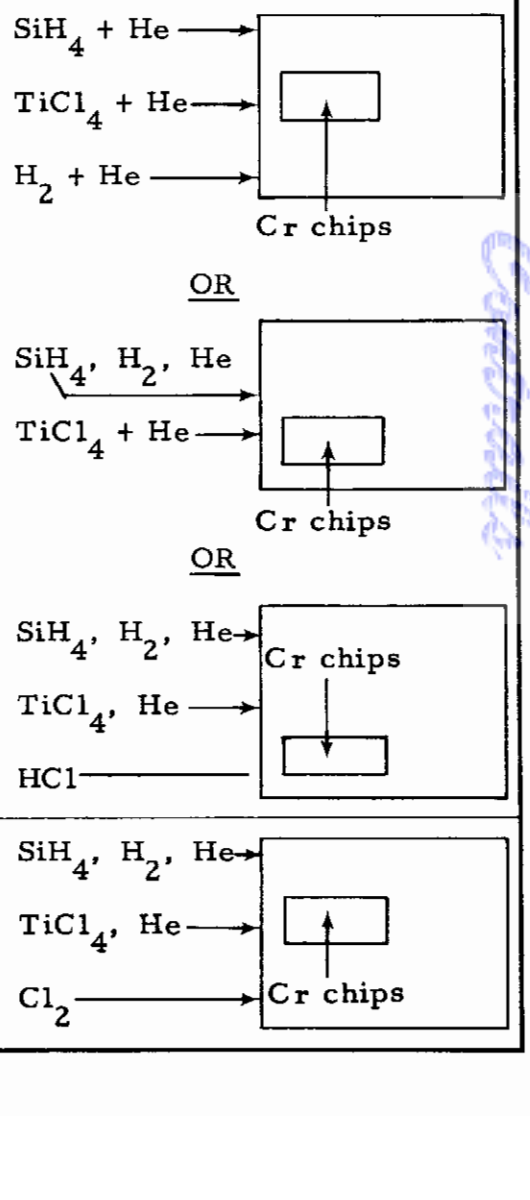
Table I

PRELIMINARY RUNS: LIST OF ROUTES FOR INTRODUCING CHEMICAL FEEDS

Chemical Feeds	Comments		Sketch Flow Diagram For Rotary Chamber Reactor
	Favorable	Unfavorable	
$SiCl_4 + Cr^* \rightarrow$ $SiCl_x + CrCl_z$	• Ease of handling $SiCl_4$ • Generate $CrCl_z$ at higher temperature • Independent flow measurement for $TiCl_4$	• No method for independent measurement of Cr • No knowledge of reacting species $SiCl_x$ and $CrCl_z$ ($y = ?$, $Z = ?$)	
$TiCl_4 + Cr^* \rightarrow$ $TiCl_y + CrCl_z$	• Ease of handling $TiCl_4$ • Achieve partial reduction of $TiCl_4$	• No method for independent measurement of Cr • No knowledge of reacting species $TiCl_y$ and $CrCl_z$	
$TiCl_4 + Ti^* \rightarrow$ $TiCl_y$	• Ease of handling $TiCl_4$ • Achieve $TiCl_4$ partial	• No method for independent measurement of Cr • No knowledge of reacting species $TiCl_y$	

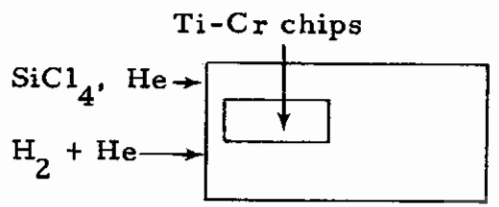
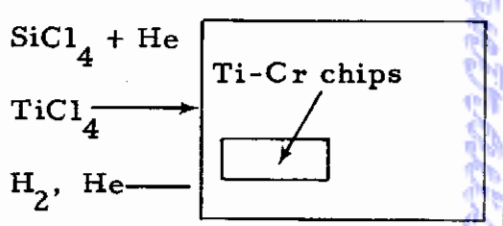
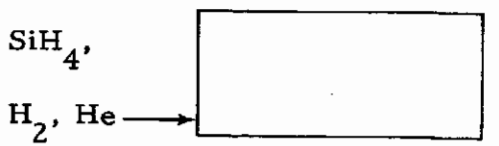
*Solid Chips

Table I (Contd)

Chemical Feeds	Comments		Sketch Flow Diagram For Rotary Chamber Reactor
	Favorable	Unfavorable	
SiH_4 ⟶ Si + Others	• Help Equilibrium by reducing HCl in reduction of trideposition	• No method for independent measurement of Cr • No knowledge of reacting species $TiCl_y$, $CrCl_z$	
Cl_2 + Cr* ⟶ $CrCl_z$	• Ease of handling $SiCl_4$ and $TiCl_4$ • Independent variations of Cr concentration		

*Solid Chips

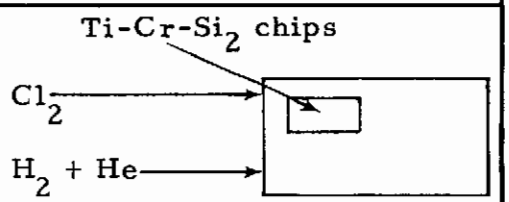
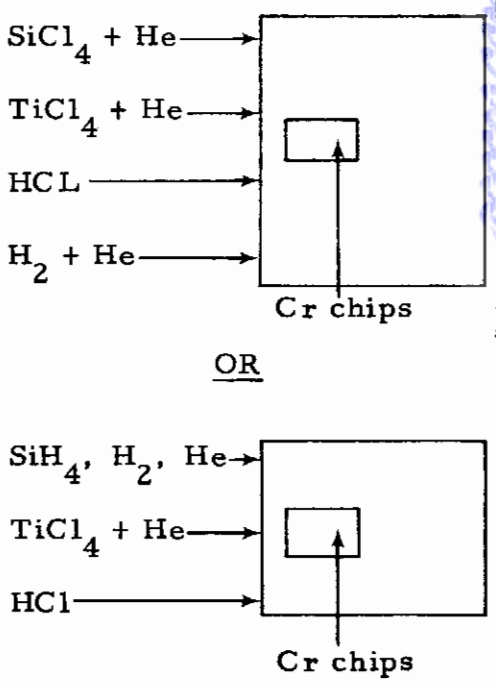
Table I (Contd)

Chemical Feeds	Comments		Sketch Flow Diagram For Rotary Chamber Reactor
	Favorable	Unfavorable	
$SiCl_4$ + TiCr** → $SiCl_x$ + $TiCl_y$ + $CrCl_z$	• Only necessary to measure $SiCl_4$ flow • Difficult to achieve desired Si/Ti/Cr concentrations	• No knowledge of x, y, z • Difficult to determine Ti loss Cr loss in straightforward manner • No independent variation of Ti and Cr	
$TiCl_4$ + TiCr** → $TiCl_y$ + Cl_z	• Only measure two feed streams $TiCl_4$ and $SiCl_4$	• No independent variation of Cr • Are kinetics equal for Ti and Cr reaction	 OR 

*Solid Chips

**Solid Alloy Chips

Table I (Contd)

Chemical Feeds	Comments		Sketch Flow Diagram For Rotary Chamber Reactor
	Favorable	Unfavorable	
$Cl_2 + CrTiSi_2$ (**) → $SiCl_x + TiCl_y +$ $CrCl_z$ alloy	• Only measure one feed stream Cl_2 • Questionably if desired Si/Ti/Cr concentration can be achieved	• No independent variation of Si • No independent variation of Ti • No independent variation of Cr	
$HCl + Cr$ (*) → $CrCl_z$	• Measure only HCl for Cr concentration • Independent variation of Cr concentration • Independent measurement of SiCl (or SiH_4) and $TiCl_4$	•	

*Solid Chips

**Solid Alloy Chips

A sketch of the equipment used in the process study of these two routes is illustrates in Figure 6. The reaction zone in the figures was used to simulate the high reaction temperatures which was encountered in the rotating reaction chamber. Inert gas bubblers were used for $SiCl_4$ and $TiCl_4$ flows.

The experimental results for the $SiCl_4$-Cr and $TiCl_4$-Cr reactions are detailed in Table II. For the $SiCl_4$-Cr reaction, the experimental results disclosed cursory reaction feasilibity. In each experiment, the $SiCl_4$ was passed over solid Cr chips at high reaction temperatures. Each time the solid Cr chips experienced a weight loss indicating chlorination of the chips and transfer of the chromium chloride product to the vapor. The Cr chips remaining after each experiment had a dark coating. X-ray analysis of this coating from one of the runs indicated a chromium silicide (Cr_3Si).

For the $TiCl_4$-Cr reaction, the process study also revealed cursory reaction feasibility. Experimental conditions included passage of $TiCl_4$ over solid Cr chips at reaction temperatures within scope of proposed conditions for the rotating reaction chamber. In each of the experiments, a loss of weight was sustained by the chips disclosing chlorination and transfer of the chromium chloride product into the vapor phase. Since this route was conducted at sufficiently high temperature and provided the $CrCl_z$ in the vapor phase for subsequent hydrogen reduction, the $TiCl_4$-Cr reaction was selected for use in the subsequent program.

2. SiH_4 Decomposition Reaction

The SiH_4 decomposition reaction was identified in Table I as a means for introducing the gas phase silicon species of the chemical feeds into the rotating reaction chamber. The SiH_4 represents a non-halide source of silicon and its use could be advantageous because it reduced the HCl content from the trideposition reaction.

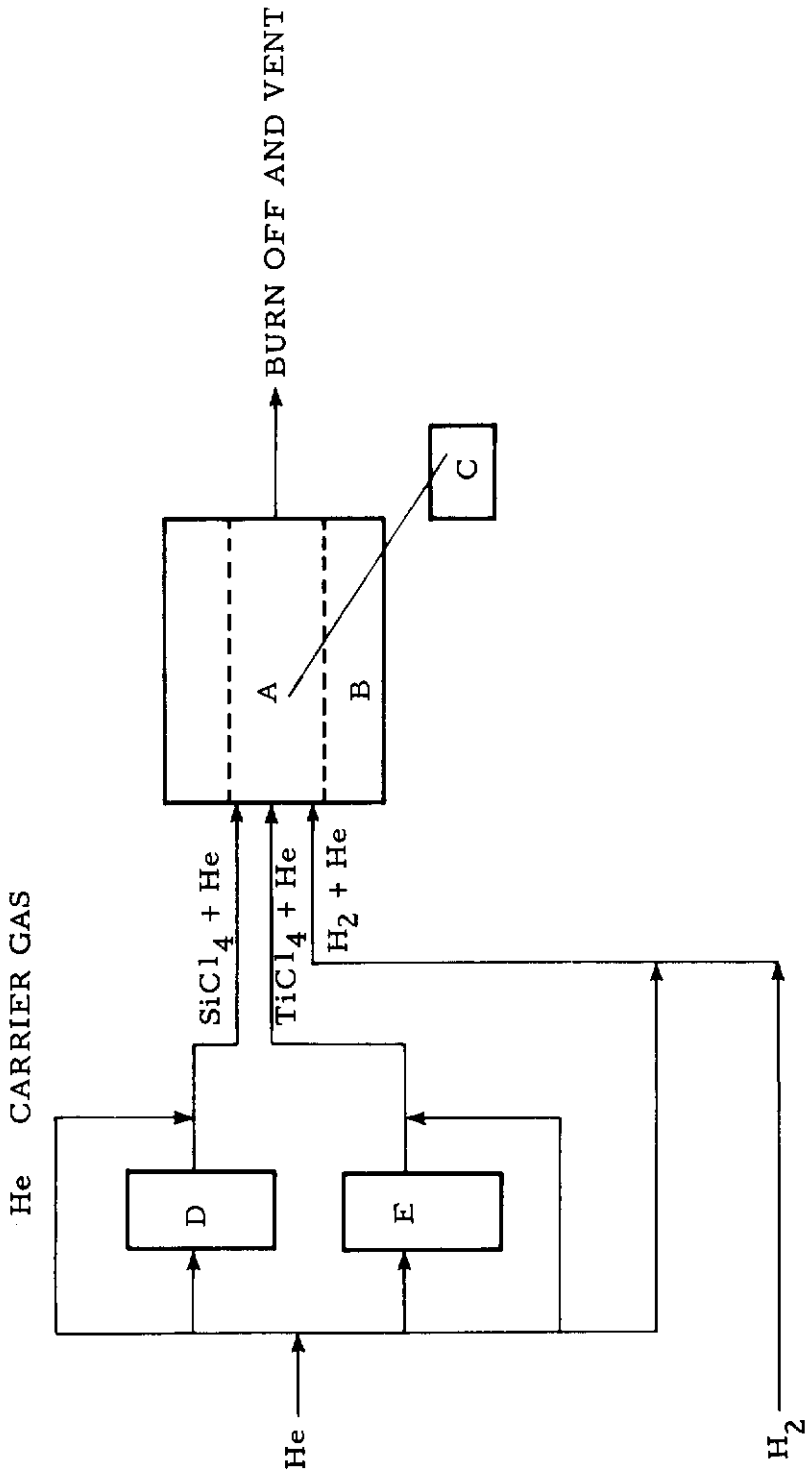


Figure 6. Preliminary Runs: Process Studies Equipment Diagram

Table II

PRELIMINARY RUNS: RESULTS FOR $SiCl_4$-Cr and $TiCl_4$-Cr REACTIONS

Run Number	He Flow (ml/min)				H_2 Carrier	H_2 Flow (ml/min)	Reaction Temp. (°C)	Wt Loss of Chips, mg	
	$SiCl_4$		$TiCl_4$						
	Bubbler	Carrier	Bubbler	Carrier				Cr	Si
CLY-1-68	10	1000	—	—	—	—	950	39.0	—
CLY-2-68	30	1000	—	—	—	—	950	25.3	—
CLY-3.1-68	10	1000	—	—	—	—	950	11.4	—
CLY-3.2-68	40	—	—	—	—	—	—	36.5	—
CLY-3.3-68	60	—	—	—	—	—	—	56.4	—
CLY-3.4-68	80	—	—	—	—	—	—	64.8	—
CLY-4-68	—	—	1000	500	1000	500	1000	Not measured	
CLY-5-68	—	—	500	1000	1000	500	980	13.0	2.3 gain
CLY-6-68	—	—	500	1000	500	1000	1000	217.3	—
CLY-7-68	—	—	1000	500	500	1000	1000	152.2	—
CLY-8-68	—	—	1000	500	500	1500	1000	203.5	—
CLY-9-68	1000	—	1000	500	500	1500	1000	140.8	—
CLY-10-68	89	—	1500	500	500	1500	1000	80.8	—
CLY-11-68	89	Some	1000	500	500	1500	1000	113.1	—
CLY-12-68	89	—	2000	500	500	1500	1000	—	—
CLY-13-68	89	≃500	2000	≃500	500	1500	1000	Error	—
CLY-14-68	89	≃500	2000	≃500	500	1500	1000	200.0	—
CLY-15-68	89	≃500	2000	≃500	500	1500	1000	410.0	—

After a literature search for decomposition temperatures and safe handling rules for the SiH_4, several cursory experiments were conducted for the decomposition reaction. The experimental results are listed in Table III.

In the first experiment, the SiH_4 feed tube was placed at the entry of the furnace and did not extend into the furnace hot-zone to preclude plugging by premature SiH_4 decomposition. The feed tube did not plug and solid deposits were obtained on quartz reactor walls and the sample specimen located inside the furnace hot zone. Subsequent efforts of (1) combined feeding of H_2, He and SiH_4 in same feed tube, and (2) graphite wool insulation enclosing the feed tube were not successful in precluding premature SiH_4 decomposition when the feed tube was extended into the furnace hot-zone and each time the feed tube plugged prior to completion of the experiment.

The described preliminary runs with the SiH_4 decomposition reaction were made with a stationary reactor while the rotating reaction chamber equipment was being completed. Additional preliminary runs were made using the rotating reaction chamber.

The first experiment using the rotating reaction chamber was conducted with satisfactory operation of the equipment. This included sufficient cooling of the locking unit-quartz chamber neck connection to prevent partial melting of seal material and resulting gas leakage at the connection point. However, the SiH_4 feed tube plugged after about five minutes.

In the next run, the feed tube was repositioned so that is was several inches from the high temperature reaction zone inside the rotating chamber. The feed tube did not plug during this run. Observation made after the run revealed that the SiH_4 did not enter the rotating chamber sufficiently for required reaction. The SiH_4 feed tube did extend into the chamber for reaction in the next run, but the feed tube plugged prior to

Table III

PRELIMINARY RUNS: SiH_4 DECOMPOSITION REACTION

Run No.	He Flow (ml/min) $TiCl_4$		H_2 Flow (ml/min)	He Carrier (ml/min)	Reaction Temperature (°C)	Comments
	Bubbler	Carrier				
CLY-24-68	2000	500	1500	500	850	The SiH_4 feed tube placed at entry of furnace hot zone to protect against plugging by early SiH_4 decomposition. Feed tube did not plug during run. Solid deposits obtained on quartz reactor walls and sample specimen located inside furnace hot zone.
CLY-25-68	2000	500	1500	500	850	H_2 diluted with He and SiH_4 were introduced through SiH_4 feed tube. Increased velocity was intended to protect against plugging. SiH_4 feed tube extended into furnace hot zone. The SiH_4 feed tube plugged after 5 min. Solid deposits achieved on feed tube, quartz reactor walls and sample specimen.
CLY-26-68	2000	500	1500	500	850	Experiment conducted with graphite cloth insulation wrapped around SiH_4 feed tube and H_2-He-SiH_4 common introduction. With insulation and common feeding, feed tube extended into furnace hot zone. The SiH_4 feed tube plugged after 20 minutes operation. Solid deposits obtained with powder-like consistency.
CLY-27-68	2000	- - -	1500	500	600	Lower reaction temperature used in experiment. Graphite cloth insulation not used. Common feeding of H_2-He-SiH_4 feed tube located inside hot zone. The SiH_4 feed tube did not plug during run but solid deposits were noted inside the tube following the run. Solid deposits obtained on reactor walls and one sample specimen.

completion of the run. Subsequent runs to preclude premature SiH_4 decomposition included: (1) hydrogen and SiH_4 introduction in common feed tube, (2) hydrogen flow in annulus with SiH_4 feed flow in annulus center tube, (3) helium flow in annulus including determination of center tube temperatures at several flows and (4) argon flow in annulus. These attempts to preclude premature SiH_4 decomposition were only partially successful (i.e., increasing length of time before plugging occurred).

The argon was used in the last attempts because of its lower thermal conductivity compared to hydrogen and helium. Argon annulus flow provided the lowest center tube temperature.

Complete data and observations for the SiH_4 decomposition reaction are listed in Table IV for these preliminary runs with the rotating reaction chamber equipment.

3. $TiCl_4$-Ti and HCl-Cr Reactions

Of the possible routes for introducing the chemical feeds into the rotating reaction chamber, the $TiCl_4$-Ti reaction was identified in Table I as a route for achieving parital reduction of $TiCl_4$ prior to the trideposition reaction. The partial reduction could enhance the trideposition reaction by reducing the number of moles of HCl in the reaction product.

Several experiments were conducted to determine the cursory feasibility and conversion for the $TiCl_4$-Ti reaction. The stationary reactor equipment used in the experiments contained a small furnace which was used to approximate reaction conditions for rotating reaction chamber equipments. The initial experiments indicated reaction feasibility. This was indicated by the loss of weight of the Ti chips when $TiCl_4$ (diluted with He) was passed over them.

Table IV

PRELIMINARY RUNS: SiH_4 DECOMPOSITION REACTION WITH ROTATING REACTION CHAMBER EQUIPMENT

Run Number	He Flow (ml/min)		SiH_4 Flow (ml/min)		H_2 Flow (ml/min)		Reaction Temperature °C	Observations
	$TiCl_4$ Bubbler	$TiCl_4$ Diluent	SiH_4 Stream	He Diluent in SiH_4	H_2 Stream	He Diluent in H_2		
CLY-28-68	2000	500	4-5	500	1500	500	1000	• The experiment was conducted in the new rotary chamber equipment. • The used fan and furnace-door heat shield kept the seal material (used for locking unit and quartz chamber) from burning. • The SiH_4 feed tube plugged 5 minutes after start of experiment. • Experiment conducted without SiH_4 after plugging. • Graphite substrate sample sustained weight gain indicating deposit on sample. • The SiH_4 feed tube was placed at approximate mid-point of the chamber of the quartz rotating reactor.
CLY-29-68	2000	1000	4-5	1000	2000	500	1000	• The SiH_4 feed tube was repositioned for the experiment. It was placed several inches from the entry of the high temperature zone of the chamber of the quartz rotating reactor. • The feed tube did not plug during the experiment. • During experiment, brownish-colored mass was noted in vapors from exhaust burn off. It was suspected to be SiH_4 not fully entering the rotating reaction chamber. • When the reactor was removed, it appeared the SiH_4 feed gas had not entered the chamber containing the substrate samples. • The graphite substrate samples sustained some weight gain.
CLY-30-68	2000	2000	4-5	—	5400	—	1000	• The SiH_4 feed tube extended into chamber to provide silicon source for trideposition reaction. • Hydrogen and SiH_4 were introduced through same feed tube. • Unable to complete experiment due to SiH_4 feed tube becoming plugged after 5-8 minutes. • Graphite substrate samples experienced very small weight gain.
CLY-31-68	2000	2000	4-5	—	5500	5500	1000	• Hydrogen feed introduced in annulus with SiH_4 feed tube comprising center tube of the two-tube annulus system. Hopefully, this arrangement would help prevent early SiH_4 decomposition which plugs feed tube. • In another feed system, helium was introduced in annulus with thermowell tube comprising center tube for analogous temperature indication of SiH_4 feed tube. • Initial part of experiment completed. • Thermowell leak developed causing shutdown of run as silver solder used for sealing the thermocouple tube melted at conditions experienced in run.
CLY-32-68	2000	2000	4-5	—	5500	5500*	1000	• Similar set up as previous run except different thermowell used having a stainless steel weld. • Calibrated thermocouple used in experiment indicate temperature in annulus center tube. • With He flowing in annulus, temperature indications in center tube were: 1 min - 70° C, 5 min - 540° C, 13 min - 846° C, and 20 min - 874° C. • Final leveling off temperature was 874° C with cooling via He flow in annulus.
CLY-33-68	2000	2000	—	—	5500	11000*	1000	• Helium flow in annulus increased to 11 ℓ/min to further cool annulus center tube. • Lower temperature observed in annulus center tube, but still not sufficient to prevent early SiH_4 decomposition. • Final leveling off temperature of 816° C was achieved in the experiment.
CLY-34-68	2000	2000	—	—	5500	6200 to 6800**	1000	• Helium flow in annulus replaced with argon. Argon has lower conductivity - about 10 percent of He - than helium. • Experiment conducted to determine effect of lower conductivity on lowering of annulus center tube temperature. • With argon low of about 6-7 ℓ/min, lowering of temperature achieved. • Temperature leveled off at about 736° C.
CLY-35-68	—	—	4-5	—	—	6200**	1000	• In the run, argon flowed in annulus and SiH_4 flowed in center tube. • Experiment conducted to determine if argon annulus flow would provide sufficient cooling to early SiH_4 decomposition which plugs feed tube. • Satisfactory SiH_4 flow achieved in first part of run. But feed tube plugged after 8 min. • Next experiment in rotary equipment shakedown will utilize $SiCl_4$ as the source of silicon.

* He flowing in annulus.

** Argon flowing in annulus.

Four experiments were conducted to determine extent of $TiCl_4$ partial reduction (i.e., conversion of $TiCl_4$) using the same Ti chips charge in each run. The partial reduction was about 40-60% conversion depending on conditions and chip history in these runs. The results are summarized in Table V.

The results of the four runs are shown graphically in Figure 7 as weight loss of Ti chips versus He flow through $TiCl_4$ bubbler. The graph indicates increase of weight loss with increase of flow. On the basis of these favorable findings, the $TiCl_4$-Ti reaction was selected for use in the subsequent program including parameter variation and optimization studies.

The HCl-Cr reaction was also previously identified as a feed entry route for providing the chromium chloride in the trideposition reaction. It further represents a route to provide variable Cr-concentration independent other metal Si and Ti components of the reaction.

Feasibility of the HCl-Cr reaction was ascertained at conditions similar to those anticipated with the rotating reaction chamber equipment. The HCl converted when passed over the Cr chips was calculated using data from another CVD project at Texas Instruments. Table VI shows the HCl conversions calculated using this data. The results reveal that 80% or more of the HCl was converted to the chromium chloride in most of the tabulated runs. Based on these findings, the HCl-Cr reaction was selected as a chromium chloride back-up route for use in the event that the other titanium and silicon chloride routes did not provide the appropriate Cr/Ti/Si reaction concentrations.

TABLE V

PRELIMINARY RUNS: $TiCl_4$ – Ti REACTION

Run No.	He Flow (ml/min) $TiCl_4$		Reaction Temperature (°C)	Wt. Loss Of Ti Chips (mg)	$TiCl_4$ Conversion* (mol%)
	Bubbler	Carrier			
CLY-17-68	2000	500	1000	287.2	- - -
CLY-18-68	2000	500	850	110.0**	- - -
CLY-19-68	4000	500	850	Tube Plugged	- - -
CLY-20-68	2000	500	850	228.6	40.5
CLY-21-68	1000	500	850	149.7	52.8
CLY-22-68	4000	500	850	573.1	50.5
CLY-23-68	2000	500	850	341.0	60.5

OTHER RUN CONDITIONS OR OBSERVATIONS:

Time of run: 30 minutes.
Charge of Ti chips varied in runs 17, 18, and 19.
Same charge of Ti chips used in 20, 21, 22, and 23.

* $TiCl_4$ conversion (mol %) = $\frac{TiCl_4 \text{ converted (mol/min)}}{TiCl_4 \text{ feed (mol/min)}}$ where: $TiCl_4$ converted is calculated from weight loss of Ti chips

** Suspected inaccurate weight loss of Ti chips due to large weight balance which was not used in any other runs calculated above.

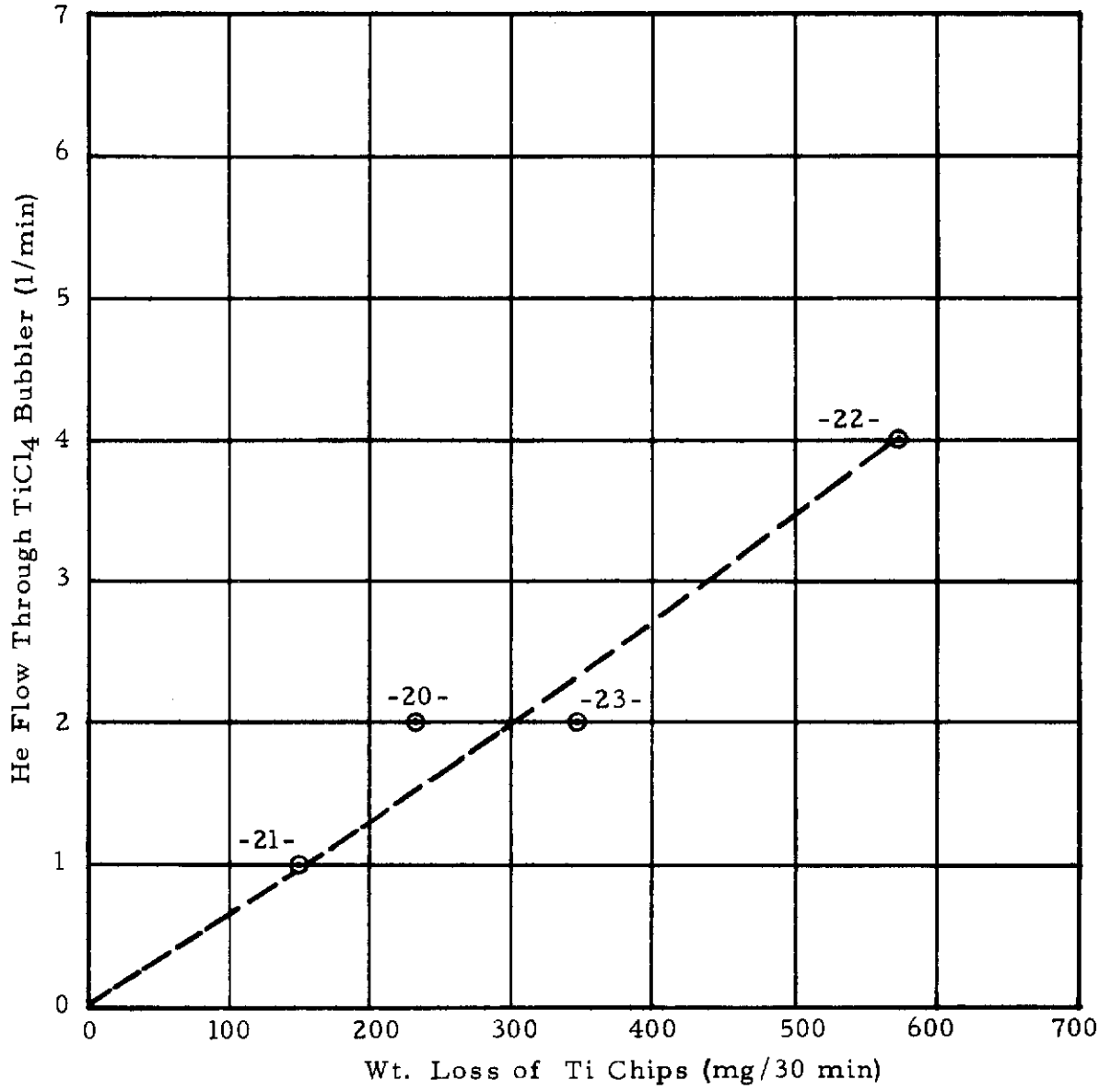


Figure 7. Preliminary Runs: Weight Loss of Ti Chips for $TiCl_4$-Ti Reaction

TABLE VI

PRELIMANRY RUNS: HCl-Cr REACTION CONVERSION OF HCl PASSED OVER SOLID Cr CHIPS

Run Number		5351	5452	5553	5755	5856	5957	6058	6159	5260	6361	6462	6563
Flow	He (l/min)	2.0	2.0	3.0	3.0	3.0	4.0	3.0	3.0	3.0	4.0	4.0	4.0
	HCl (cc/min)	250	250	250	250	250	250	250	250	250	330	250	330
Temperature (°C)		1000	1000	950	1000	1000	1000	1000	1000	1000	1000	1000	1000
HCl Conversion* (mol %)		100	80	85.5	80	87	81.5	70.5	83.5	64.5	84	85	86

OTHER RUN CONDITIONS:

Hcl diluted with He passed downward over solid chips in vertical quartz reactor.
Solid Cr chips charge in the range of several hundred grams.

$$*\text{HCl Conversion (mol \%)} = \frac{\text{HCl Converted (mol/min)}}{\text{HCl Feed (mol/min)}}$$

where: HCl converted is calculated from weight loss of chips.

4. Trideposition Reaction Using Si, Ti and Cr Chloride Feeds

One of the basic problems arising from using the SiH_4 decomposition reaction as the gas phase silicon species for the trideposition was early decomposition of the SiH_4 in the feed entry tube. Since the previous work[1] with a laboratory stationary reactor had provided chromium-titanium-silicon coating using the respective metal chloride feeds, the next preliminary runs were conducted with silicon, titanium and chromium chloride feeds. These runs were made using the rotating reaction chamber equipment.

Preliminary runs for the trideposition reaction using these metal chloride feeds indicated feasibility of the coating reaction for the conditions studied. For these runs, graphite and metal substrate samples were placed inside the rotating reaction chamber. During the deposition time, the silicon, titanium and chromium chlorides, hydrogen and inert gas diluent were continuously introduced into the rotating reaction chamber containing the substrate samples. Substrate sample weight gains and other data for the trideposition reaction, using metal chloride feeds, are recorded in Table VII. In general, the results were favorable in that the substrate samples experienced weight gains indicating deposition of coating on the substrates in the reaction environment.

These favorable results (i.e., coating deposit achieved on substrate using silicon titanium and chromium chloride feeds) provided the trideposition reaction chemistry base for starting up the next program activity involving parameter variations.

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[1] Wakefield, Gene F., "Final Report on Refractory Metal Coatings by Chemical Vapor Deposition," Technical Report AFML-TR-66-397 (December 1966).

Table VII

PRELIMINARY RUNS: RESULTS FOR TRIDEPOSITION REACTION USING SILICON, TITANIUM AND CHROMIUM CHLORIDE FEEDS

Run Number	Inert Gas Flows (ℓ/min)				H_2 Flow (ℓ/min)		Inert Gas	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reactor Temperature (°C)	Weight Gain of Substrate Sample (mg)				
	$SiCl_4$ Bubbler	$SiCl_4$ Diluent	$TiCl_4$ Bubbler	$TiCl_4$ Diluent	H_2 Stream	Inert Gas					Graphite Substrates	Metal Substrate			
												1	2	3	Average
CLY-36-68	.089	.50	2.0	.50	1.5	.50	He	5.089	30	1000	-	-	-	-	-
CLY-37-68	.148	1.0	4.0	1.0	3.0	1.0	He	10.148	30	1000	9.5	-	-	-	-
CLY-38-68	.045	.25	1.0	2.4	2.35	.65	He	6.695	30	1000	15.2	-	-	-	2.2*
CLY-39-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	30	1000	11.8	-	-	-	4.6*
CLY-40-68	.145	.50	4.0	.50	4.7	1.30	He	10.145	30	1000	16.7	6.0	6.0	4.7	5.6
CLY-41-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	120	1000	38.7	13.7	19.1	14.4	15.7
CLY-42-68	.089	.50	2.0	.50	6.5	1.30	He	10.889	30	1000	25.2	2.8	2.7	4.7	3.4
CLY-43-68	.045	.25	1.0	.50	6.5	.65	He	8.945	30	1000	3.2	4.3	3.3	4.3	4.0
CLY-44-68	.089	.50	2.0	.50	6.5	1.30	He	10.889	120	1000	76.1	9.9	10.4	10.0	10.1
CLY-45-68	.045	.25	2.0	.50	6.5	.65	He	9.945	30	1000	6.3	4.7	5.1	5.1	5.0
CLY-46-68	.045	.25	2.0	.50	6.5	.65	He	9.945	120	1000	73.9	9.8	10.4	8.0	9.4
CLY-47-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	120	1050	31.2	15.3	15.7	28.2	19.7
CLY-48-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	30	1050	16.3	11.1	11.1	11.7	11.3
CLY-49-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	30	950	4.8	2.7	2.6	1.7	2.3
CLY-50-68	.089	.50	2.0	.50	4.7	1.30	He	9.089	120	950	8.5	9.6	10.3	11.0	10.3

OTHER RUN CONDITIONS AND OBSERVATIONS:

- Several substrate samples used in run CLY-36-68 sustained a weight gain.
- Six metal substrate samples used in run CLY-37-68 experienced a weight gain of 39.1 mg.
- Two ceramic substrates were used in runs CLY-42-68 through CLY-48-68 in addition to graphite and metal substrate samples. In runs CLY-43-68 through CLY-48-68, the ceramic substrates from immediate preceding run were used.
- Graphite substrates from immediate preceding run were used in runs CLY-45-68 through CLY-48-68.
- Slight variation in size of graphite and metal substrate samples,

*Two metal substrates were used in runs CLY-38-68 and CLY-39-68. The respective weight gains were 4.4 and 9.2 mg. The average respective weight gains per metal substrate were 2.2 and 4.6 mg.

B. PARAMETER VARIATION

The trideposition reaction with hydrogen reduction of silicon, titanium and chromium chloride feeds was used as the chemistry base for parameter variation runs with the rotating reaction chamber equipment. Six parameters were investigated including reaction temperature, deposition time, reactant concentrations, rotation speed and flow rate. The investigation disclosed that the coating deposit from the trideposition reaction was increased with increase of the following parameters: reaction temperature; deposition time; Si, Ti and Cr chloride concentrations; H_2 concentration; rotation speed and flow rate. These disclosures and base parameter values gleaned from the runs formed the basis for the next activity of optimization and production demonstration studies with the manufacturing processing equipment.

1. Reaction Temperature

Parameter variation experiments using silicon, titanium and chromium chloride feeds indicated coating deposit increase with reaction temperature increase. This reaction temperature effect on coating deposit was observed for variable temperature runs in 930-1150°C range. Reaction temperatures up to 1230°C were achieved in subsequent other parameter experiments.

Complete data for parameter variation runs with silicon, titanium and chromium chloride feeds are recorded in Table VIII.

The initial parameter variation experiments were conducted by varying the temperature and holding other parameters constant to determine reaction temperature effect on the coating deposit (determined as weight gain of substrates). These initial experiments used facsimile samples of graphite and columbium for the substrates and utilized reaction conditions similar to the previous effort. Results of three experiments illustrating the reaction temperature effect — reaction temperature increase provides coating deposit increase — are summarized in Table IX for 930-1050°C range.

Table VIII

PARAMETER VARIATION: RESULTS USING SILICON, TITANIUM AND CHROMIUM CHLORIDE FEEDS

Run Number	Inert Gas Flow (ℓ/min)				Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chip (mg)	H_2 Flow (ℓ/min)		Inert Gas	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temperature (°C)	Rotation Speed (rpm)	Weight Gain of Metal Substrate (mg)			
	$SiCl_4$ Bubbler	$SiCl_4$ Diluent	$TiCl_4$ Bubbler	$TiCl_4$ Diluent			H_2 Stream	Inert Diluent Gas						1	2	3	Average
CLY-50-68	.089	.50	2.0	.50	--	--	4.7	1.50	He	9.089	30	1030-1050	11	17.3	17.0	18.0	17.4
CLY-52-68[1]	.089	.50			--	--	4.7	1.50	He	9.089	30	1030-1050		--	--	25.8	25.8
CLY-53-68[2]	.045	.25			--	--	6.5	.65	Ar	9.945	120	930-1000		14.8	11.1	12.3	12.7
CLY-54-68	.045		2.0		--	--				9.945		1130-1150		20.8	21.2	31.9	24.5
CLY-55-68	.045		4.0		1034	--			Ar	12.044		1180-1200		54.3	53.1	58.3	55.2
CLY-56-68	.144		6.8		4036.9	--			He	14.544		1180-1200		42.0	43.0	46.6	43.9
CLY-57-68	.144		6.8		127.9	3504			He	14.544		1180-1200		42.2	44.2	53.9	48.9
CLY-58-68	.045		4.0		374.9	392.4	6.5		Ar	12.44		1180-1200		110.3	104.0	82.9	99.0
CLY-59-68	.045		4.0		2186.4	--	6.0		Ar	11.445		1210-1230		21.0	29.3	27.9	26.1
CLY-60-68	.045		4.0		236.2	1641.6	6.0			11.445		1176-1196		22.5	24.0	28.7	25.1
CLY-61-68	.090		6.50		1911.6	2027.7	6.3			14.3		1225-1250		6.0	6.7	6.9	6.5
CLY-62-68					4161.4	--	6.0			14.0		1225-1250	11	40.8	25.4[3]	46.9	37.7
CLY-63-68[4]					1035.7	--						1225-1250	5	12.6	13.3	14.7	13.5
CLY-64-68[4]					1842.8	--						1225-1250	2	22.4	18.2	20.6	20.4
CLY-65-68[5]					2141.9	--						1225-1250	5	3.7	3.2	4.3	3.7
CLY-66-68	.090	.25	6.50	.50	7442.7	--	6.0	.65		14.0		1230	11	6.4	6.4	8.1	7.0
CLY-67-68	.045	.125	3.25	.25	4267.7	--	3.0	.325		7.0			11	6.1	5.4	4.7	5.4
CLY-68-68	.228	.25	6.50	.50	5765.1	--	6.0	.65		14.135			3	29.9	29.1	26.8	28.6
CLY-69-68	.090				3158.0	--				14.0			11	8.5	11.1	9.6	9.4
CLY-70-68					4270.7	--								15.3	18.1	9.1	14.2
CLY-71-68[7]					--	--								--	--	--	--
CLY-72-68		.25			1148.8	--	6.0							10.8	11.1	13.0	11.6
CLY-73-68		3.91			4627.4	--	3.0							11.5	10.2	11.3	11.0
CLY-74-68[6]		.25			8747.0	--	6.0						11	24.2	24.2	19.6	22.7
CLY-75-68		3.91			7258.5	--	3.0						3	16.2	14.4	20.0	16.8
CLY-76-68	.090	.25	6.50	.50	6974.3	--	6.0	.65		14.0			3	8.4	9.7	9.7	9.2
CLY-77-68	.045	.125	3.25	.25	4511.9	--	3.0	.325		7.0			3	3.6	4.1	5.2	4.3
CLY-78-68	.045	.125	3.25	.25	4432.9	--	3.0	.325	Ar	7.0	120	1230	11	4.5	4.3	6.4	5.0

OTHER RUN CONDITIONS AND OBSERVATIONS:

- Completed rotameter calibration for Ar inert gas prior to CLY-59-68
- Started using columbiuem substrates obtained for steel prior to CLY-59-68
- Dual thermocouple installed in furnace prior to CLY-61-68
- Acid etched and cleaned rotating reaction chamber used in CLY-62-68 through CLY-68-68
- Refilled $TiCl_4$ bubbler prior to CLY-66-68
- Installed new thermowell for reaction temperature prior to CLY-66-68
- Refilled $TiCl_4$ and $SiCl_4$ bubblers prior to CLY-72-68

FOOTNOTES

1. Weight gain on graphite substrates of 19.4 mg.
2. Weight gain on graphite substrates of 147.1 mg.
3. Slightly smaller size than other two substrates.
4. Different reactor geometry for gas feed inlets in runs CLY-63-68 and CLY-64-68.
5. Low liquid level detected in $TiCl_4$ bubbler.
6. Different reactor geometry for $SiCl_4$ and H_2 gas feed inlets.
7. Couldn't complete run because of emergency hydrogen purifier shutdown.

Table IX

REACTION TEMPERATURE EFFECT ON COATING DEPOSIT IN 930°C TO 1050°C RANGE

Run No.	Reaction Temperature (C°)	Coating Deposit (mg)	
		Graphite Substrates	Metal Substrates
CLY-49-68	930 - 950	4.8	2.3
CLY-39-68	980 - 1000	11.8	4.6
CLY-48-68	1030 - 1050	16.3	11.3

OTHER RUN CONDITIONS:

Slight variation in size of graphite and metal substrates. Deposition time of 30 minutes.

Complete data are listed in Table VII. Weight gain shown for metal substrate is average for three samples.

Subsequent parameter variation experiments were conducted at higher reaction temperatures. A comparison of two such experiments at identical process conditions except temperature is recorded in Table X to show that the increase in coating deposit with temperature occurred at reaction temperatures to 1150°C.

Prior to conducting the above experiments at higher reaction temperatures, a temperature range kit was obtained, installed and calibrated for use in the rotating reaction chamber equipment.

Maximum reaction temperature of 1230°C was achieved in experiments completed after temperature range kit installation.

Table X

REACTION TEMPERATURE EFFECT ON COATING DEPOSIT IN 980°C TO 1150°C RANGE

Run No.	Reaction Temperature (°C)	Coating Deposit (mg)	
		Graphite Substrates	Metal Substrates
CLY-53-68	980 - 1000	19.4	12.7
CLY-54-68	1130 - 1150	147.1	24.5

OTHER RUN CONDITIONS:

Slight variation in size of graphite and metal substrates. Deposition time of 120 minutes.

Complete data are listed in Table VIII. Weight gain shown for metal substrate is average for three samples.

2. Deposition Time

Initial parameter variation experiments disclosed that coating deposit increases with increase of deposition time. The deposition time effect on coating deposit was investigated for three reaction temperatures in the 950°C-1050°C range. The data is recorded in Table XI.

Subsequent parameter variation experiments utilized the deposition time (i. e., 120 min) providing the greater coating deposit.

3. Si, Ti and Cr Chloride Concentration

Increase in coating deposit with silicon, titanium and chromium chloride concentration increases was suggested in parameter variation experiments. The coating deposit increase was observed with quantitative silicon and titanium chloride concentrations and with qualitative chromium chloride concentration.

Table XI

DEPOSITION TIME EFFECT ON COATING DEPOSIT

Run Number	Reaction Temperature (°C)	Deposition Time (min)	Coating Deposit (mg)	
			Graphite Substrates	Metal Substrates
CLY-39-68	980 - 1000	30	11.8	4.6
CLY-41-68	980 - 1000	120	38.7	15.7
CLY-48-68	1030 - 1050	30	16.3	11.3
CLY-47-68	1030 - 1050	120	31.2	19.7
CLY-49-68	930 - 950	30	4.8	2.3
CLY-50-68	930 - 950	120	8.5	10.3

OTHER RUN CONDITIONS:

Slight variation in size of graphite and metal substrates. Complete data are listed in Table VII. Weight gain shown for metal substrate is average for three samples.

The initial parameter variation experiments were completed with variations in silicon, titanium and chromium chloride concentrations while holding other parameters constant. Silicon and titanium chloride concentrations were measured by helium flow through the respective bubblers. Chromium chloride concentration was only qualitative (i.e., chromium chloride concentration is increased with titanium chloride concentration). The run results shown in the last two runs in Table XII suggest coating deposit increase with silicon, titanium and chromium chloride concentration increase.

Table XII

Si, Ti AND Cr CHLORIDE CONCENTRATION EFFECT ON COATING DEPOSIT

Run Number	Si and Ti Chloride Concentrations* (He Flow Through Bubbler in ℓ/min)		H_2 Flow (ℓ/min)	Coating Deposit (mg)	
	$SiCl_4$ Bubbler	$TiCl_4$ Bubbler		Graphite Substrates	Metal Substrates
CLY-43-68	.045	1.0	6.7	3.2	4.0
CLY-39-68	.089	2.0	4.7	11.8	4.6
CLY-40-68	.145	4.0	4.7	16.7	5.6

OTHER RUN CONDITIONS:
Slight variation in shape and size of graphite and metal substrates. Deposition time is 30 minutes. Complete data are listed in Table VII. Weight gain shown for metal substrate is average for three samples.
*Qualitative Cr chloride concentration increases with $TiCl_4$ bubbler.

A chromium chloride generation chamber which would provide quantitative measurement of chromium chloride was being constructed while the initial parameter variation experiments were being made. The chromium chloride is generated by passing $TiCl_4$ (contained in inert diluent gas passed through the $TiCl_4$ bubbler) over solid Cr chips according to representative reaction.

$$2TiCl_4 + Cr \xrightarrow{T} 2TiCl_3 + CrCl_2$$

Quantative measurements with the generation chamber supported the qualitative chromium chloride concentration increase with $TiCl_4$ bubbler (i.e., $TiCl_4$ bubbler flows of 3.25 and 6.5 ℓ/min provided Cr chips weight losses of 4276.7 and 7448.7 mg).

Although run CLY-43-68 in Table XII was conducted at higher hydrogen flow, its respective silicon, titanium and chromium chloride concentrations are lower than the same respective chloride concentrations of the last two runs in the table (i.e., the last two runs have higher silicon, titanium and qualitative chromium chloride concentrations). Since the coating deposit of the last two runs was higher, the CLY-43-68 run further indicated coating rate increase with silicon, titanium and chromium chloride concentrations.

Two cursory runs were conducted with an increase of titanium and chromium choloride concentrations with other parameters constant. Results, listed in Table XIII, for these runs suggested increase of coating deposit with titanium and chromium chloride concentration increases.

Subsequent parameter variation experiments were conducted with higher titanium and chromium chloride concentrations.

Table XIII

Ti AND Cr CHLORIDE CONCENTRATION EFFECT ON COATING DEPOSIT

Run Number	Ti Chloride Concentrations* (He Flow Through $TiCl_4$ Bubbler in ℓ/min)	Coating Deposit (mg)	
		Graphite Substrates	Metal Substrate
CLY-43-68	1.0	3.3	4.0
CLY-45-68	2.0	6.3	5.0

OTHER RUN CONDITIONS:

Slight variation in graphite substrate samples. Fresh graphite samples used in run CLY-43-68. Graphite samples from previous run used in run CLY-45-68. Weight gain for metal substrate is average for three samples.

*Qualitative Cr chloride concentration increases with $TiCl_4$ bubbler.

4. H_2 Concentration

Determination of hydrogen concentration effect on coating deposit was made in subsequent cursory parameter variation experiment. With hydrogen concentration measured by hydrogen flow rate, the summary tabulation in Table XIV suggested the coating deposit increased with hydrogen concentration increase.

It should be noted that the cursory determination applies at two reaction chamber rotation speeds (3 and 11 rpm) and constant flow rate (14 ℓ/min).

5. Rotation Speed

Investigation of rotation speed effect on coating deposit was made at two levels of flow rate and hydrogen concentration. The results indicated some coating deposit increase as rotation speed increase from three to eleven rpm. The data from these experiments, listed in Table XV, summarizes the results.

The rotation speed effect was observed at two flow rates, 14 and 7 ℓ/min, and hydrogen concentrations of 3 and 6 ℓ/min. The higher rotation speed of eleven rpm which resulted in greater weight gain was used in most parameter variation experiments.

6. Flow Rate

Parameter experiments made with flow rate variations suggested increase of coating deposit with increase in flow rate. The data in Table XVI illustrated coating deposit increase with flow rate increase during experiments. These experiments were conducted with the flow rate doubled, including hydrogen concentration, and flow rate doubled with hydrogen concentration constant (last two runs).

Table XIV

H_2 CONCENTRATION EFFECT ON COATING DEPOSIT

Run Number	Rotation Speed (rpm)	Flow Rate (ℓ/min)	H_2 Concentration: H_2 Flow Rate (ℓ/min)	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-72-68	11	14	6	11.6
CLY-73-68	11	14	3	11.0
CLY-76-68	3	14	6	16.8
CLY-75-68	3	14	3	9.2

OTHER RUN CONDITIONS

Some flow difficulties experienced with $SiCl_4$ and $TiCl_4$ bubblers in first part of CLY-76-68 run. Complete data are listed in Table VIII.

Table XV

ROTATION SPEED EFFECT ON COATING DEPOSIT

Run Number	Rotation Speed (rpm)	Flow Rate (ℓ/min)	H_2 Concentration: H_2 Flow Rate (ℓ/min)	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-72-68	11	14	6	11.6
CLY-76-68	3	14	6	9.2
CLY-78-68	11	7	3	5.0
CLY-77-68	3	7	3	4.3

Other run conditions and complete data are listed in Table VIII.

Table XVI

FLOW RATE EFFECT ON COATING DEPOSIT

Run Number	Rotation Speed (rpm)	Flow Rate (ℓ/min)	H_2 Concentration: H_2 Flow Rate (ℓ/min)	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-66-68	11	14	6	7.0
CLY-67-68	11	7	3	5.4
CLY-73-68	11	14	3	11.0
CLY-78-68	11	7	3	5.0

OTHER RUN CONDITIONS

- Run CLY-66-68 was conducted at twice the flow rate of run CLY-67-68 on all components including H_2 Concentration.
- Run CLY-73-68 was conducted at twice the flow rate of run CLY-78-68 while holding H_2Concentration constant.
- Complete data are listed in Table VIII.

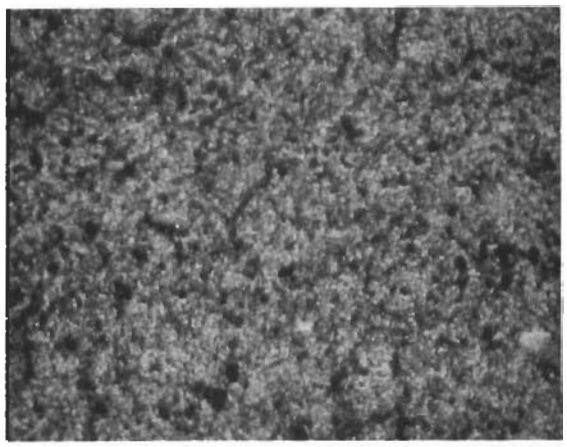
7. Coating Evaluation

Cursory electron microprobe analysis was completed on several samples prepared in parameter variation experiments. The analysis indicated that chromium, titanium and silicon depositions were achieved in the experiments since the coating deposit contained these respective components.

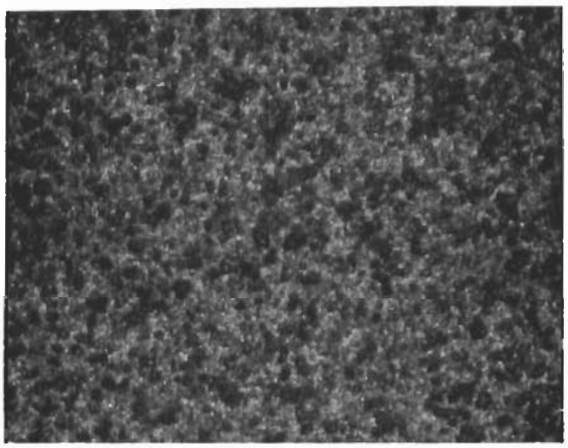
Microphotographs showing surface of coatings deposited in parameter variation experiments are presented in Figure 8.

Microphotographs of mounted sample cross sections are given in Figure 9 to show the substrate and coating deposit.

(a) CLY-68-68



(b) CLY-72-68



(c) CLY-73-68

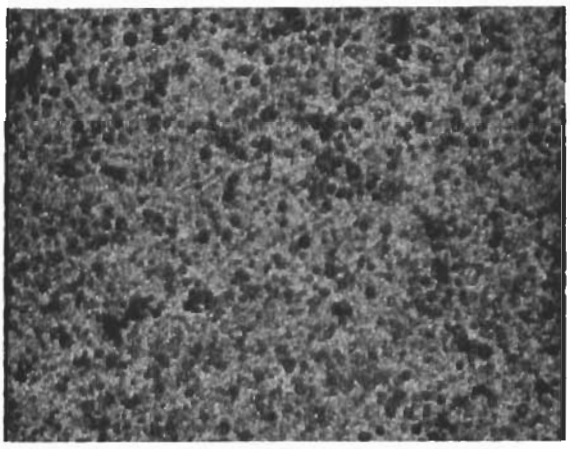
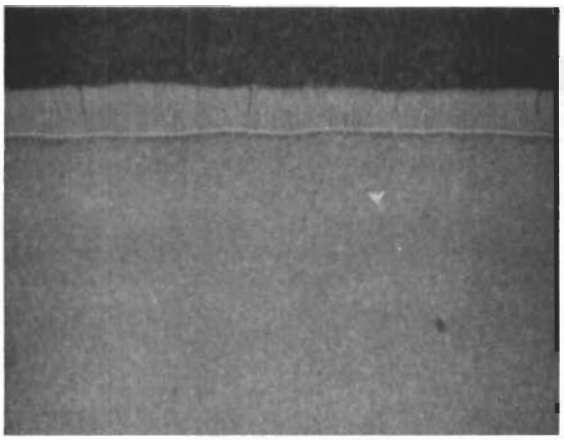
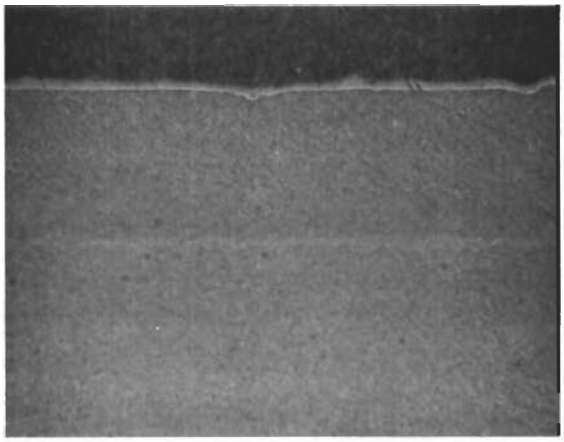


Figure 8. Parameter Variation: Microphotographs Showing Coating Surface (250X)

(a) CLY-68-68



(b) CLY-72-68



(c) CLY-73-68

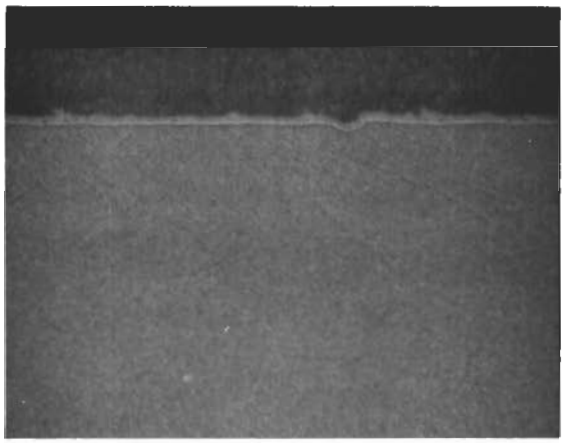


Figure 9. Parameter Variation: Microphotographs of Cross Section Showing Coating and Substrate (500X)

SECTION V

OPTIMIZATION AND PRODUCTION DEMONSTRATION STUDIES

A. OPTIMIZE PARAMETERS

Previous parameter variation disclosures were utilized as the basis for optimize parameter runs with the manufacturing processing equipment. For optimize parameters, demonstrated coating rate increases comprised the key results. Coating rate increases for the trideposition reaction were achieved with the following important variables: gas feed geometry; reaction temperature; silicon chloride concentration; flow rate; dual chamber prereduction of titanium tetrachloride; titanium tetrachloride concentration; hydrogen concentration and argon dilution level of the hydrogen gas feed. Coating rates in the runs were the highest to date with the equipment. Additionally key findings included first and second statistical series results for use in the next program activity of analysis involving statistical regression and factorial variance analyses.

1. Gas Feed Geometry Study

Prior to conducting the experiments involved to optimize parameter, several gas feed geometries were studied. This included cursory gas mixing experiments which allowed observation of gas mixing patterns. This also involved study of different reaction chamber configurations.

The gas feed geometries studied are shown in Figure 10. Results indicated appreciable difference between coating deposits obtained by use of each of the gas feed geometries.

The reaction chambers used are shown in Figure 11.

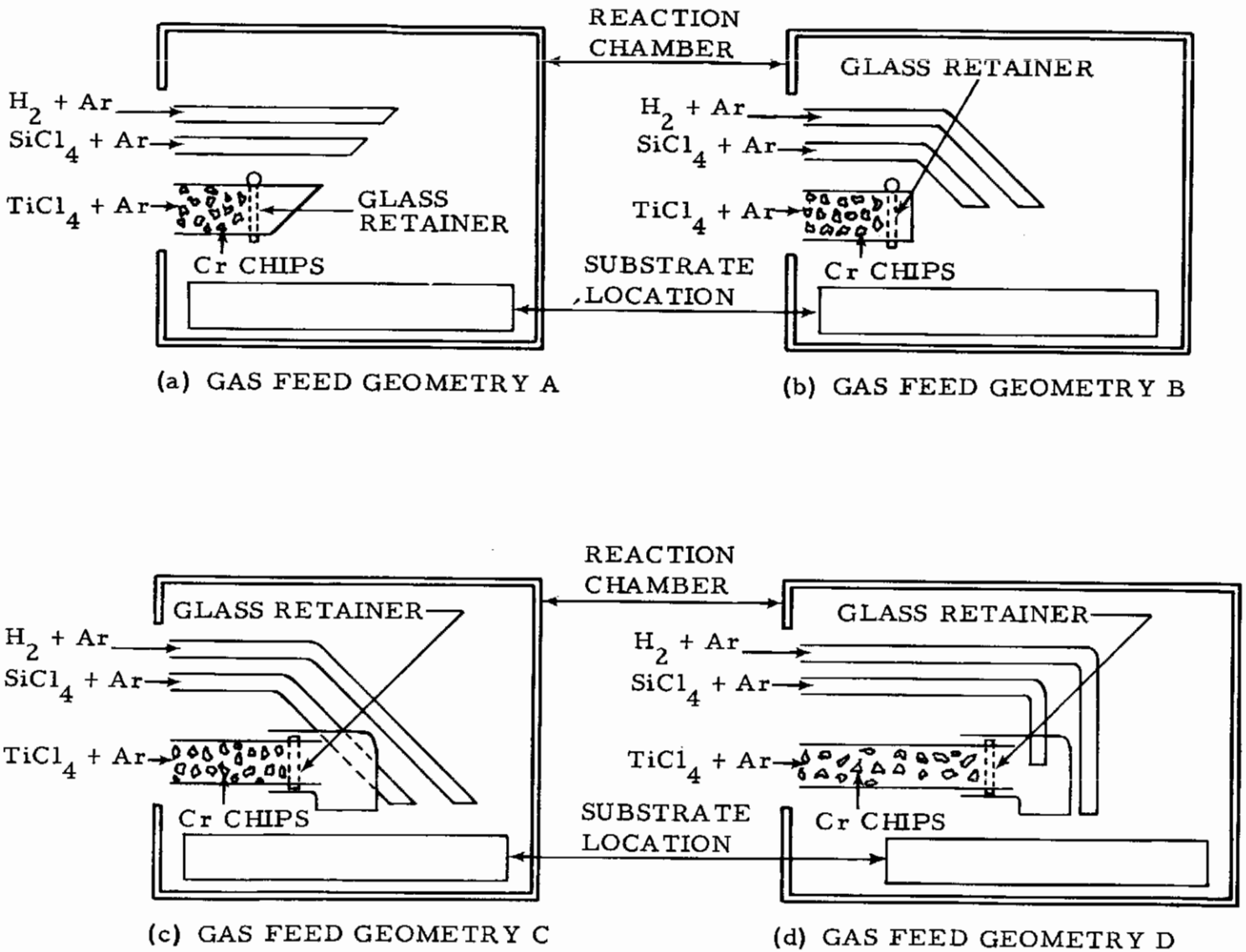
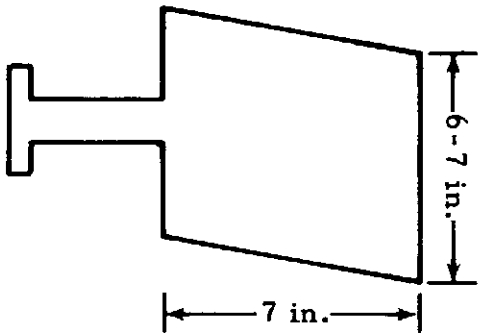
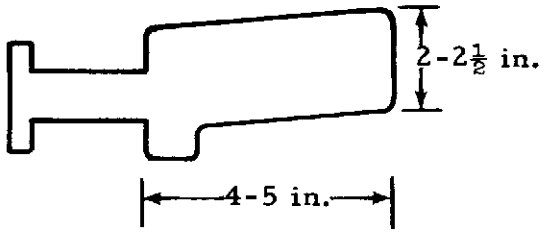


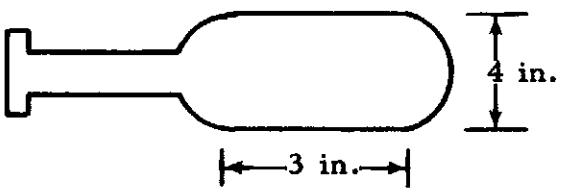
Figure 10. Optimize Parameters: Gas Feed Geometries for Introducing Gas Feed Reactants in Reaction Chamber



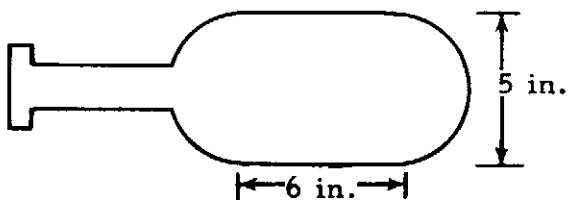
(a) Reaction Chamber A
(7-in. quartz rocking bottle)



(b) Reaction Chamber B
(special reaction chamber)



(c) Reaction Chamber c
(small reaction chamber)



(d) Reaction Chamber D

Figure 11. Optimize Parameters: Reaction Chambers Used for CVD Coating with Trideposition Reaction

Prior to conducting the initial experiments with different gas feed geometries, several cursory experiments were made to observe gas mixing inside the reaction chamber. The experiments disclosed: (a) the reaction of water vapor and $TiCl_4$ provided a white reaction product which permitted observation of the gas mixing process, (b) addition of $SiCl_4$ did not visibly alter observed gas mixing and (c) increase of diluant gas carrying water vapor to maximum flow achievable with the equipment did not alter the observed gas mixing. The observed gas mixing in the cursory experiments indicated some variation of the visible white reaction product with region inside the reaction chamber. Also, the cursory experiments indicated gas mixing could be altered with the gas feed geometry used to introduce the reactants into the reaction chamber.

The initial optimization parameter experiments with different gas feed geometries were conducted with the 7-in. quartz rocking bottle as the reaction chamber. The 7-in. quartz rocking bottle (see Figure 11a) was used in preliminary and parameter variation runs discussed earlier. Coating deposit results for two initial experiments conducted at identical conditions, except gas feed geometry, in Table XVII revealed that coating deposit was increased with gas feed geometry change (i. e., greater coating deposit was achieved with gas feed geometry B than with gas feed geometry A).

The data listed in Table XVII indicates coating deposit using gas feed geometry B was almost double that obtained using gas feed geometry A to introduce the reactants into the reaction chamber. As a result of this increase achieved with change of gas feed geometry, other gas feed geometries were investigated.

Results for other gas feed geometries investigated are tabulated in Table XVIII for runs with a constant flow rate and silicon chloride concentration.

Table XVII

GAS FEED GEOMETRY EFFECT ON COATING DEPOSIT WITH QUARTZ ROCKING BOTTLE REACTION CHAMBER

Run Number	Gas Feed Geometry	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-72-68		11.6
CLY-85-68		21.7
Other Run Conditions: Other process conditions are given in accompanying data table in Appendices.		

Table XVIII

GAS FEED GEOMETRY EFFECT ON COATING DEPOSIT WITH SMALL REACTION CHAMBER

Run Number	Gas Feed Geometry	Flow Rate Via Measured Gas Feed Flow (ℓ/min)	Silicon Chloride Concentration Via $SiCl_4$ Bubbler (Ar, ℓ/min)	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-88-68	B	3.863	.0225	14.2
CLY-89-68	C	3.863	.0225	27.7
CLY-92-68	D	3.863	.0225	36.5
Other Run Conditions: Other process conditions are given in accompanying data table in Appendices.				

The data shown in Table XVIII indicated that greatest coating deposit was achieved with gas feed geometry D (i.e., the greatest coating deposit of 36.5-mg substrate weight gain was achieved using gas feed geometry D for introducing the reactants into the reaction chamber).

It was recognized that the other parameters such as flow rate and silicon chloride concentration influence the coating deposit obtained while using any specific gas feed geometry. However, since gas feed geometry D provided the greatest coating deposit of all gas feed geometries studied, it was selected for use in the first statistical series of experiments for optimization.

2. First Statistical Series

For optimization, the first statistical series of experiments were conducted for determining the effect of three of the independent variables — reaction temperature, silicon chloride concentration and flow rate — on the coating rate for two levels of each of the dependent variables. Three other independent variables — titanium chloride concentration, hydrogen concentration and argon dilution of hydrogen gas feed — were held constant for the series. The results, including graphical plots with positive slope curves for coating rate variation, indicated that coating rate is increased in the independent variable ranges studied.

The experimental plan for the first statistical series is given in Table XIX. The general variable range selected for the series was based on results from previous preliminary runs, parameter variation experiments and gas feed geometry study. The results for the coating rate at each level of the independent variables of temperature, concentration and flow are presented in the last column of Table XIX.

Effect of reaction temperature on coating rate is graphically illustrated in Figure 12. The curves were constructed for comparing data points of constant flow rate and silicon chloride concentration. The four curves with positive slopes indicated that the coating rate is increased with reaction temperature for the variable range studied.

Table XIX

OPTIMIZE PARAMETERS: FIRST STATISTICAL SERIES OF EXPERIMENTS

Run No.	x_1	x_2	x_3	y
1	-1	1	1	0.61
2	-1	-1	-1	0.37
3	1	-1	-1	0.39
4	-1	-1	1	0.47
5	1	1	1	0.69
6	1	1	-1	0.59
7	1	-1	1	0.59
8	-1	1	-1	0.37

Variable	Description	-1	1
x_1	Reaction Temperature (^oC)	1015	1115
x_2	Silicon Chloride Concentration via $SiCl_4$ Bubbler (Ar, ℓ/min)	.0225	.045
x_3	Flow Rate via Measured Gas Feed Flow (ℓ/min)	7.73	11.59
y	Coating Rate via Average Weight Gain Rate Per Substrate (mg/min)		

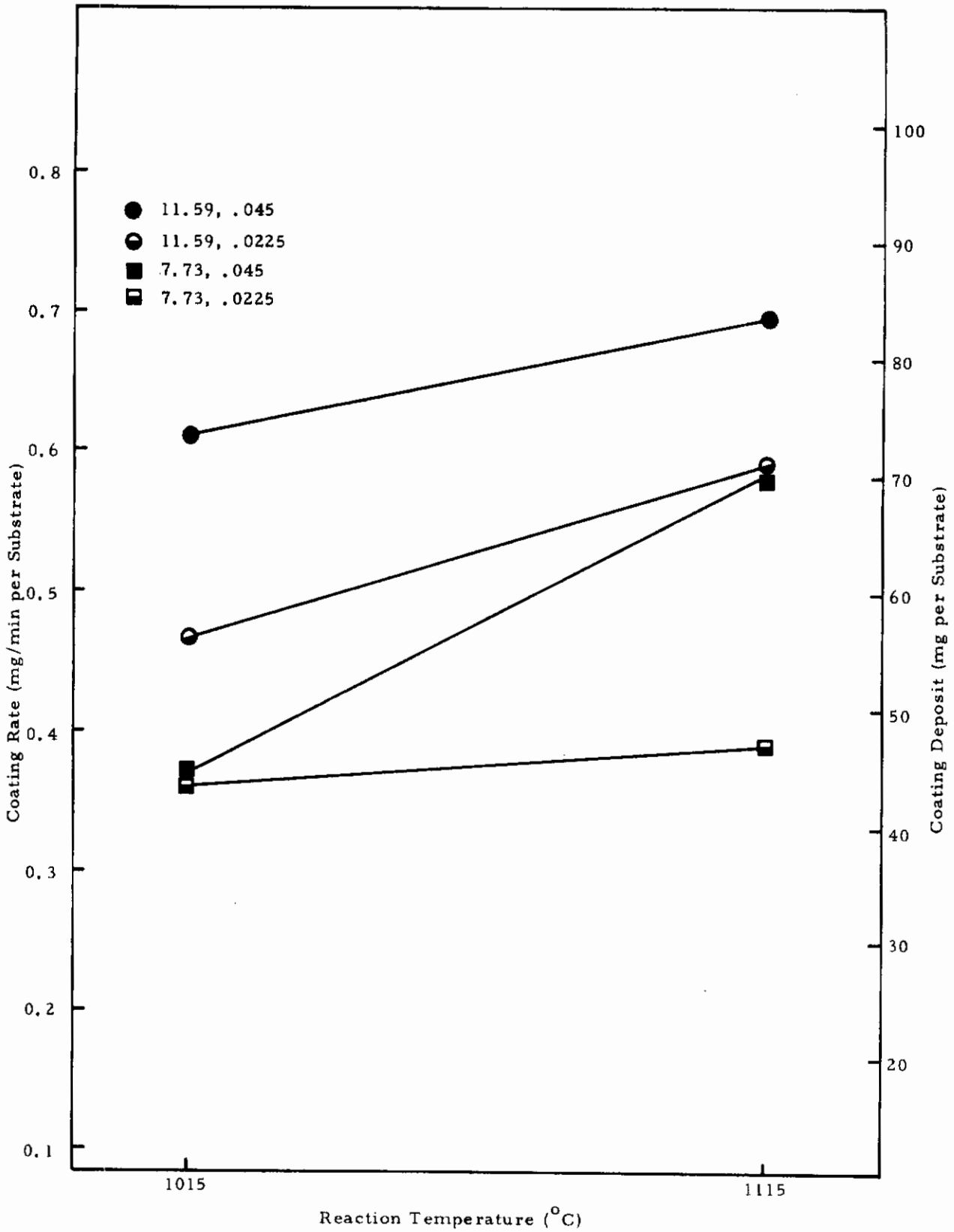


Figure 12. Optimize Parameters: Effect of Reaction Temperature on Coating Rate in First Statistical Series

Figure 13 illustrates effect of silicon chloride concentrations on coating rate. The effect shown was with constant flow rate and reaction temperature. The bottom curve in Figure 13 show little effect of silicon chloride concentration on coating rate. The remaining three curves, which have more positive slopes, indicated higher coating rate increase with silicon chloride concentration.

The effect of flow rate on coating rate is illustrated in Figure 14 at constant reaction temperature and silicon chloride concentration. Each curve constructed in Figure 14 has a positive slope and indicated the coating rate increase with flow rate for the variable range tested.

3. Argon Dilution of Hydrogen Gas Feed

While conducting the first statistical series, an exploratory run was conducted in which the hydrogen gas feed was highly diluted with argon. After completion of the first statistical series, an inspection of the coating deposit achieved in the series revealed that this exploratory run provided the highest coating deposit. Confirmation of this finding was made by repeating the exploratory run and obtaining similar high coating deposit as shown by last two runs of Table XX. The summary tabulation in Table XX illustrated the appreciable coating deposit increase due to the high level of argon dilution of hydrogen gas feed.

The effect of dual chamber prereduction of titanium tetrachloride was investigated in several runs after completion of first statistical and exploratory runs. Dual chamber prereduction is the dual reduction achieved by flowing titanium tetrachloride feed through a dual chamber containing the solid Ti and Cr chips to permit the following representative reactions:

$$3TiCl_4 + Ti\ (\text{solid chips}) \xrightarrow{T} 4TiCl_3 \qquad (1)$$

$$2TiCl_4 + Cr\ (\text{solid chips}) \xrightarrow{T} 2TiCl_3 + CrCl_2 \qquad (2)$$

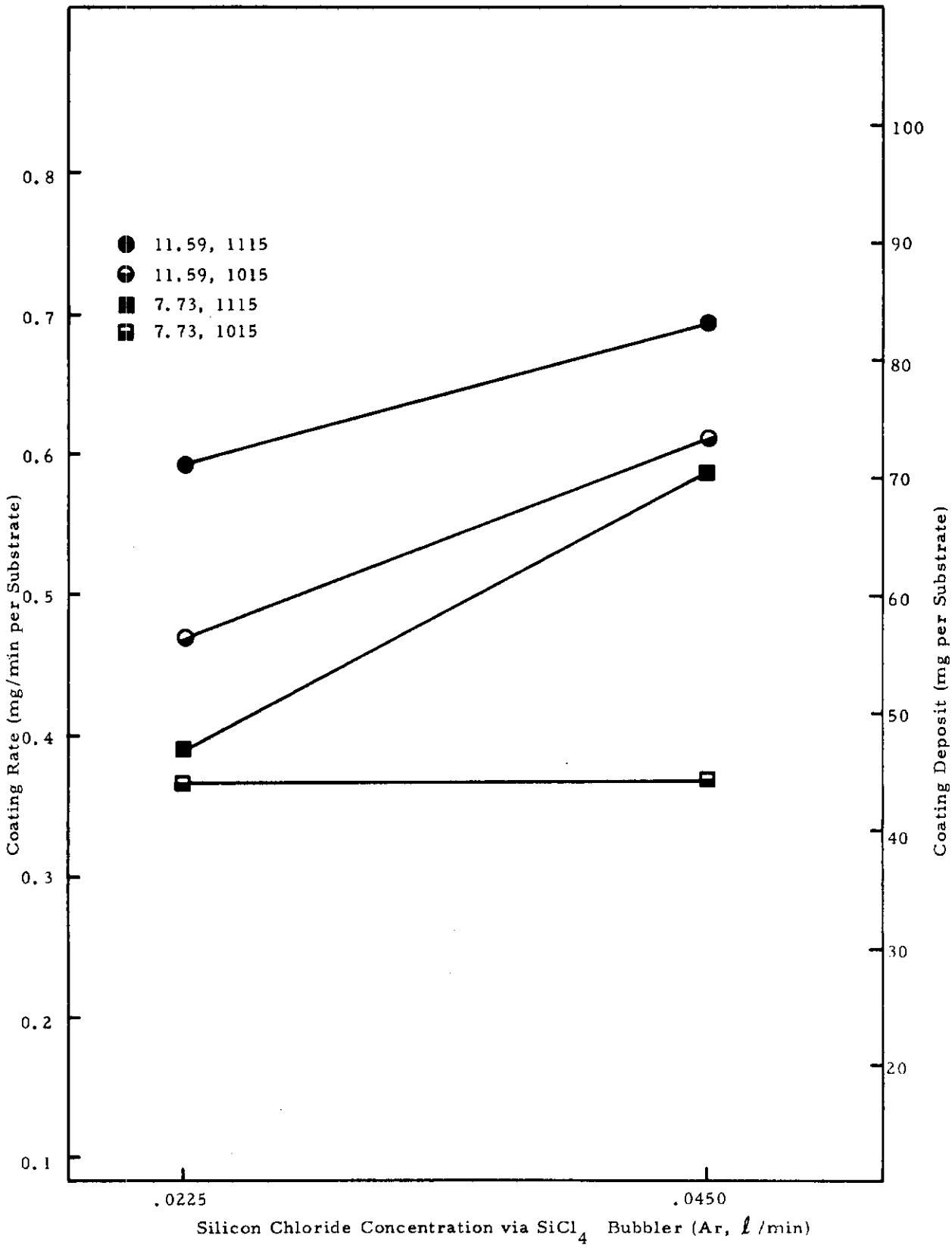


Figure 13. Optimize Parameters: Effect of Silicon Chloride Concentration on Coating Rate in First Statistical Series

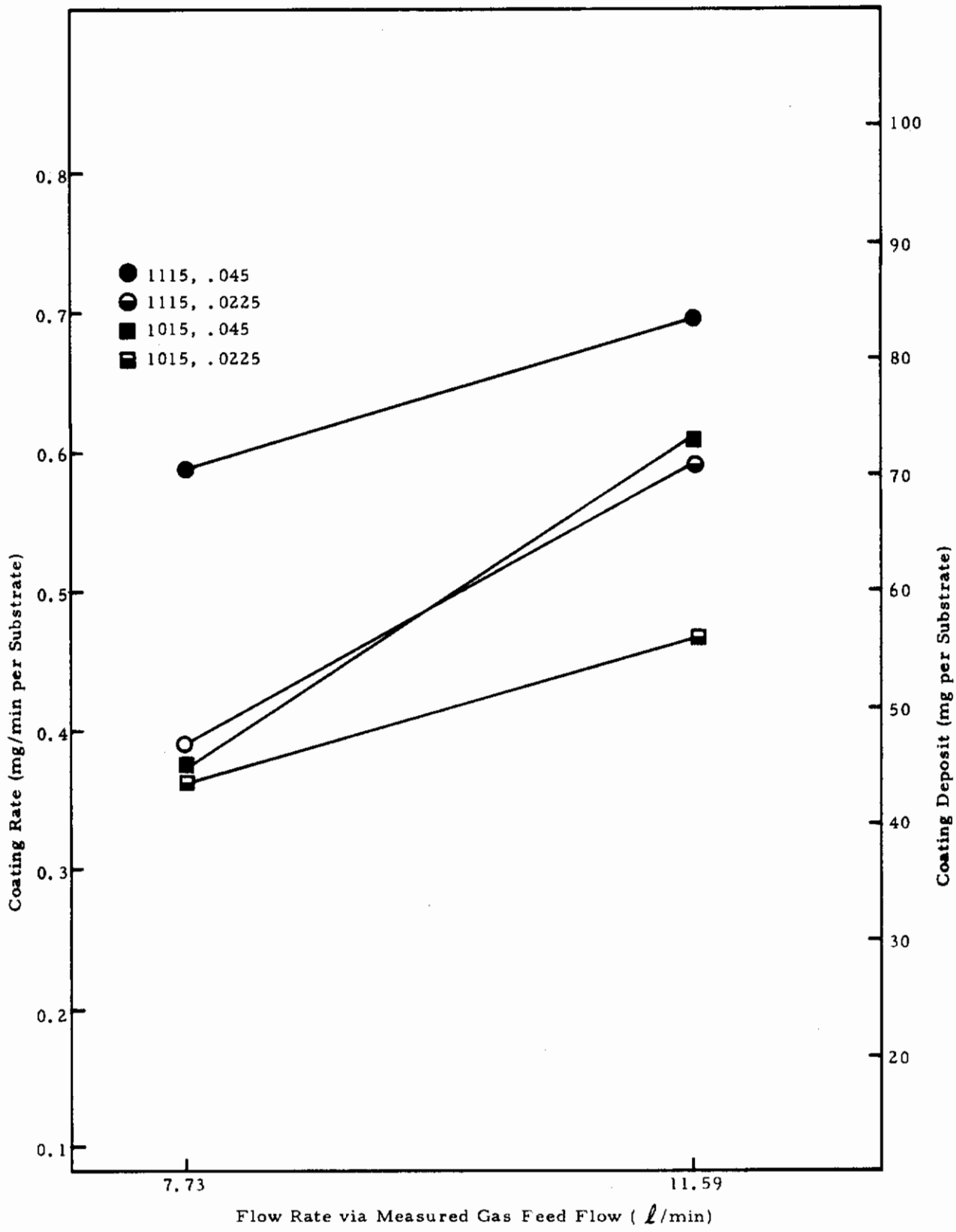


Figure 14. Optimize Parameters: Effect of Flow Rate on Coating Rate in First Statistical Series

Table XX

EFFECT OF ARGON DILUTION OF HYDROGEN GAS FEED ON COATING DEPOSIT

Run Number	Argon Dilution of Hydrogen Gas Feed	Prereduction of Titanium Tetrachloride	Coating Deposit: Avg. Substrate Weignt Gain (mg)
CLY-96-68	Low	Single Chamber	44.3
CLY-98-68	High	Single Chamber	96.6
CLY-107-68	High	Single Chamber	95.5
Other Run Conditions: Hydrogen gas feed of 3 ℓ/min. The "low" and "high" expressions used in argon dilution of hydrogen gas feed are 0.46 and 4.33 ℓ/min.			

It should be noted that the above reactions are not precise representatives of chemistry since other titanium and chromium chlorides are known to exist. The shown reactions are intedned only to represent dual chamber prereduction of titanium tetrachloride.

The investigation indicated the coating deposit achieved during dual chamber prereduction was increased over that achieved with single chamber prereduction with only Cr chips as shown by data in Table XXI.

Table XXI

EFFECT OF DUAL CHAMBER PREREDUCTION OF TITANIUM TETRACHLORIDE ON COATING DEPOSIT

Run Number	Prereduction of Titanium Tetrachloride	Coating Deposit: Avg. Substrate Weight Gain (mg)
CLY-107-68	Single Chamber	95.5
CLY-108-68	Dual Chamber	112.9
Other Run Conditions: Both runs conducted with high argon dilution of hydrogen gas feed.		

In addition to coating deposit increase indicated in Table XXI, microscopic inspection of the single and dual chamber samples revealed that the coating deposit surface of the dual chamber sample was smoother (i.e., less nodule projections) than the single chamber sample. This was confirmed by comparison made of additional deposit surfaces prepared by both single and dual chamber prereductions. As a result of these findings, the dual chamber prereduction of titanium tetrachloride was selected for use in the second statistical series of experiments.

4. Second Statistical Series with Dual Chamber Prereduction

The second statistical series of experiments to optimize parameters was designed to determine effect of the three independent variables which were held constant in first statistical series (i.e., titanium tetrachloride concentration, hydrogen concentration and argon dilution of hydrogen gas feed). The completed series, at two levels for each independent variable are presented in Table XXII. For the series, the independent variables studied in the first statistical series were maintained at the constant optimum level as determined by first statistical series results.

The second statistical series resulted in coating rate increases; which, in general, surpassed coating rates achieved in the first statistical series. Graphical plots are shown in Figures 15, 16 and 17. The positive slope curves, illustrating coating rate increase, indicated that argon dilution of the hydrogen gas feed influences coating rate more than titanium and hydrogen concentrations.

The effect of titanium chloride concentration on coating rate is depicted graphically in Figure 15. The effect depicted by each curve in the figure was obtained while holding hydrogen concentration and argon dilution of hydrogen gas feed constant. The positive slope curves in the figure indicate that there is a coating rate increase due to titanium chloride concentration.

Table XXII

OPTIMIZE PARAMETERS: SECOND STATISTICAL SERIES OF EXPERIMENTS WITH DUAL CHAMBER PREREDUCTION OF TITANIUM TETRACHLORIDE

Run No.	X_4	X_5	X_6	Y
1	-1	1	1	0.619
2	-1	-1	-1	0.469
3	1	-1	-1	0.535
4	-1	-1	1	0.576
5	1	1	1	0.831
6	1	1	-1	0.567
7	1	-1	1	0.624
8	-1	1	-1	0.510

Variable	Description	-1	1
X_4	Titanium Chloride Concentration via $TiCl_4$ Bubbler (Ar, ℓ/min)	3	6
X_5	Hydrogen Concentration via H_2 Flow (ℓ/min)	3	6
X_6	Argon Dilution of Hydrogen Gas Feed (ℓ/min)	3	6
Y	Coating Rate via Average Weight Gain Rate Per Substrate (mg/min)	—	—

Figure 16 shows effect of hydrogen concentration on coating rate. The effect depicted by curves was obtained while holding the titanium chloride concentration and argon dilution of hydrogen gas feed constant. The curves suggest a small increase in coating rate with hydrogen concentration.

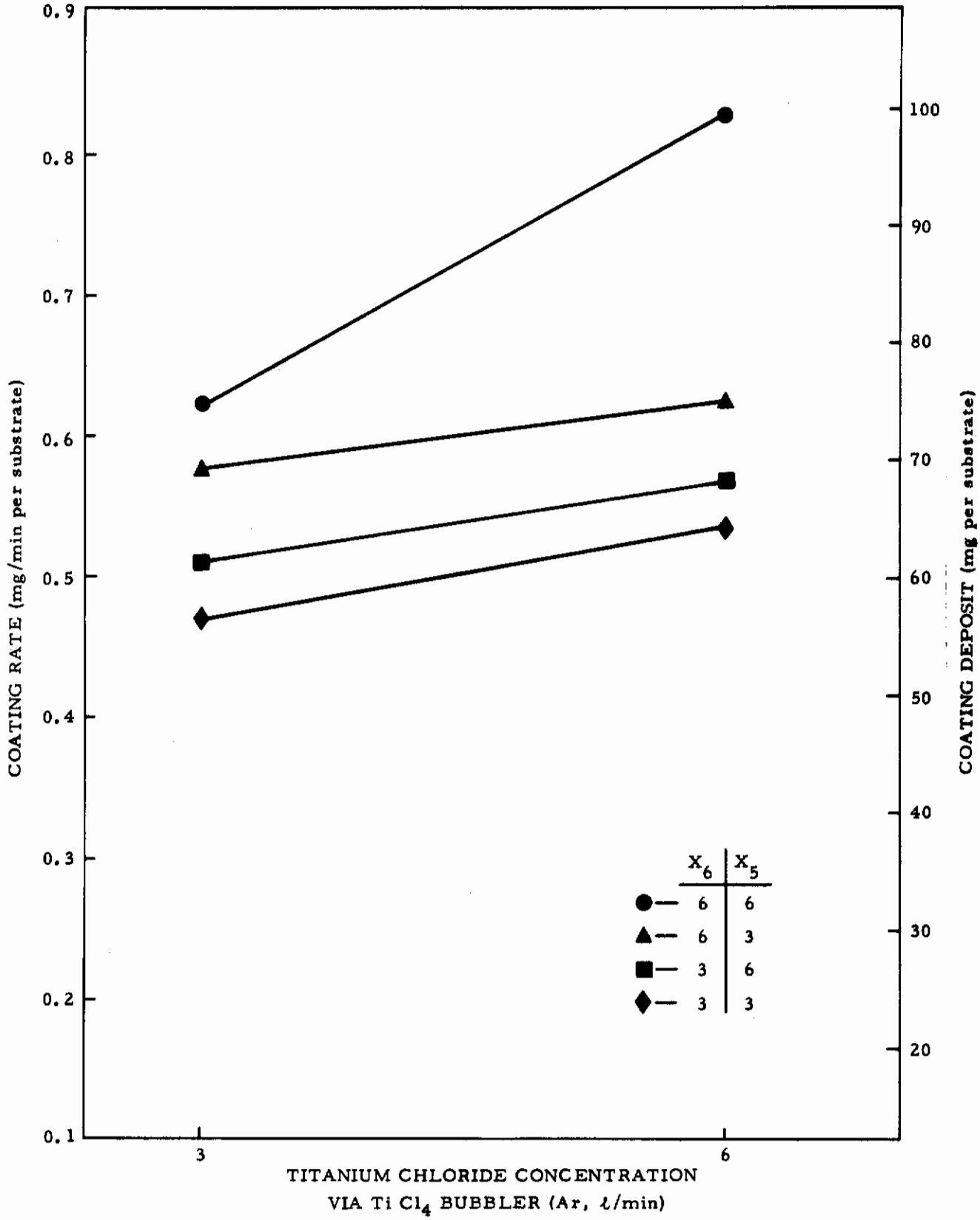


Figure 15. Optimize Parameters: Effect of Titanium Chloride Concentrations on Coating Rate in Second Statistical Series

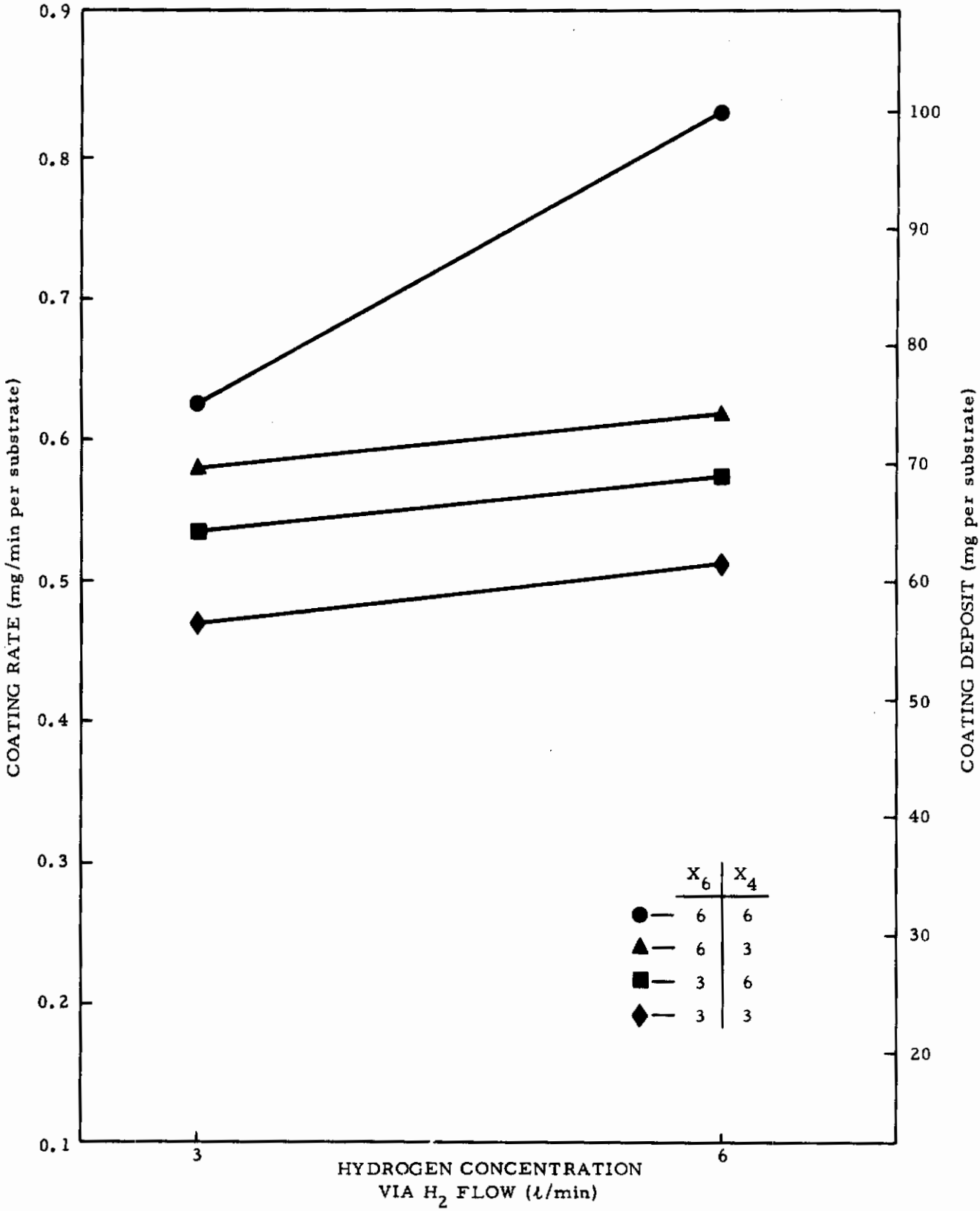


Figure 16. Optimize Parameters: Effect of Hydrogen Concentration on Coating Rate in Second Statistical Series

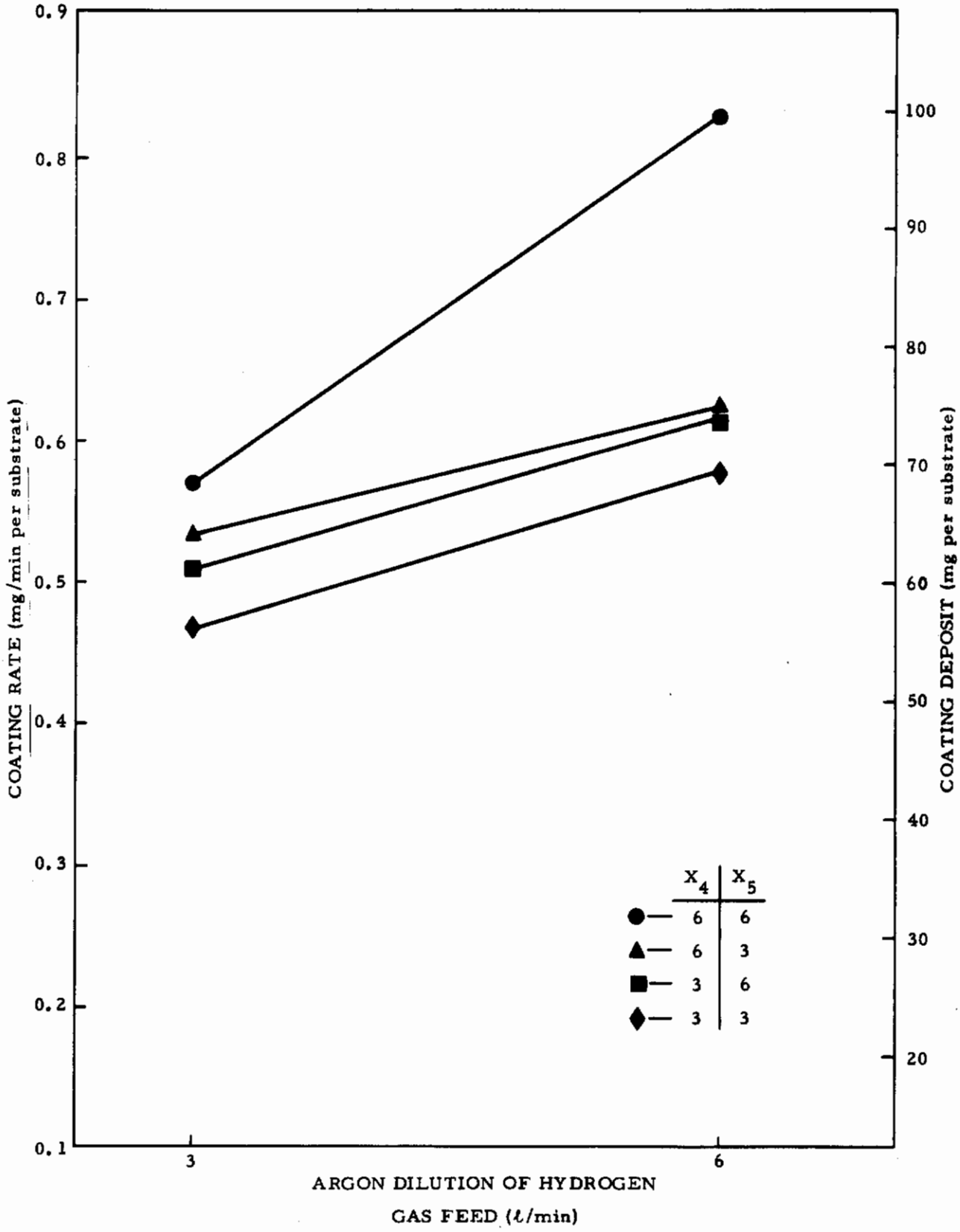


Figure 17. Optimize Parameters: Effect of Argon Dilution of Hydrogen Gas Feed on Coating Rate in Second Statistical Series

The effect of argon dilution of hydrogen gas feed on coating rate is indicated by Figure 17. The effect depicted by the curve was obtained while holding the titanium chloride and hydrogen concentrations constant. The positive sloped curves illustrate an increase in coating due to argon dilution of hydrogen gas feed. It is noted that these positive slope curves have higher slopes than the corresponding positive slopes of the other two independent parameters. This suggests that argon dilution of the hydrogen gas feed has more effect on coating rate than titanium chloride concentration and hydrogen concentration for the range of variables studied.

The above suggestion tends to confirm earlier findings made in the exploratory runs to optimize parameters: argon dilution of hydrogen gas feed is an independent parameter providing appreciable increase in coating deposit.

B. ANALYSIS

Regression and factorial variance analyses of the first and second statistical series results were performed to provide information for reference to use in subsequent program activities. Multiple regression analysis with T-test indicated that flow rate and argon dilution of hydrogen gas feed appreciably influence coating rate. For F-test, factorial analysis of variance confirmed the indicated coating rate influence at 95% confidence level. The factorial analysis additionally disclosed that variation was not attributable to first order interactions. On basis of these findings, flow rate and argon dilution were maintained at high levels in the next experiments (deposit phase runs) with the rotating reaction chamber equipment.

1. Regression Analysis

Multiple regression analysis of the first statistical series results was made for coating rate as a function of the three independent variables: reaction temperature, silicon chloride concentration and flow rate. The regression analysis results are listed in Table XXIII. The computed T-value for each variable (X_1 = 2.99, X_2 = 2.99 and X_3 = 4.35) exceeds the T-value (2.36) for 95 percent confidence level. This indicates the X_1, X_2, and X_3 influence on coating rate. On the basis of T-test, the X_3 variable has the greatest effect.

Table XXIII

ANALYSIS: MULTIPLE REGRESSION ANALYSIS OF FIRST STATISTICAL SERIES

Variable	Regression Coefficient	T Value	T for 95% Level
X_1 (Reaction Temperature)	1.1×10^{-3}	2.99	2.36
X_2 (Silicon Chloride Concentration)	4.89	2.99	2.36
X_3 (Flow Rate)	4.15×10^{-2}	4.35	2.36
Intercept: -1.22691			
Standard Error of Estimate: 0.05196			
Multiple Correlation Coefficient: 0.94983			

Multiple regression analysis results are listed in Table XXIV for the second statistical series. The tabulated regression analysis results apply for coating rate as a function of the three independent variables: titanium chloride concentration, hydrogen concentration and argon dilution of hydrogen gas feed. The computed T-values for X_4 and X_6 (i.e., $X_4 = 2.37$ and $X_6 = 3.53$) exceed the T-value for 95 percent confidence level (i.e., $T = 2.36$), and indicate a significant effect by X_4 and X_6 on coating rate. The smaller value, 2.00, for X_5 indicates less influence. On basis of T-test, the X_6 variable, argon dilution of hydrogen gas feed, has the greatest effect on coating rate for the variable range studied in the second statistical series.

Table XXIV

ANALYSIS: MULTIPLE REGRESSION ANALYSIS OF SECOND STATISTICAL SERIES

Variable	Regression Coefficient	T Value	T for 95% Level
X_4 (Titanium Chloride Concentration	3.19×10^{-2}	2.37	2.36
X_5 (Hydrogen Concentration)	2.69×10^{-2}	2.00	2.36
X_6 (Argon Dilution of Hydrogen Gas Feed)	4.74×10^{-2}	3.53	2.36
Intercept: 0.11325			
Standard Error of Estimate: 0.05702			
Multiple Correlation Coefficient: 0.92017			

2. Factorial Analysis of Variance

Factorial analysis was completed for first statistical series using the Yates' method, as discussed by Davies;[1] for calculation of effects and mean squares. The results for analysis of variance, including F-value calculated from experimental data and F-value required for 95 percent confidence level, are presented in Table XXV.

In Table XXV, the columns for source of variation and F-values are utilized. The main effects in source of variation for rows 1, 2 and 3 corresponds to variations in the three independent variables X_1, X_2 and X_3. The other source of variation (interactions) corresponds to interactions of the respective independent variables. It is noted that F-values of main effects of 1, 2 and 3 exceed the F-values of interactions (i.e., $X_1 = 8.97$, $X_2 = 8.97$ and $X_3 = 19.0$ vs 1.18, 0.074 and 0.073 respectively). These higher F-values indicate that the coating rate variation is attributable to the three independent variables studied in first statistical series, and is not attributable to first order interactions of the variables. Furthermore, on basis of F-test at 95 percent confidence level, the highest F-value of 19 for X_3 indicates that flow rate has the greatest influence on coating rate for variable range studied. Flow rate in the second statistical series exceeded flow rate in first statistical series on basis of this finding.

Factorial analysis of variance for the second statistical series is presented in Table XXVI. In the table, with first column for source of variation, the main effects in source of variation column for 4, 5 and 6 corresponds to variations in the three independent variables X_4, X_5 and X_6 which are titanium chloride concentration, hydrogen concentration and argon dilution of hydrogen gas feed respectively.

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[1] Davies, O. L., Editor, The Design and Analysis of Industrial Experiments, p. 264, Hafner Publishing Company, New York, New York, 1963.

Table XXV

ANALYSIS: FACTORIAL ANALYSIS OF VARIANCE FOR FIRST STATISTICAL SERIES

Source of Variance	Degrees of Freedom	Sums of Squares	F Value*	F Required**
Main Effects				
1	1	2.42×10^{-2}	8.97	7.71
2	1	2.42×10^{-2}	8.97	7.71
3	1	5.12×10^{-2}	19.0	7.71
Interactions				
12	1	0.32×10^{-2}	1.18	7.71
13	1	0.020×10^{-2}	0.074	7.71
23	1	0.020×10^{-2}	0.073	7.71
123	1	0.720×10^{-2}	- - -	- - -
TOTAL	7	11.041×10^{-2}	- - -	- - -

NUMBER OF VARIABLES: 3

NUMBER OF REPLICATES: 1

Variance	Variance Identification	No. of Levels
1	Reaction Temperature	2
2	Silicon Chloride Concentration	2
3	Flow Rate	2

GRAND MEAN: 0.51

*Based on combining all four interactions

**95 percent confidence level

Table XXVI

ANALYSIS: FACTORIAL ANALYSIS OF VARIANCE FOR SECOND STATISTICAL SERIES

Source of Variance	Degrees of Freedom	Sums of Squares	F Value *	F Required **	F Required ***
Main Effects					
4	1	1.83×10^{-2}	5.64	4.54	7.71
5	1	1.30×10^{-2}	4.01	4.54	7.71
6	1	4.05×10^{-2}	12.4	4.54	7.71
Interactions					
45	1	0.301×10^{-2}	0.924	4.54	7.71
46	1	0.234×10^{-2}	0.722	4.54	7.71
56	1	0.392×10^{-2}	1.20	4.54	7.71
456	1	0.373×10^{-2}	---	---	---
TOTAL	7	8.485×10^{-2}	---	---	---

NUMBER OF VARIABLES: 3

NUMBER OF REPLICATES: 1

Variance	Variance Identification	No. of Levels
4	Titanium Chloride Concentration	2
5	Hydrogen Concentration	2
6	Argon Dilution of Hydrogen Gas Feed	2

GRAND MEAN: 0.591

*Based on combining all four interactions

**90 percent confidence level

***95 percent confidence level

The other source of variation (interactions) corresponds to interaction of the respective independent variables. It is noted that F-values of main effects of 4, 5 and 6 exceed the F-values of interactions (i.e., X_4 = 5.64, X_5 = 4.01 and X_6 = 12.4 vs 0.924, 0.722 and 1.20 respectively). These higher F-values indicate that the coating rate variation is attributable to the three independent variables studied in second statistical series, and is not attribu able to first order interactions of the variables. Furthermore, on basis of F-test at 95 percent confidence level, the highest F-value, 12.4 for X_6, indicates that argon dilution of hydrogen gas feed exerts highest influence of the independent variables.

The argon dilution of hydrogen gas feed was maintained at high level in the next experiments, deposit phase runs, on basis of above favorable effect in factorial analysis of variance.

C. ADDITIONAL OPTIMIZATION AND PRODUCTION

Additional optimization and production studies were started by utilizing previous program analysis findings from first and second statistical series which were conducted with round rod substrates of columbium composition.

In deposit phases, acceptable coating deposits were achieved on threaded substrates — 1-in. threaded stud refractory fasteners of columbium alloy Cb 752 composition — in variable loading runs with the processing equipment. For coating oxidation samples, a statistically designed plan was formulated and conducted to determine the influence of the seven process variables on important coating properties (including rate, deposit and oxidation resistance). The effect of each process variable was established by the Yate's method in analysis of test which also included a specific method for selecting process variable values for oxidation improvement.

Duplicate best coating runs demonstrated that differently shaped substrates — 1 1/2-in. hex head bolt refractory fasteners of Cb 752 composition — could be CVD coated at high reactor loading of ten substrates per run. Produce fastener runs further verified that the CVD-rotating reaction chamber technology was applicable for coating additional different shapes — bolts, studs, rods and flat panels — in one run. Coating was achieved with reactor loading of twenty total substrates per run which is within scope of potential production equipment.

Cyclic oxidation optimization provided significant coating oxidation property improvement and uniform coverage of different shapes. Three shapes — hex head bolt, threaded stud and hex nut refractory fasteners — were CVD coated at a loading level of thirty substrates per run (i.e., ten of each shape) with uniform coating coverage of very little variation from the mean. Additionally, statistical base optimization runs — based on statistical plan results from coating oxidation samples and analysis of test — were completed to define the apparent optimum region. A tenfold coating oxidation property improvement over earlier results was achieved by coating the refractory fasteners in the apparent optimum region.

For production demonstration batches, specific refractory fasteners — 1 1/2-in. long hex head bolts and complimenting 1/4-in. dia. hex nuts — were coated at increased reactor loading of thirty to fifty substrates per run. A total of more than twenty demonstration runs were made with uniform substrate coverage at this current coating capability level. In previous work which served as a basis for this scale-up program, coating capability involved one substrate per run. The current coating capability of fifty substrates per run greatly exceeds the previous results and illutrates that the optimized technology is within the scope of practical production equipment.

1. Deposit Phases

Deposit phase runs with threaded substrates — refractory fasteners of columbium alloy composition — were made using independent variable values obtained from first and second statistical series which were conducted with round rod substrates of columbium composition. The coating deposits achieved on the threaded substrates in the runs were acceptable and within the same order of magnitude as coating deposits obtained with the round rod substrates.

Deposit phase runs with variable quantity substrate loading in the reactor were completed as part of the program objective involving process establishment of potential production equipment. The variable quantity substrate run results disclosed coating rate and coating deposit variations when substrate loading in reactor was increased from 3 to 12 substrates.

Figure 18 illustrates the variation of coating rate with substrate loading. The right vertical axis in the figure shows the variation of coating deposit. The curve constructed in the figure indicates that coating rate and coating deposit were decreased as substrate loading was increased from 3 to 12 substrates in the reactor. The coating deposit variation is about 50 percent with the 400 percent loading increase. Also, the coating deposit (about 130 mg per threaded substrate) achieved at substrate loading of 10 was within the acceptable range for the next experiments, coating oxidation samples.

2. Coating Oxidation Samples

A statistically designed plan was formulated and conducted in coating oxidation samples runs. The purpose was to determine influence of the seven process variables on coating properties of interest (coating rate, coating deposit and oxidation resistance of coating) while conducting a minimum number

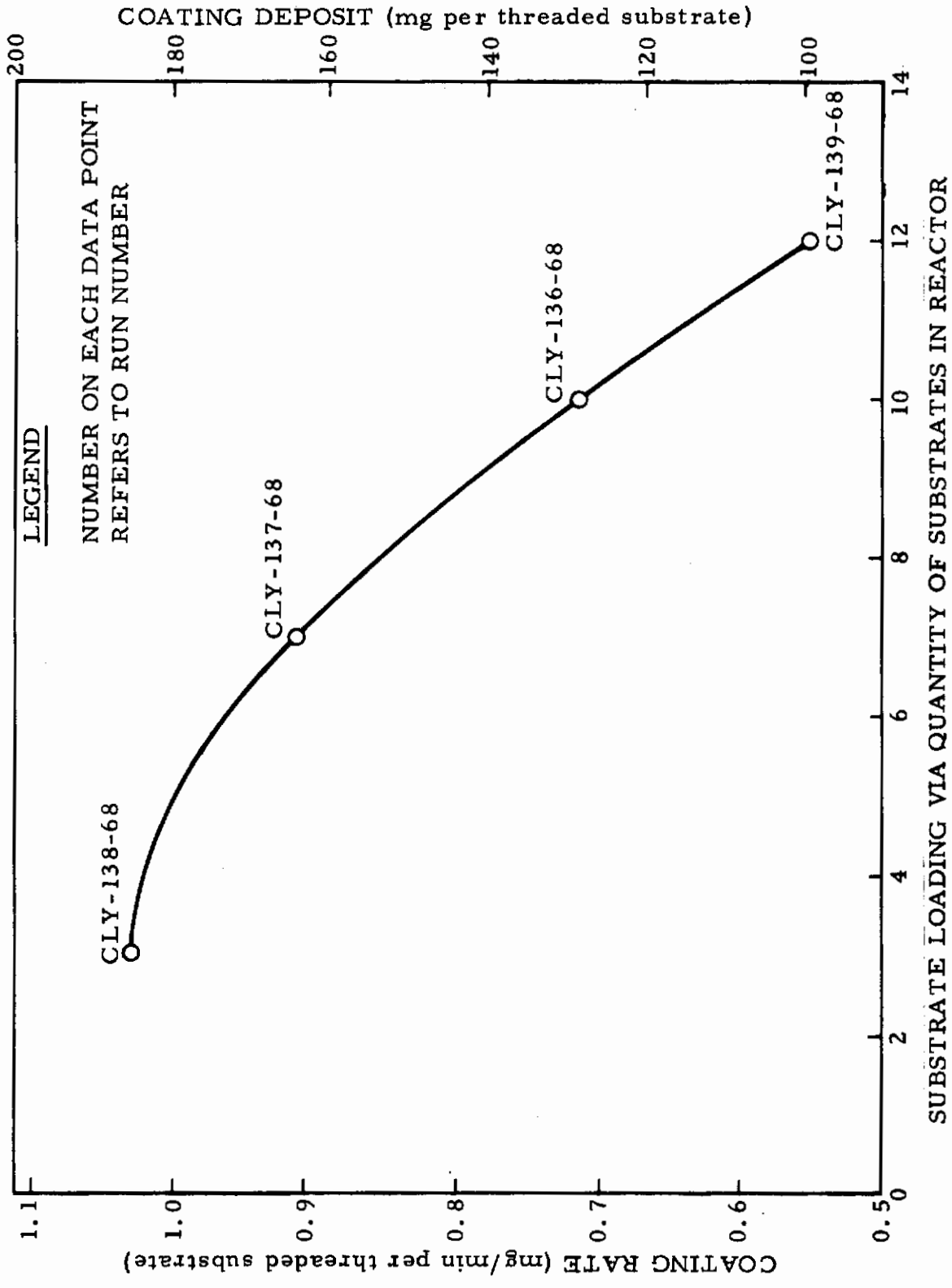

Figure 18. Deposit Phases: Effect of Substrate Loading on Coating Rate in Deposit Phase Runs

of experiments utilizing previous program findings. A fractional design was selected which minimized experiments by requiring only one-sixteenth of total factorial design for process variable effects and neglecting first-order interactions. Previous program findings were utilized in selection of process variable base levels in the fractional design. The fractional plan and results for coating properties at each experiment level are presented in Table XXVII.

The influence of the process variable on coating properties listed in the table was determined by Yate's method. The calculated effect tended to confirm earlier reported results applicable to different process variable value ranges. The calculated results disclosed that the coating rate and the coating deposit on substrates increased with corresponding increases in reaction temperature, silicon chloride concentration, flow rate, titanium chloride concentration and hydrogen concentration. Reaction temperature, silicon chloride concentration and titanium chloride concentration exhibited more influence on coating rate and coating deposit than the other process variables for the variable range studied in coating oxidation sample runs. The coating property disclosure applies for 1-in. threaded stud substrates which were coated at high loading levels of six and ten substrates per run.

A detailed tabulation of process conditions and results for coating oxidation sample runs is presented in Appendix IX. A summary tabulation showing loading level (quantity of substrates coated in the run) and coating deposit (quantity of coating deposited on the substrate) is given in Table XXVIII. It is noted in the table that eight demonstration runs were conducted at a loading level of ten substrates per run with a complimenting coating deposit 80 to 160 mg per substrate.

Table XXVII

COATING OXIDATION SAMPLES: PLAN AND RESULTS FOR INITIAL COATING OXIDATION SAMPLE RUNS

Run No.	Process Variables							Results: Coating Properties of Interest			
	X_1	X_2	X_3	X_4	X_5	X_6	X_7	Y_1	Y_2	Y_3	Y_4
1	-1	-1	-1	-1	-1	-1	-1	.513	92.1	2.0	.5
2	+1	+1	-1	-1	+1	+1	-1	1.210	218.5	26.5	9.0
3	+1	-1	+1	-1	+1	-1	+1	.920	165.5	17.3	1.0
4	-1	+1	+1	-1	-1	+1	+1	.457	82.0	9.8	2.0
5	+1	-1	-1	+1	-1	+1	+1	.605	109.7	11.8	6.5
6	-1	+1	-1	+1	+1	-1	+1	.776	141.7	2.0	27.5
7	-1	-1	+1	+1	+1	+1	-1	.617	111.1	103.5	42.0
8	+1	+1	+1	+1	-1	-1	-1	1.160	209.8	2.0	34.0

Process Variables and Coating Properties	Description	Low Level	High Level	Unit	Base Level
		-1	+1	---	---
X_1	Reaction Temperature (°C)	1000	1100	50	1050
X_2	Silicon Chloride Concentration via $SiCl_4$ Bubbler (Ar, ℓ/min)	.040	.080	.020	.060
X_3	Flow Rate via Measured Gas Feed Flow (ℓ/min)	17	21	2	19
X_4	Titanium Chloride Concentration via $TiCl_4$ Bubbler (Ar, ℓ/min)	4	6	1	5
X_5	Hydrogen Concentration via H_2 Flow (ℓ/min)	4	6	1	5
X_6	Argon Dilution of Hydrogen Gas Feed (ℓ/min)	4	6	1	5
X_7	Substrate Loading via Quantity of Substrate in Reactor	6	10	2	8
Y_1	Coating Rate via Average Weight Gain Rate per Threaded Substrate (mg/min)				
Y_2	Coating Deposit via Average Weight Gain per Threaded Substrate (mg)				
Y_3	Initial Coating Oxidation Resistance at 2200°F via Average Test Time in High Temperature Oxidation Environment Before Failure (hr)				
Y_4	Initial Coating Oxidation Resistance at 2400°F via Average Test Time in High Temperature Oxidation Environment Before Failure (hr)				

Table XXVIII

COATING OXIDATION SAMPLES: LOADING LEVEL AND COATING DEPOSIT RESULTS FOR COATING OXIDATION SAMPLE RUNS

Run Number	Loading Level: Quantity of Substrates	Coating Deposit: Weight Gain of Substrate (mg)											Substrate Identification
		1	2	3	4	5	6	7	8	9	10	Avg.	
CLY-147-68	6	131.7	132.8	138.2	115.2	129.3	124.0	—	—	—	—	128.5	Threaded Substrate
CLY-148-68	6	92.9	93.6	92.4	91.2	91.5	91.0	—	—	—	—	92.1	Threaded Substrate
CLY-149-68	10	162.0	163.0	168.5	168.4	166.0	164.8	165.5	165.9	166.6	164.5	165.5	Threaded Substrate
CLY-150-68	10	111.2	109.6	113.5	112.2	111.8	108.0	106.4	109.1	109.1	107.0	109.7	Threaded Substrate
CLY-151-68	6	114.5	115.2	106.9	111.9	106.6	112.0	—	—	—	—	111.1	Threaded Substrate
CLY-152-68	6	220.5	189.5	242.9	216.8	223.8	217.7	—	—	—	—	218.5	Threaded Substrate
CLY-153-68	10	59.8	90.2	80.1	56.2	90.0	91.2	89.5	91.8	90.7	80.7	82.0	Threaded Substrate
CLY-154-68	10	147.1	138.8	134.1	145.4	134.4	136.6	142.0	144.1	147.0	147.9	141.7	Threaded Substrate
CLY-155-68	6	205.0	207.8	210.7	210.3	200.4	224.5	—	—	—	—	209.8	Threaded Substrate
CLY-156-68	10	136.6	130.5	133.2	127.3	134.2	134.9	135.7	132.2	135.5	139.3	134.9	Threaded Substrate
CLY-157-68	10	117.0	104.9	101.7	103.4	108.4	103.4	107.3	106.6	110.3	106.0	106.9	Threaded Substrate
CLY-158-68	10	93.4	93.1	93.6	95.1	93.4	94.3	94.7	96.7	95.7	98.4	94.3	Threaded Substrate
CLY-159-68	10	137.9	136.8	134.9	139.0	143.0	138.4	139.9	142.3	141.1	140.4	139.4	Threaded Substrate

- 1-in. Threaded Stud Substrate
- Reaction Chamber C (small reaction chamber)

Completion of this program activity of coating oxidation samples revealed that 1-in. threaded stud substrates may be CVD coated at loading levels of six and ten substrates per run which is within the scope of potential production equipment. Additionally, it provided necessary data for the next activity — analysis of test — involving process variable effects on coating oxidation resistance.

3. Analysis of Test

In analysis of tests, the effect of process variables on coating oxidation resistance was determined for samples from coating oxidation sample runs. Yate's method was utilized for calculating the effects. The calculated results based on 2400°F oxidation test results for the coatings are shown in Table XXIX.

Table XXXIX

ANALYSIS OF TESTS: EFFECT OF PROCESS VARIABLES ON OXIDATION RESISTANCE OF COATING BASED ON 2400°F OXIDATION TEST RESULTS

Process Variable				Effect of Process Variable on Oxidation Resistance of Coating	
	Identification	Unit	Base Level	Calculated Effect	Remarks
X_1	Reaction Temperature (°C)	50	1050	-.27	Decrease of reaction temperature below 1050°C base level should improve coating oxidation resistance.
X_2	Silicon Chloride Concentration via $SiCl_4$ Bubbler (Ar, ℓ/min)	.020	.060	+.28	Increase of silicon chloride concentration should increase coating oxidation resistance.
X_3	Flow Rate via Measured Gas Feed Flow (ℓ/min)	2	19	+.44	Coating oxidation resistance is increased with increase of flow rate.
X_4	Titanium Chloride Concentration via $TiCl_4$ Bubbler (Ar, ℓ/min)	1	5	+1.22	Large calculated effect of +1.22 suggests that titanium chloride concentration possesses greatest influence on oxidation resistance for variable range studied.
X_5	Hydrogen Concentration via H_2 Flow (ℓ/min)	1	5	+.45	Second largest calculated effect of +.45 indicates hydrogen concentration increase favorable influences coating oxidation resistance.
X_6	Argon Dilution of Hydrogen Gas Feed (ℓ/min)	1	5	-.44	Lowering of level of argon dilution of hydrogen gas feed improves coating oxidation resistance.
X_7	Substrate Loading via Quantity of Substrate in Reactor	2	8	-.67	Negative calculated effect indicates coating oxidation with decrease of substrate loading.

Explanation:

- Process variable effects calculated by Yate's method
- Effects are based on results for 2400°F oxidation testing of samples from initial coating oxidation sample runs.
- 1-in. threaded stud substrates
- Reaction Chamber C (small reaction chamber)
- Gas Feed Geometry D

In Table XXIX, a positive value in the column for calculated effect indicates that coating oxidation resistance is improved with positive increase of that test process variable. Within this scope, the calculated results indicate that coating oxidation resistance at 2400°F is improved with increase of silicon chloride concentration, flow rate, titanium chloride concentration and hydrogen concentration. The negative values in the calculated effect column suggest that coating oxidation resistance is improved with decrease of reaction temperature, argon dilution of hydrogen gas feed and substrate loading. Of these calculated effects for improvement with process variable increase, it appears that titanium chloride concentration and hydrogen concentration possess more influence on oxidation resistance than the other process variables for the variable range studied.

These findings for process variable effects on coating oxidation resistance were utilized in experiments for coating oxidation improvement. For their implementation, the respective values in the calculated effect and unit columns in Table XXIX are used. The product of the calculated effect and unit values is determined for each process variable. This product is then added (subtracted if the calculated effect is negative) to the base level of the variable to provide a new process variable value for oxidation improvement.[2]

Multiple regression analysis for coating oxidation resistance as a function of coating thickness and composition was made for samples prepared at two coating thickness levels according to contract specifications. The cursory correlation applied for 2200°F and 2400°F coating oxidation resistance. Due to low computed T values and composition data spread, it was concluded that the correlations comprised only a rough estimation method.

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[2] Li, C.H., "Work Sheet Gives Optimum Condition," Chemical Engineering, 151-156, April 7, 1968.

In further work for analysis of tests, multiple regression analysis correlations were compiled for 2200°F and 2400°F coating oxidation resistance as a function of the seven process variables (reaction temperature, silicon chloride concentration, flow rate, titanium chloride concentration, hydrogen concentration, argon dilution level and substrate loading). The correlations including regression coefficients and computed T values are presented in Table XXX. In the table for 2400°F coating oxidation resistance, the columns for regression coefficient and computed absolute T values are used. The positive values in the regression coefficient column suggest that 2400°F coating oxidation resistance is improved with increase of silicon chloride concentration, flow rate, titanium chloride concentration and hydrogen concentration. In the column giving the computed T value for each of these process variables, it is noted that their computed T values exceed T values for 90% and 95% confidence levels. Within this scope, the tabulated results further indicate influence of silicon chloride concentration, flow rate, titanium chloride concentration and hydrogen concentration for coating oxidation resistance improvement at 90% and 95% confidence levels.

The findings from completion of this program activity — especially the indicated influence of the process variables on coating oxidation performance — provided a good method for process variable value selections in remaining program activities concerned with improving coating oxidation resistance.

4. Duplicate Best Coating

Selection of process variable values was completed for experiments in the plan for duplicating the best coating. The plan for duplicating best coating runs involved using program results for 1-in. threaded studs as substrates and the small reaction chamber (Reaction Chamber C in Figure 11c) as the reactor.

Table XXX

ANALYSIS OF TESTS: CURSORY MULTIPLE REGRESSION ANALYSIS CORRELATIONS FOR 2200°F AND 2400°F COATING OXIDATION RESISTANCE

Process Variable	Variable Value Range Studied for Correlation	Regression Coefficient		Computed Absolute T Value		T Value for Confidence Level	
		2200°F Coating Oxid. Res. Y_3 (hr)	2400°F Coating Oxid. Res. Y_4 (hr)	2200°F Coating Oxid. Res. Y_3 (hr)	2400°F Coating Oxid. Res. Y_4 (hr)	95%	90%
X_1 Reaction Temperature (°C)	988-1100	-.239	-.064	1.10	1.80	2.20	1.80
X_2 Silicon Chloride Concentration via $SiCl_4$ Bubbler (Ar, ℓ / min)	.040-.110	-140.6	191.7	.279	2.32	2.20	1.80
X_3 Flow Rate via Measured Gas Feed Flow (ℓ /min)	16.5-21	3.40	1.96	.629	2.22	2.20	1.80
X_4 Titanium Chloride Concentration via $TiCl_4$ Bubbler (Ar, ℓ /min)	3.75-6	3.48	11.68	.322	6.59	2.20	1.80
X_5 Hydrogen Concentration via H_2 Flow (ℓ /min)	2.5-6	6.49	3.54	.644	2.15	2.20	1.80
X_6 Argon Dilution of Hydrogen Gas Feed (ℓ /min)	1.25-6	2.58	-1.97	.295	1.38	2.20	1.80
X_7 Substrate Loading via Quantity of Substrate in Reactor	6-10	-3.94	-2.99	.740	3.43	2.20	1.80
Intercept		188.9	-8.69				
Standard Error of Estimate		31.23	5.12				
Multiple Correlation Coefficient		1.59	.978				
Mean Value for Correlation		15.3	11.6				

Correlation Specifics

- Y_3 and $Y_4 = aX_1 + bX_2 + cX_3 + dX_4 + eX_5 + fX_6 + gX_7$ + Intercept
- a, b, c, d, e, f, and g = Regression coefficient in above tabulation
- Y_3 = Coating Oxidation Resistance at 2200°F via Average Test Time in High Temperature Oxidation Environment Before Failure (hr)
- Y_4 = Coating Oxidation Resistance at 2400°F via Average Test Time in High Temperature Oxidation Environment Before Failure (hr)
- Correlation based on samples from coating oxidation sample runs
- 1-in. threaded stud substrate
- Reaction Chamber C (small reaction chamber)
- Gas Feed Geometry D

The steps in this plan were (a) repeating runs which provided best coating oxidation resistance at 2400°F testing, (b) repeating runs which provided best oxidation resistance at 2400°F testing with substrate reactor loading of ten and (c) conducting additional runs utilizing findings of previous activity — analysis of tests — for process variable effects on coating oxidation resistance. For the additional runs, process variables of silicon chloride concentration, flow rate, titanium chloride concentration and hydrogen concentration were increased from their base level values on the basis of calculated effect for coating oxidation improvement. The substrates were 1 1/2-in. hex head bolts of specified columbium alloy composition.

Initial experiments with 1 1/2-in. hex head bolts and small reaction chamber disclosed that, after short periods of operation, the gas feed geometry system was broken by the different rotation volume of hex head bolt substrates. To solve this problem another reaction chamber (Reaction Chamber D in Figure 11d) was fabricated.

Complete process conditions and results for the duplicate best coating runs are presented in Table XXXI. The first two runs in the tabulation were made at process conditions which provided best 2400°F coating oxidation resistance with 1-in. threaded stud substrates according to steps (a) and (b) in the above stated plan for duplicating best coating runs. The remaining runs comprise the additional runs for coating oxidation improvement. All runs in the table were made with high substrate reactor loading of ten substrates.

Table XXXI

DUPLICATE BEST COATING: PROCESS CONDITIONS AND RESULTS FOR DUPLICATE BEST COATING RUNS

Run Number	Inert Gas Flows (ℓ/min) $SiCl_4$ Bubbler	$SiCl_4$ Diluant	$TiCl_4$ Bubbler	$TiCl_4$ Diluant	Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Gas Flows (ℓ/min) H_2 Feed	Inert Diluant Gas	Inert Gas Identification	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quantity of Substrates	Coating Deposits Average Weight Gain of Substrate (mg)	Substrate Identification	Reaction Chamber Identification	Gas Feed Geometry Identification	Dual Chamber Identification	Cr and Ti Chips Charge
CLY-160-69	.080	.42	6.0	0.50	Yes	Yes	6.0	4.0	Ar	17.0	240	1000	11	10	178.4	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh
CLY-161-69	.040	2.46	6.0	0.50	Yes	Yes	6.0	6.0	Ar	21.0	300	1000	11	10	147.2	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh
CLY-162-69	.078	2.822	8.6	0.50	Yes	Yes	6.5	3.5	Ar	22.0	300	1000	11	10	297.3	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh
CLY-163-69	.096	2.204	12.2	0.50	Yes	Yes	8.0	2.0	Ar	25.0	300	960	11	10	306.8	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh
CLY-164-69	.120	1.38	15.0	0.50	Yes	Yes	10.0	–	Ar	27.0	60	900	11	10	81.4	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh
CLY-165-69	.120	1.38	17.0	0.50	Yes	Yes	10.0	–	Ar	29.0	270	900	11	10	330.7	1 1/2 Hex Head Bolt	D	D	Chamber B	Fresh

OTHER RUN CONDITIONS

- 1 1/2 hex head bolt (dimension: 1 1/2 in. long x 1/4 in. diameter with 1/2 in. of 1/4-20 refractory threads one end and hex head other end, material: Cb 752 alloy)
- In run CLY-164-69, resistance heating element burned out after one hour of run time.

Run Number	Quantity of Substrate	Coating Deposit: Weight Gain of Substrate (mg) 1	2	3	4	5	6	7	8	9	10	Avg.	Substrate Identification
CLY-160-69	10	146.5	159.6	170.8	182.7	183.6	193.5	194.7	193.0	191.3	167.8	178.4	1 1/2 Hex Head Bolt
CLY-161-69	10	125.4	152.0	147.7	143.6	143.6	138.0	157.3	163.2	156.1	145.6	147.2	1 1/2 Hex Head Bolt
CLY-162-69	10	300.5	294.4	297.0	297.8	302.0	294.7	294.1	294.0	295.6	302.6	297.3	1 1/2 Hex Head Bolt
CLY-163-69	10	314.6	305.0	311.4	302.2	305.5	305.4	296.7	296.7	317.3	313.7	306.8	1 1/2 Hex Head Bolt
CLY-164-69	10	67.5	66.7	99.3	82.9	63.0	69.1	94.1	79.2	86.1	106.0	81.4	1 1/2 Hex Head Bolt
CLY-165-69	10	326.5	337.9	331.6	333.6	328.7	327.8	329.8	332.9	329.3	329.0	330.7	1 1/2 Hex Head Bolt

The distribution and mean of coating deposit and rate are shown in Figure 19 for a representative duplicate best coating run. The partially darkened columns correspond to coating deposit and rate for each substrate (i.e., individual data for each substrate). The darkened column is the mean value for the ten substrates coated in the run. The individual data and mean value in the figure illustrate that there was little distribution of coating deposit and rate among the ten substrates coated in the run.

Completion of duplicate best coating runs demonstrated that the fabricated reaction chamber (Reaction Chamber D) may be utilized for coating 1 1/2-in. hex head bolt substrates at high substrate reactor loading of ten substrates per run. Further, the 1 1/2-in. hex head bolts were coated at high loading with very small variation of quantity of coating deposited on each substrate.

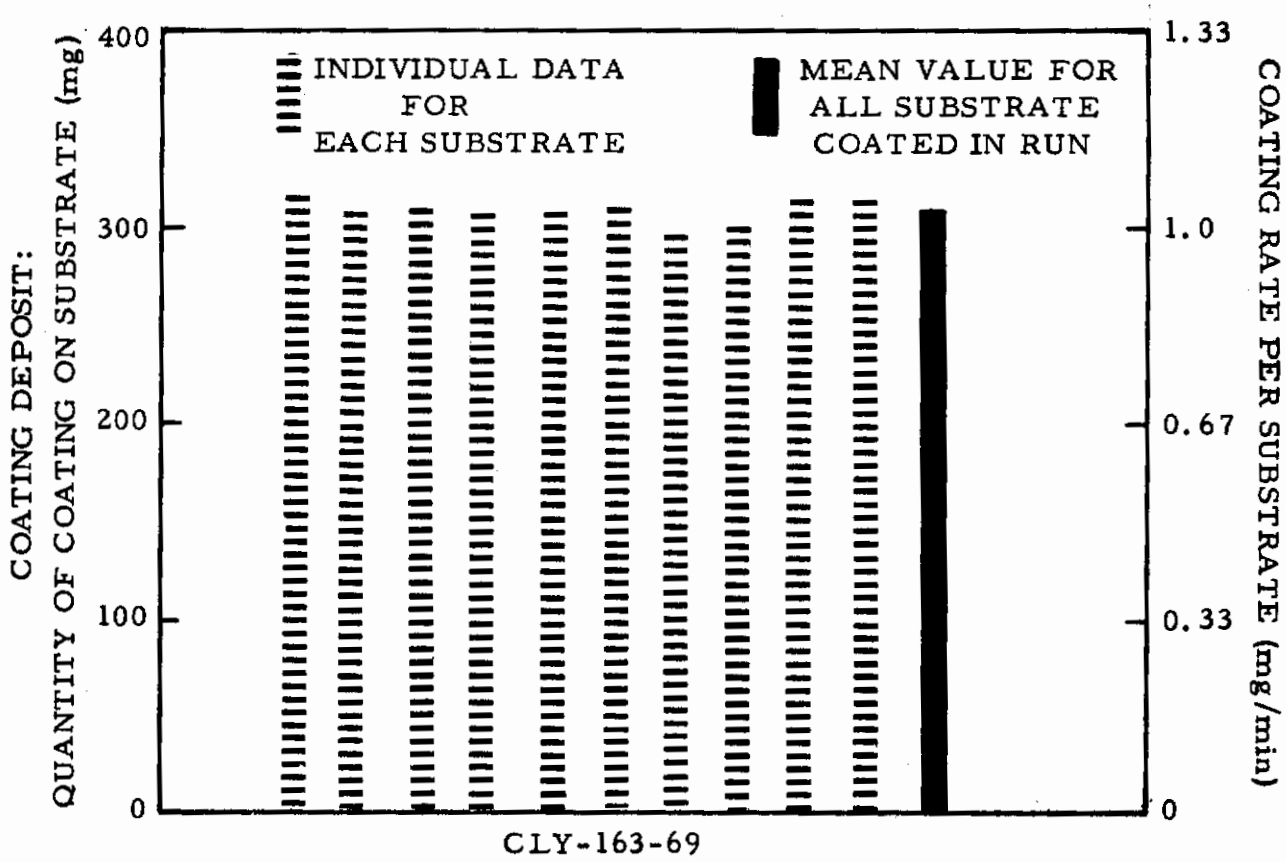


Figure 19. Duplicate Best Coatings: Mean and Distribution for Coating Deposit and Rate for Representative Duplicate Best Coating Run (1 1/2-in. Hex Head Bolt Substrate)

5. Product Fasteners

For "produce fasteners," process variable values were gleaned from duplicate best coating runs which were completed with 1 1/2-in hex head bolt substrates. The initial "produce fastener" runs within the scope were started using the reaction chamber just fabricated (i.e., Reaction Chamber D). These initial runs revealed that a larger reaction chamber was required for coating different shaped substrates — such as threaded studs, hex head bolts, hex nuts, flat panels and round rods — at high substrate reactor loadings within contract specifications. Procurement of a larger reaction chamber for use as the reactor in product fastener runs was started and completed.

Produce fastener runs were made with this larger rotating reaction chamber. The results for a representative run are shown in Figure 20 which plots coating deposit (i.e., quantity of coating deposited on a substrate) for the different shaped substrates coated in the run. Based on individual substrate data and mean value for each differently shaped substrate, the graphical plots indicate little coating deposit variation from the mean. This is especially true for the 1-in. threaded stud, 1 1/2-in. round rod and 1 1/2-in. hex head bolt. This small coating deposit variation is within acceptable limits. It is further noted that twenty of the different shaped substrates were coated in the run.

Completion of produce fastener runs demonstrated that, with the larger reaction chamber, the CVD-rotating reaction chamber technology is applicable to coating a variety of differently shaped substrates — including 1 1/2-inl hex head bolts, 1-in. threaded studs, 1 1/2-in. round rods and flat panels. Further, the completed produce fastener runs revealed that these different shaped substrates may be coated at loadings within the scope of process development of practical production equipment according to contract specifications.

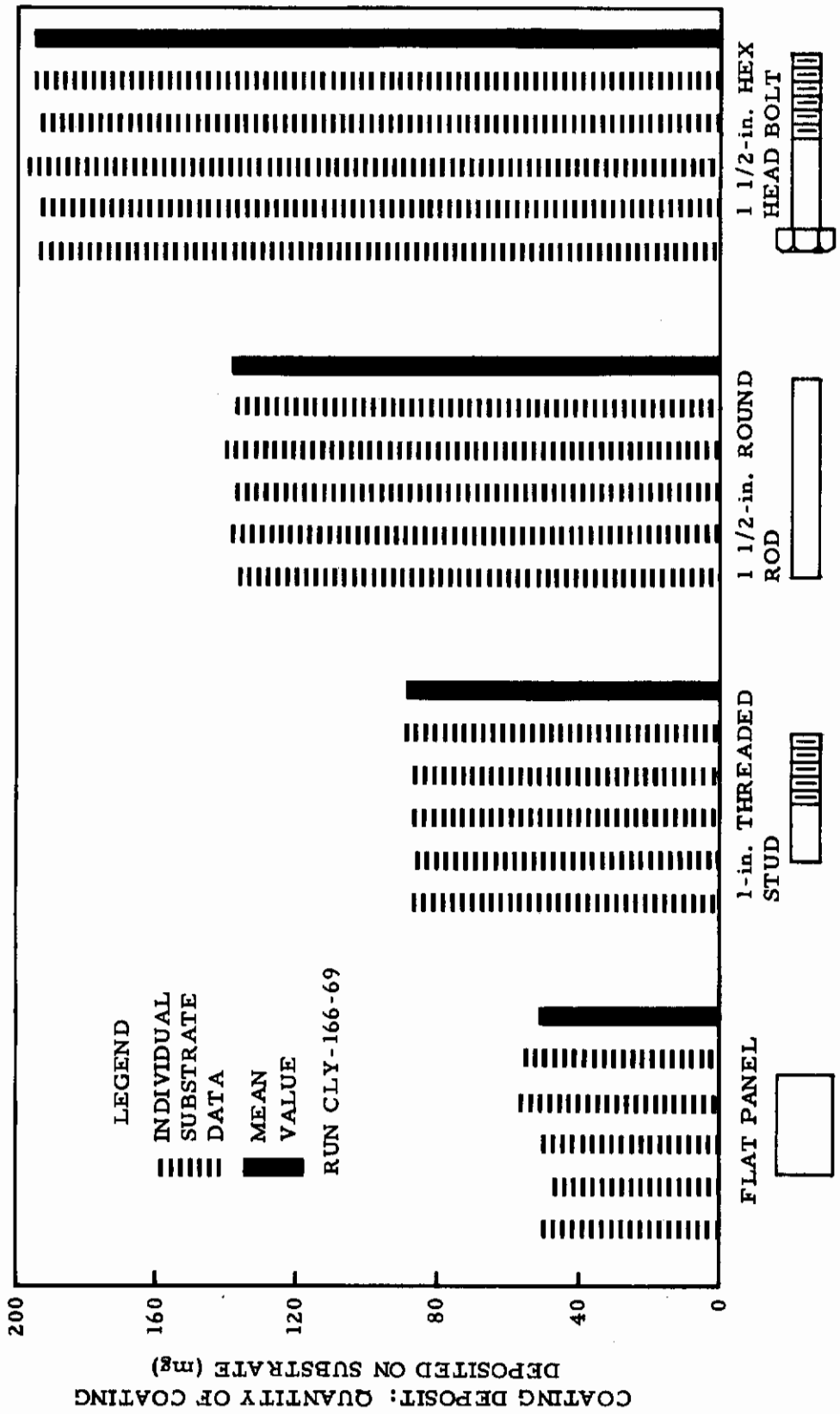


Figure 20. Produce Fasteners: Mean and Distribution for Coating Deposit for Different Shaped Substrated Coated in Representative Produce Fastener Run

6. Cyclic Oxidation Optimization

Using previous results as a starting point, cyclic oxidation runs provided significant coating oxidation property improvement and uniform coating coverage of different shapes. Uniform coating coverage with very little coating deposit and coverage variation from the mean was achieved for three different shapes — hex head bolt, threaded stud and hex nut refractory fasteners — prepared at loading level of coating thirty substrates per run (i.e., ten of each shape). The uniform coverage permitted attachment of the coated hex nut to complimenting coated threaded bolt and stud substrates suggesting that the CVD coated components are still amenable for use in their original application. For coating oxidation property improvement, mean test times to failure of eighty plus hours for protection in a 2400°F oxidation environment were obtained for coated 1 1/2-in. round rods. The round rod substrates were coated in statistical base optimization runs to define apparent optimum region. Use of the apparent optimum region for coating 1 1/2-in. hex head bolt refractory fasteners provided a tenfold improvement. Results indicated mean time to failure exceeding twenty hours, compared to previous several hours protection. For comparison, the uncoated fastener fails with severe oxidation after only one-half hour. Coating thickness was several mils (mostly 3-4 mil range) for providing high temperature oxidation protection of the base substrate. These coating oxidation property test times to failure of eighty and twenty plus hours surpass all previous results for substrates coated at current high reactor loading level (coating twenty to thirty substrates per run) with several shapes.

For cyclic oxidation runs, Figure 21 presents representative results for coating deposit mean and distribution based on individual substrate data and mean value of the distribution. The figure applies for three differently shaped refractory fasteners — hex head bolt, threaded stud and hex nut — which were coated in the same deposition run at high reactor loading level of coating thirty substrates (i.e., ten of each shape). The fairly uniform height of the partially darkened — individual substrate columns for each different shape in the figure - reveals very little coating deposit and coverage variation from the mean.

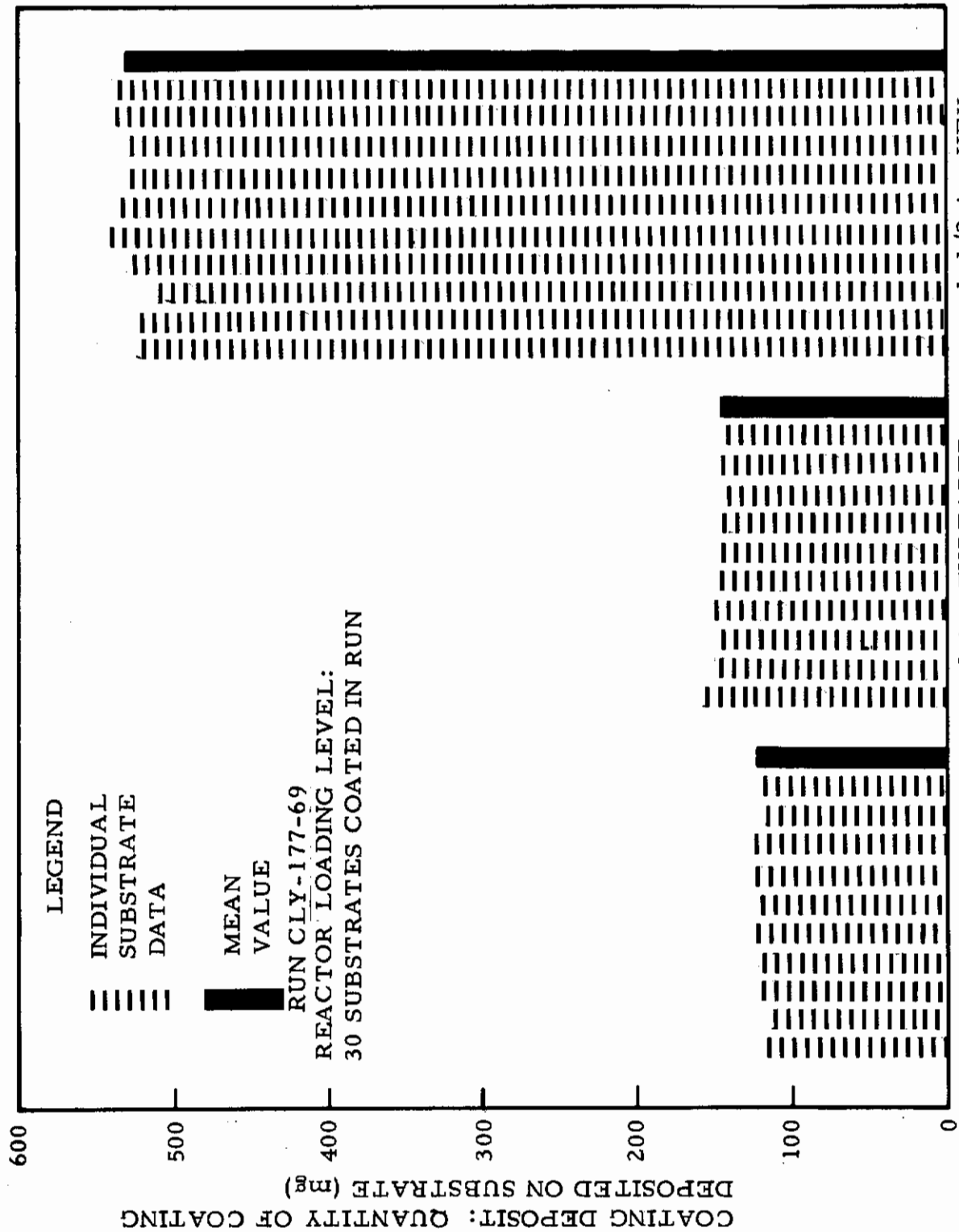


Figure 21. Cyclic Oxidation: Mean and Distribution of Coating Deposit on Differently Shaped Refractory Fasteners Coated at High Reactor Loading Level

The uniform coating coverage of the three differently shaped refractory fasteners is shown in Figure 22. For the bottom two samples, attachment of the coated hex nut to the respective coated threaded substrates (threaded stud and hex head bolt refractory fasteners) suggested that the CVD coated components were amenable for use in their original application.

For coating oxidation property improvement, results of the statistical base optimization runs to locate the apparent optimum region are contained in Figure 23. The coating oxidation property (i.e., test time to failure illustrated by the darkened columns and the left vertical axis) was determined as the mean time from testing four coated samples in the 2400°F oxidation environment. The figure illustrates the coating oxidation property improvement with successive statistical base optimization runs (i.e., process parameter changes illustrated by horizontal axis). The improvement is demonstrated by the increasing height of the darkened columns (i.e., test times to failure exceeding 10, 20, 30, 60, 70, and 80 and 40 hours with the left vertical axis). The coating thickness of several mils (mostly in the 3-mil range) on the 1 1/2-in. round rod substrates is given by the partially darkened columns and right vertical axis. The mean test time to failure of eighty plus hours protection in the 2400°F oxidation environment indicated in the "apparent optimum region" surpasses all previous results for samples prepared at this reactor loading level (total: coating twenty substrates per deposition run, individual substrate shape: ten round rods and ten threaded studs).

Figure 24 displays results for "apparent optimum region" from 2600°F cyclic oxidation testing. The figure applies for 1 1/2-in. round rod substrates coated in the statistical base optimization runs.

Use of the statistical base optimization runs (i.e., process parameter values gleamed from the apparent optimum region) for coating 1 1/2-in. hex head bolt refractory fastener substrates provided significant coating oxidation property improvement. Figure 25 illustrates the improvement by comparing previous and current test times to failure. In the figure, mean test time to failure was determined as mean time from testing four coated samples to gross failure in the 2400°F oxidation environment.

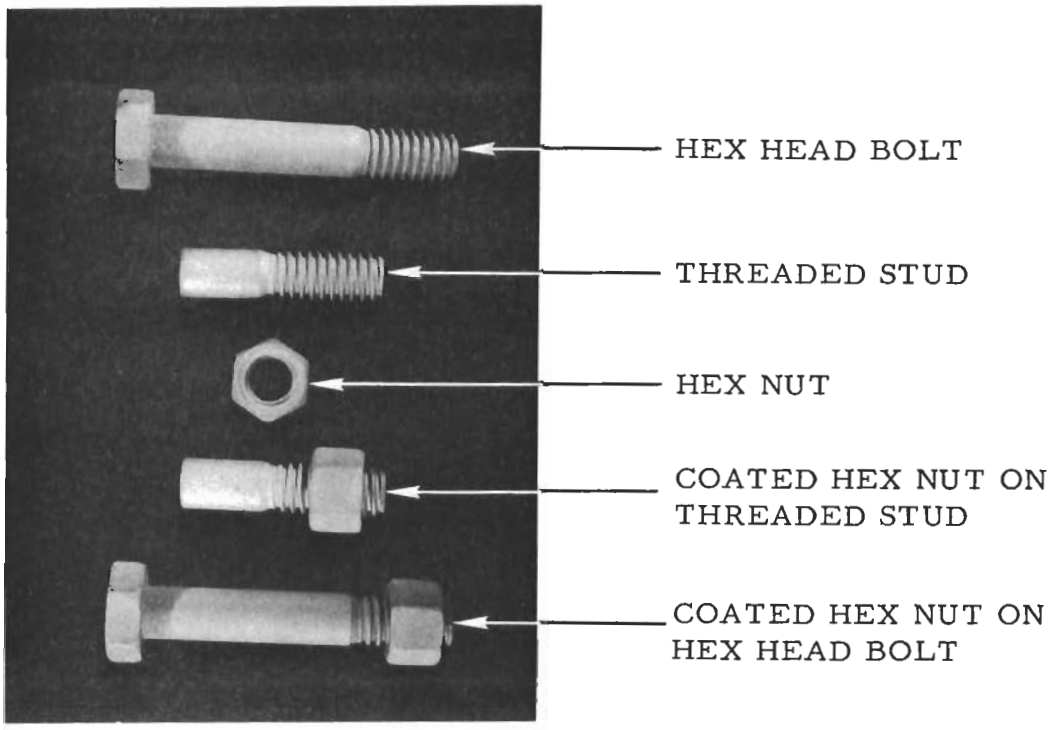


Figure 22. Cyclic Oxidation: Uniform Coating Coverage of Differently Shaped Refractory Fasteners Permits Attachment of Coated Threads and Nut (High Reactor Loading Level: 30 Substrates Coated in Run CLY-177-69)

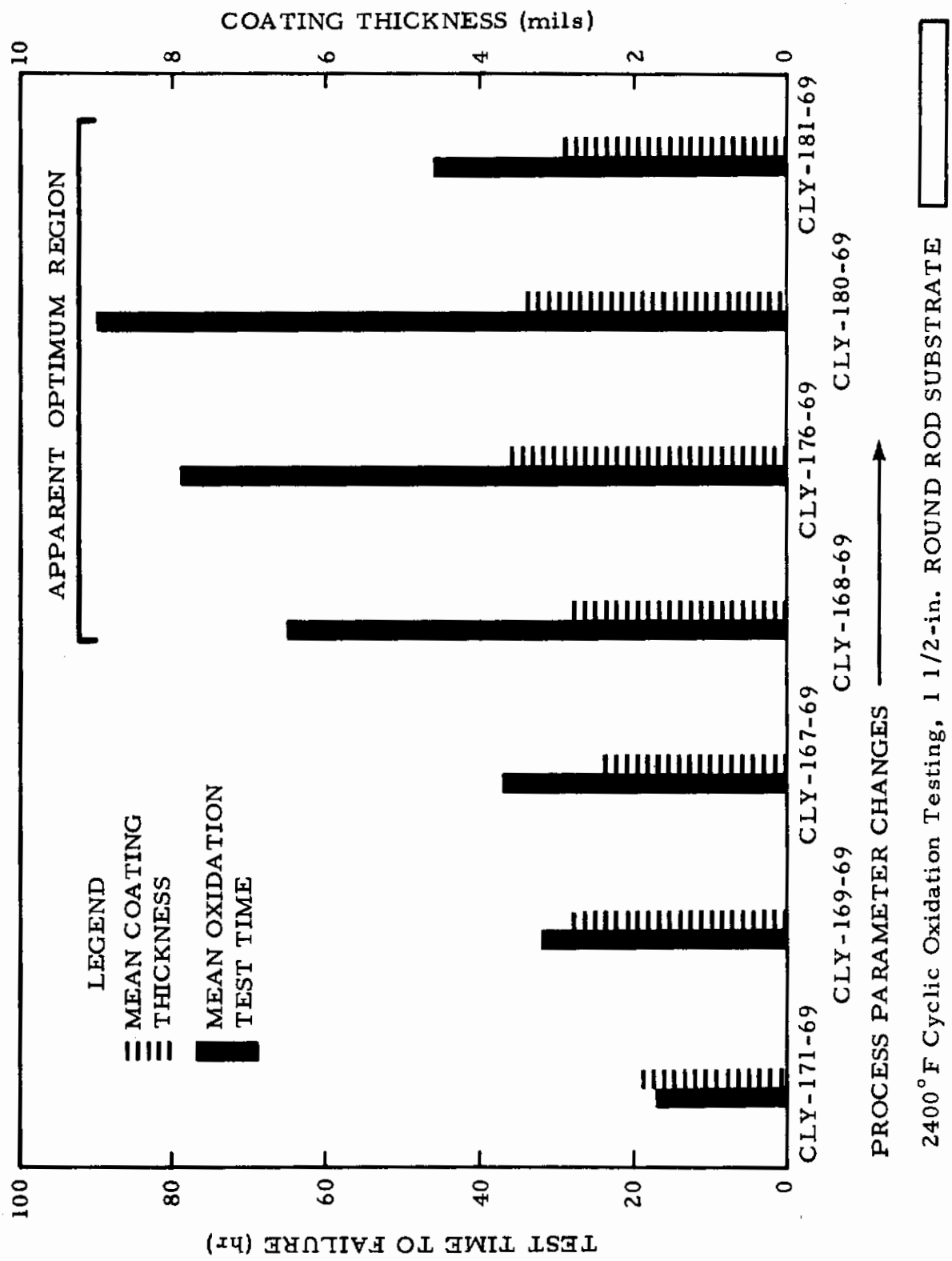


Figure 23. Cyclic Oxidation: Statistical Base Optimization Runs Locate Optimum Region for 2400°F Coating Oxidation Property Improvement

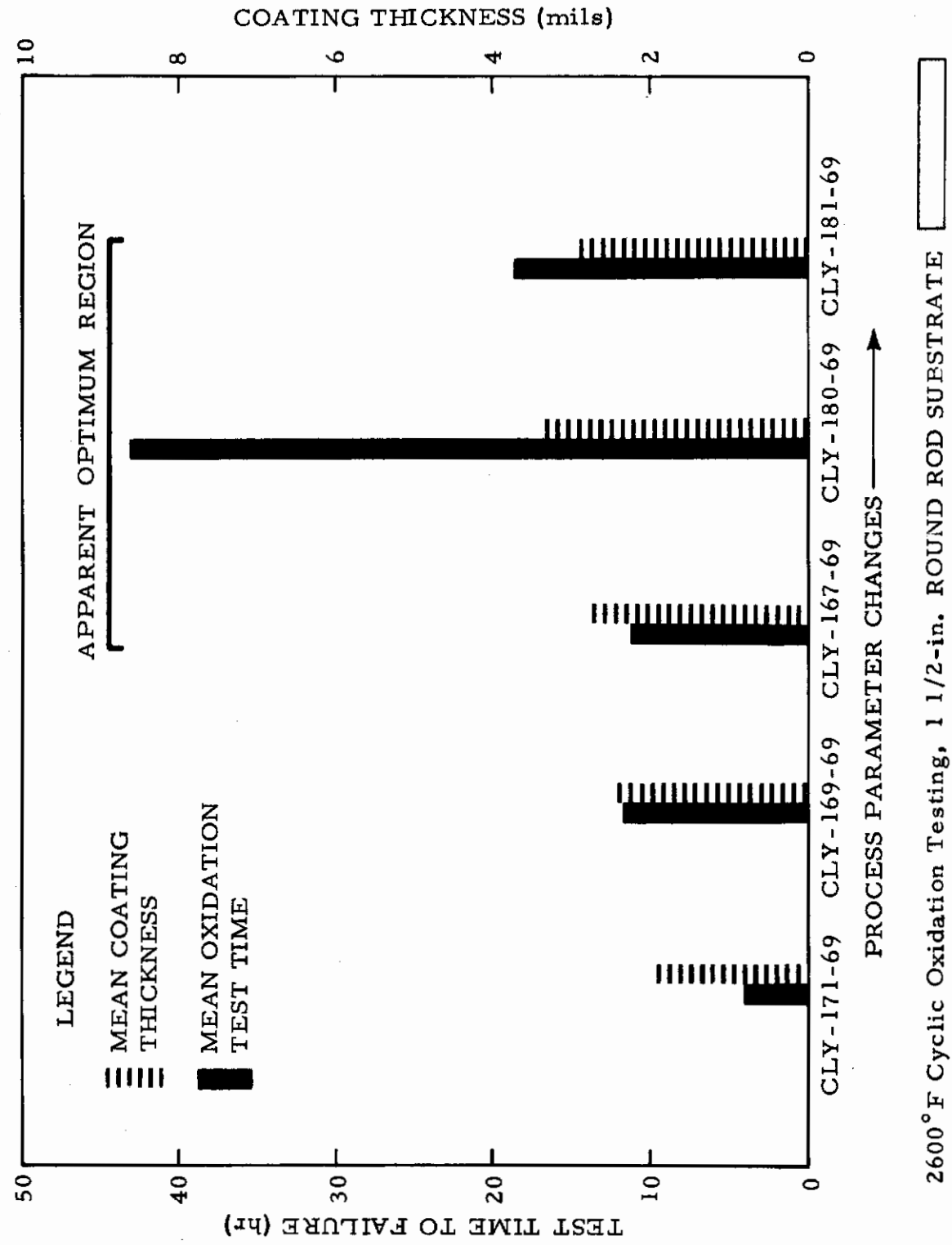


Figure 24. Cyclic Oxidation: Statistical Base Optimization Runs Locate Optimum Region for 2600°F Coating Oxidation Property Improvement

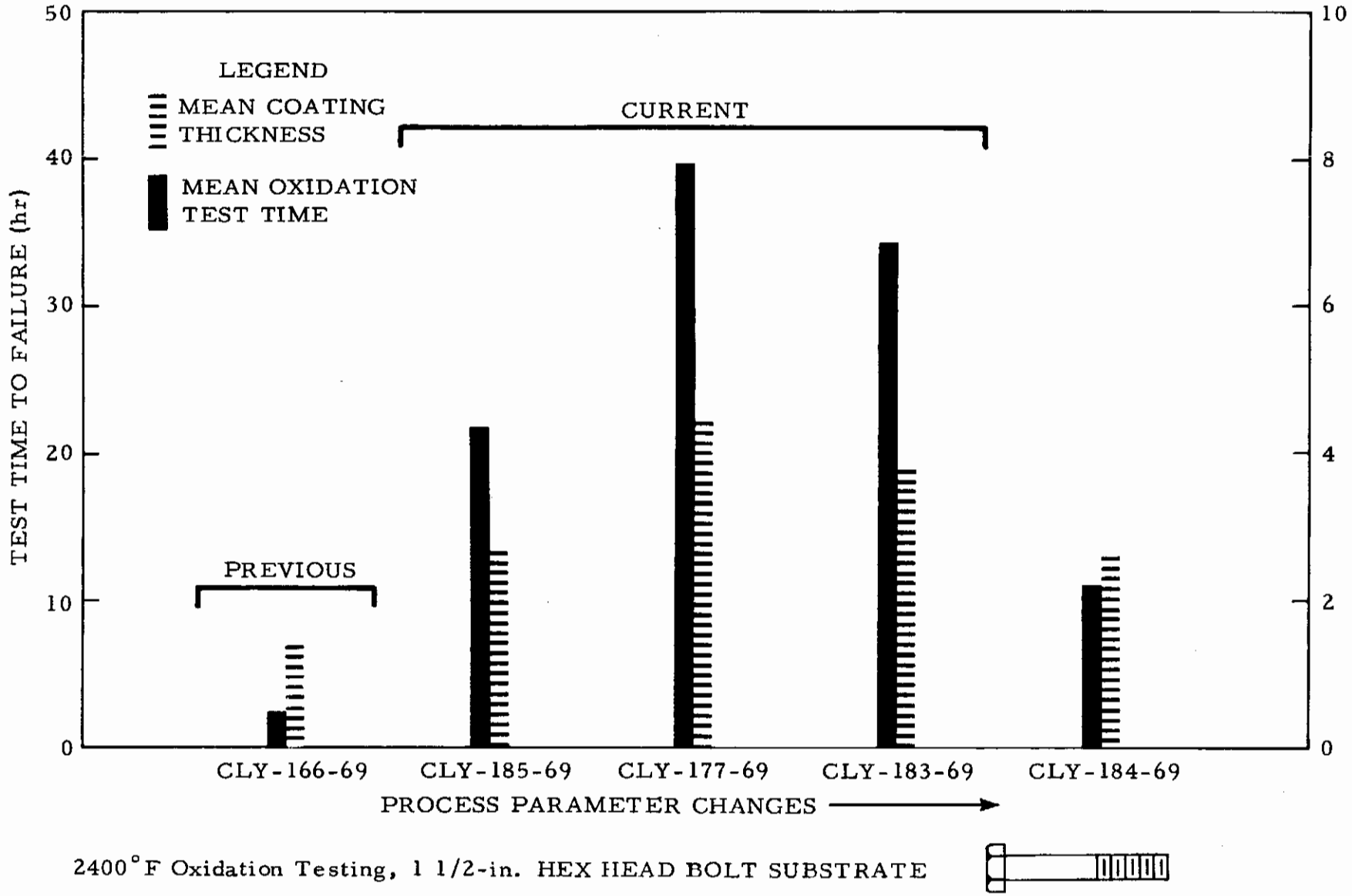


Figure 25. Cyclic Oxidation: Use of Statistical Base Optimization Runs Provides Coating Oxidation Property Improvement for Protecting Hex Head Bolt Refractory Fasteners

Previously, mean test time to failure for the coating was only several hours protection of substrate from high temperature oxidation. Current results, for three different runs as disclosed in the figure, indicate a mean time to failure exceeding twenty hours which comprises a tenfold improvement over previous results. This twenty plus hours protection before gross failure exceeded all previous results for samples coated at this reactor loading level (coating twenty to thirty substrates total per deposition run with several substrate shapes comprising the total).

Completion of this program activity of cyclic oxidation disclosed that differently shaped substrates — including refractory fasteners such as hex head bolts, threaded studs and hex nut — may be coated at a high reactor level of coating twenty to thirty substrates per run with uniform coating coverage of the substrate. Further, the cyclic oxidation program activity results — specifically the process parameter values gleaned from the apparent optimum region — comprise a base for coating refractory fasteners at increased loading in the next program activity — production demonstration batches.

7. Production Demonstration Batches

Coating of refractory fasteners-hex head bolts and hex nuts — required for "production demonstration batches" was completed at increased loading. A comparison of previous and current results disclosed that the current coating capability of coating thirty to fifty substrates per run exceeds all previous results. Twenty plus demonstration runs were conducted at this current coating capability level with uniform substrate coverage. For the four batches selected from the demonstration runs for external testing, 2400°F cyclic oxidation test results revealed twenty plus hour coating protection of the refractory fastener substrates.

The previous program activity, cyclic oxidation, served as a base for coating of the refractory fasteners. Specific use involved coating the refractory fasteners with process parameter values gleaned from the apparent optimum region.

Representative results at the increased coating capability are illustrated in Figure 26 which plots coating deposit mean and distribution for the columbium alloy refractory fasteners. The figure additionally compares previous and current coating capabilities which are denoted by the two horizontal darkened lines with turned down ends above the individual and mean data. The current coating capability comprises coating fifty substrates per deposition run (i. e., evidenced by shown individual substrate coating deposit data on thirty hex head bolts and twenty hex nuts located below the horizontal darkened line for current coating capability). In previous work which served as a basis for starting this scale-up program, coating capability involved coating one substrate per deposition run (i. e., evidenced by shown data on single flat panel). The current coating capability of fifty substrates per run exceeds all previous results for refractory fasteners and is within the scope of process demonstration of practical production equipment.

Process conditions and results for additional production demonstration batches are given in Appendix XIX. A total of more than twenty demonstration runs were conducted in the coating capability range of thirty to fifty substrates per run. Uniform coating coverage (with only minimum percentage of coating deposit variation within the individual substrates) was achieved in the twenty plus production runs.

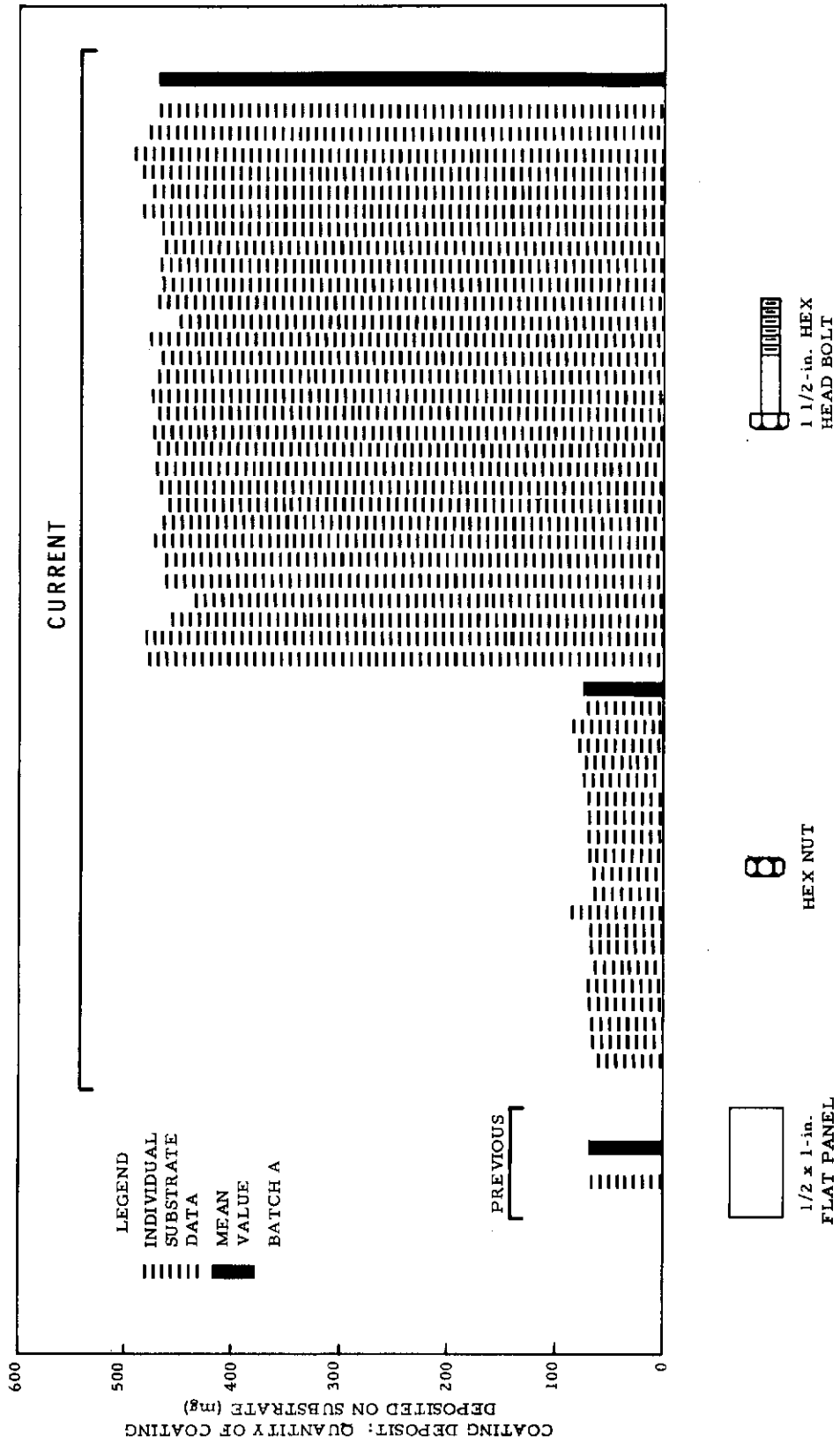


Figure 26. Production Demonstration Batches: Coating Deposit Mean and Distribution Illustrating Current Coating Capability for Refractory Fasteners

SECTION VI
COATING EVALUATION STUDIES

A. OXIDATION TESTING

Oxidation test results for protection of the substrate by the coating deposit were made on the samples obtained from the first statistical series tests. The samples were subjected to a 2500°F oxidation environment in the initial testing. The test results are shown in Figure 27 by plotting weight gain (caused by oxidation) against the test time in the environment. The curves indicate that satisfactory initial oxidation resistance for several hours is provided by some first statistical series samples.

Oxidation test results for second statistical series samples are shown in Figure 28. The curves indicate that satisfactory initial oxidation protection for several hours was provided by nearly all second statistical series samples. Upon exposure to test time exceeding ten hours, 3 of the 8 second statistical series samples provided satisfactory oxidation protection for the substrate. In general, oxidation resistance of second statistical series samples was better than results for first statistical series samples. Round rod substrates of columbium composition were utilized in both first and second statistical series.

For deposit phase runs, threaded substrates — 1-in. threaded stud refractory fasteners of columbium alloy composition Cb 752 — were utilized. Oxidation test results for representative samples are illustrated in Figure 29. Each data point in the figure corresponds to weight gain without visible substrate oxidation. The last data point for each curve is that weight gain determined prior to visible substrate oxidation which was observed at next weighing. The curves disclose both satisfactory initial oxidation resistance for several hours and substrate protection for long exposure to test time exceeding 10 hours.

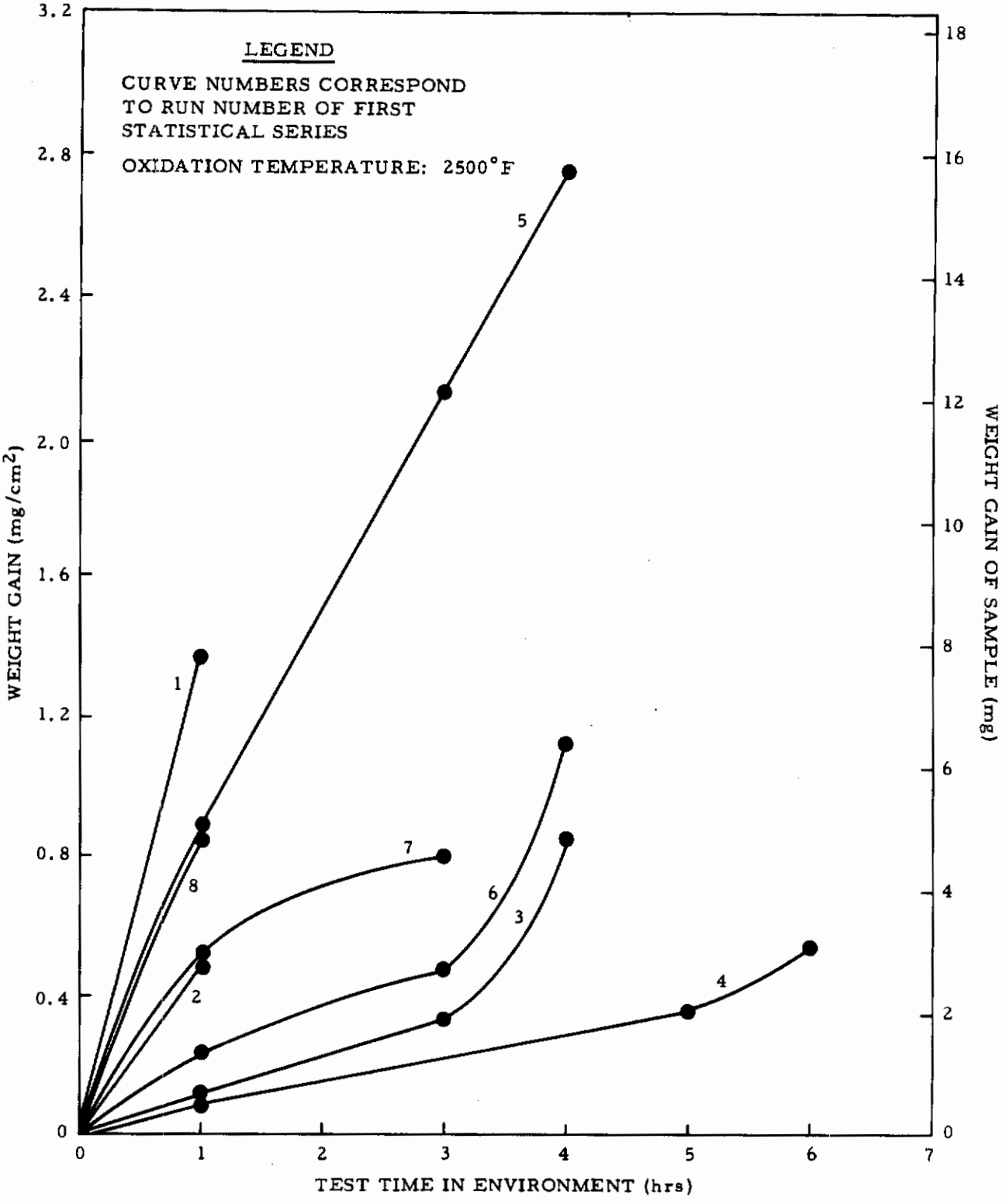


Figure 27. Oxidation Testing: Oxidation Test Results for First Statistical Series Samples

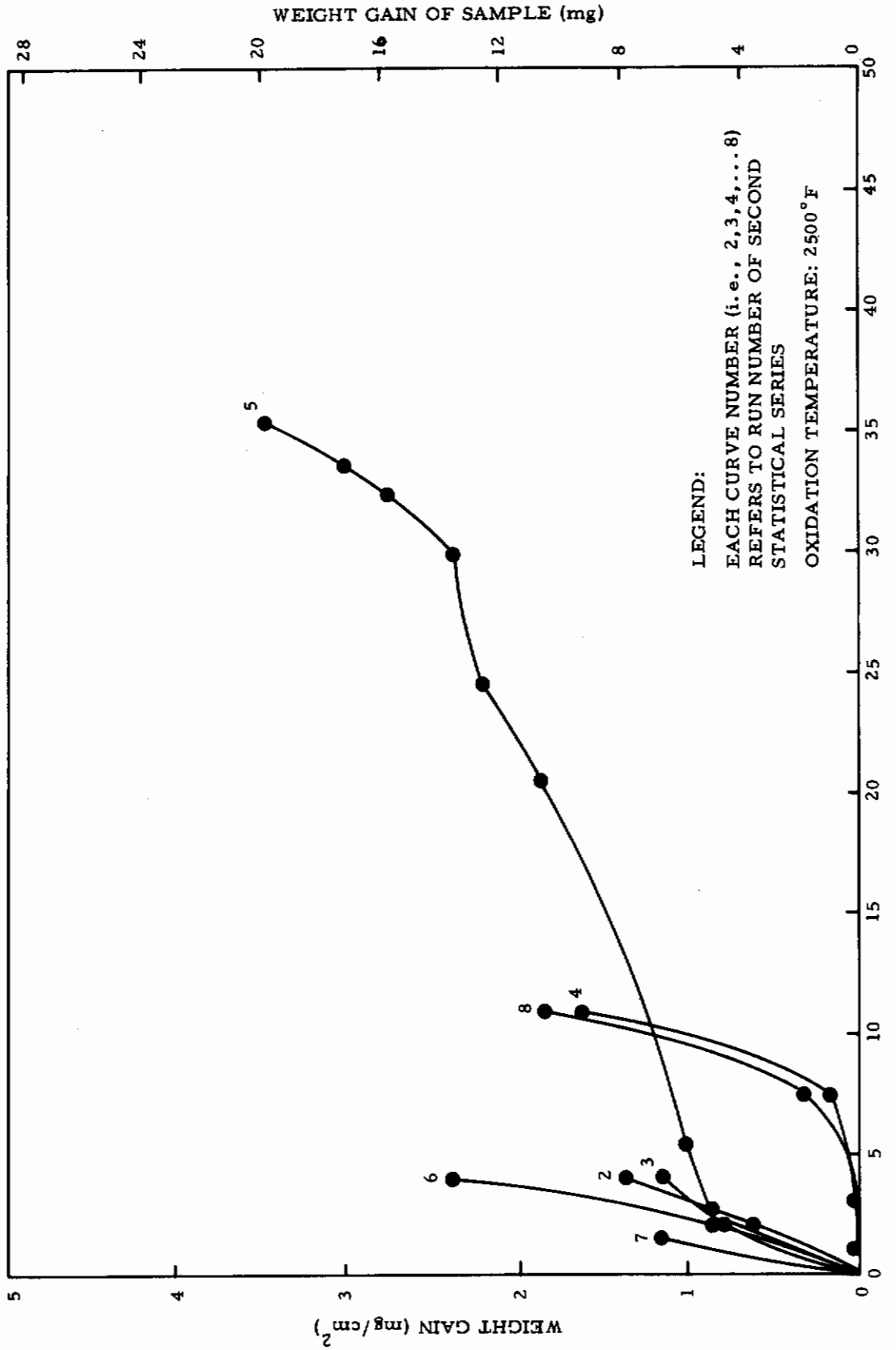


Figure 28. Oxidation Testing: Oxidation Test Results for Second Statistical Series Samples

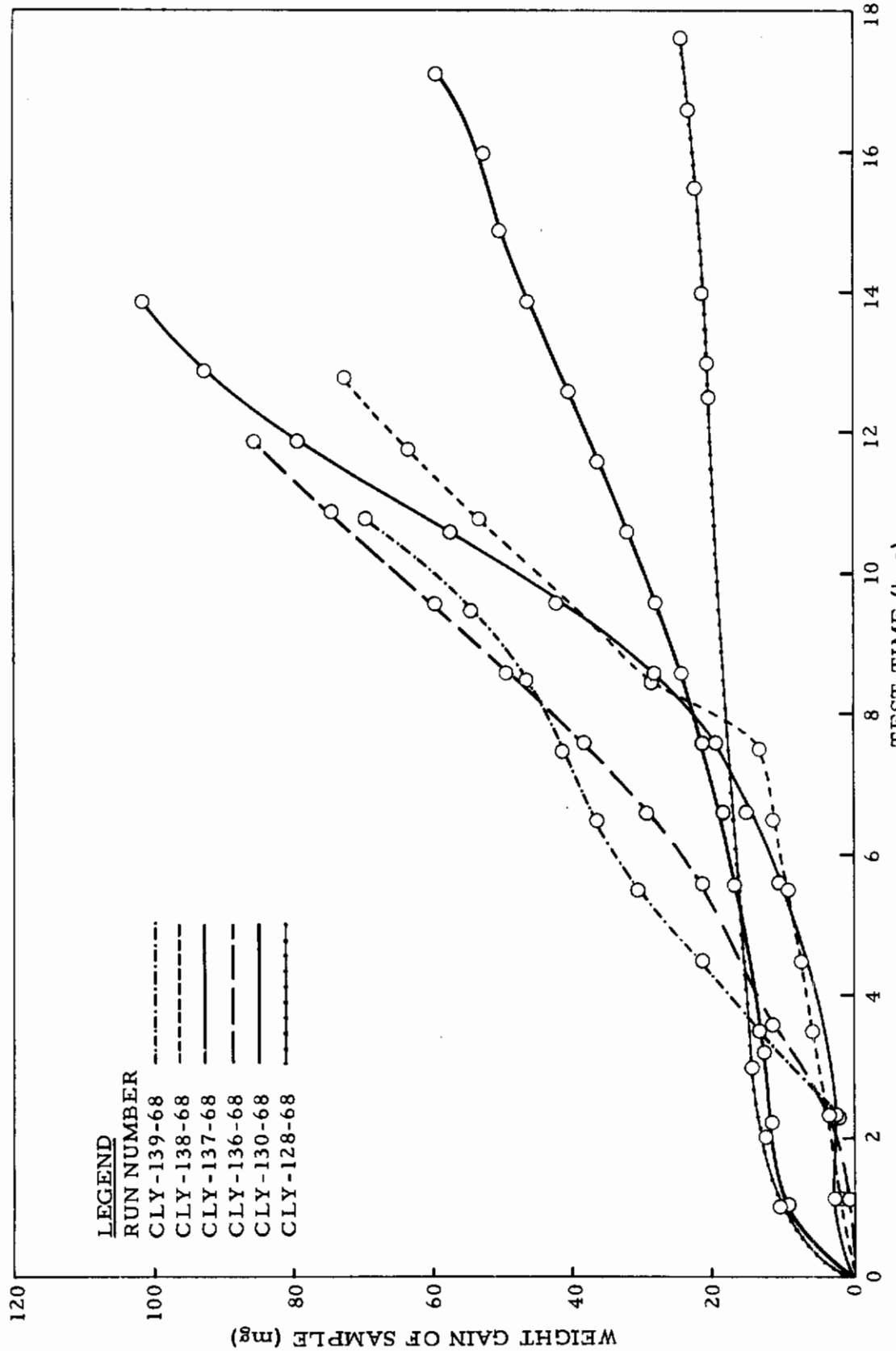


Figure 29. Oxidation Testing: Oxidation Test Results at 2500°F for Representative Deposit Phase Run Samples

In general, oxidation test results for "deposit phase runs with threaded substrates" surpassed results for first and second statistical series with round rod substrates. For first and second statistical series, 3 samples provided oxidation protection for test time exceeding 10-hours. In deposit phases, adequate oxidation protection for test time exceeding 10-hours was provided by all 6 representative samples shown in Figure 29.

Oxidation test results at 2200°F are shown in Figure 30 for representative samples from coating oxidation sample runs. The curves constructed in the figure illustrate the coating oxidation resistance for protection of threaded substrates. Five of the samples provided adequate oxidation resistance for test time exceeding eighteen hours in the high temperature oxidation environment.

Figure 31 presents oxidation test results at 2400°F for representative coating oxidation sample runs. It is noted, in the figure, that three samples provided threaded substrate protection from oxidation for a test time greater than thirty hours. In general, oxidation test results for coatings from coating oxidation sample runs showed improvement over previous results from first statistical series, second statistical series and deposit phases because of process variable changes.

Additional 2400°F oxidation testing was performed on samples prepared in coating oxidation sample runs. The additional testing involved four samples from runs conducted at high substrate loading level (i.e., 10 substrates per run). Figure 32 presents the mean and distribution of the additional 2400°F oxidation test results for the coated 1-in. threaded studs. The undarkened columns in the figure indicate the distribution of test time to failure with each of the four samples tested. The mean value is disclosed by the darkened column. In the figure, the run providing the best 2400°F oxidation test results is run CLY-154-68 with mean time to failure of 27.4 hr. These results served as a base for starting the next experiments — duplicate best coatings — with 1 1/2-in. hex head bolt substrates.

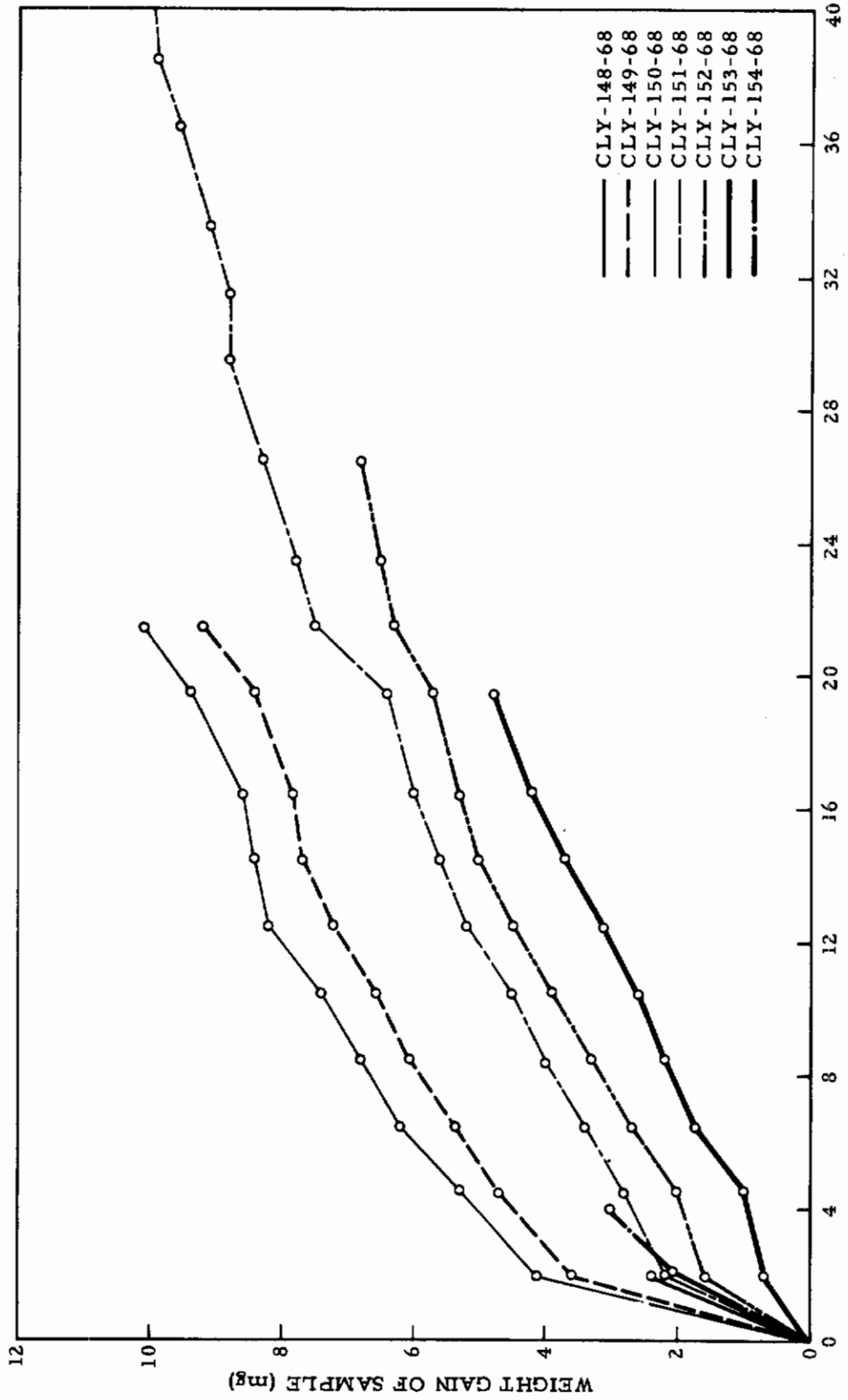


Figure 30. Oxidation Testing: Oxidation Test Results at 2200°F for Representative Coating Oxidation Sample Runs

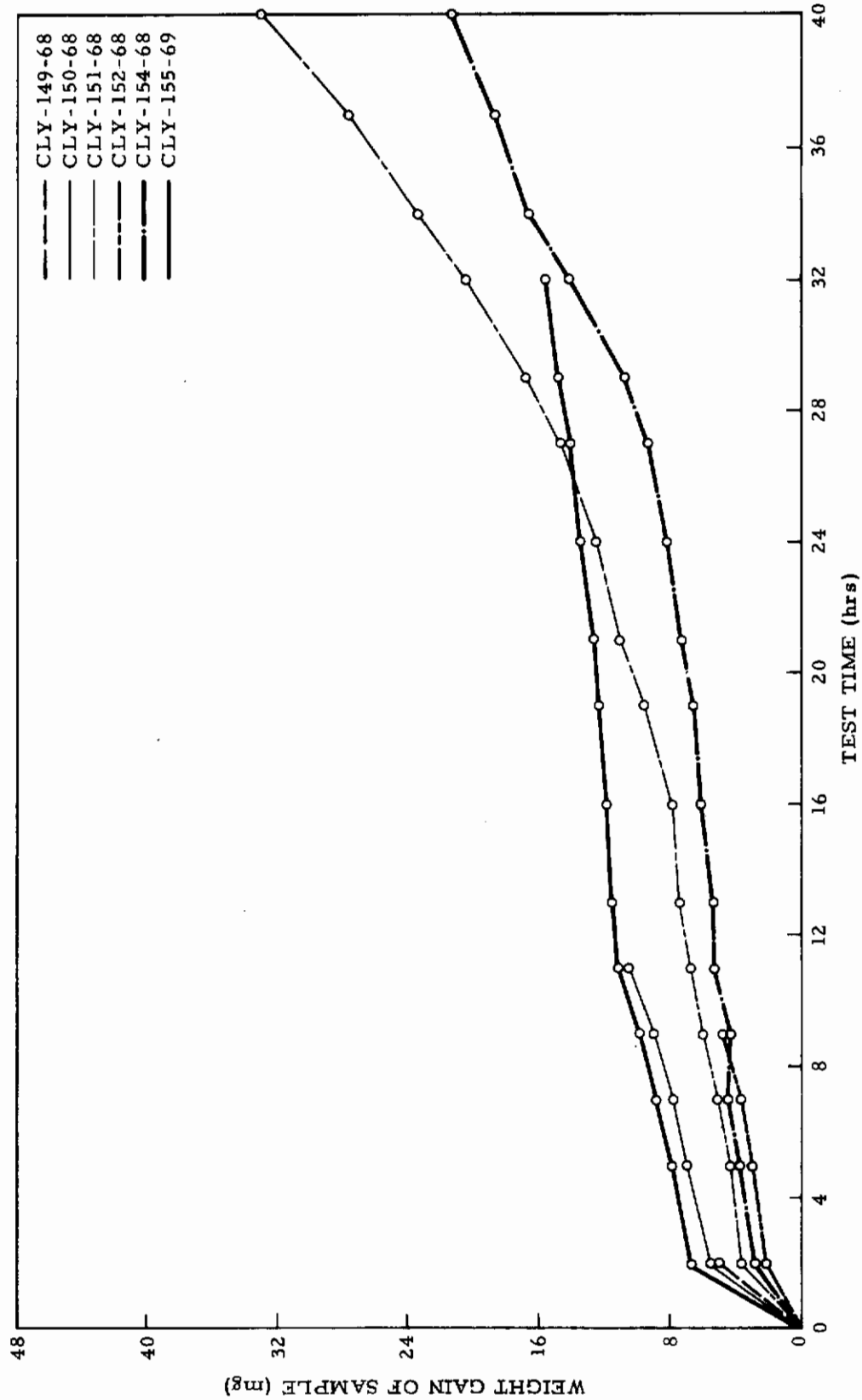


Figure 31. Oxidation Testing: Oxidation Test Results at 2400°F for Representative Coating Oxidation Sample Runs

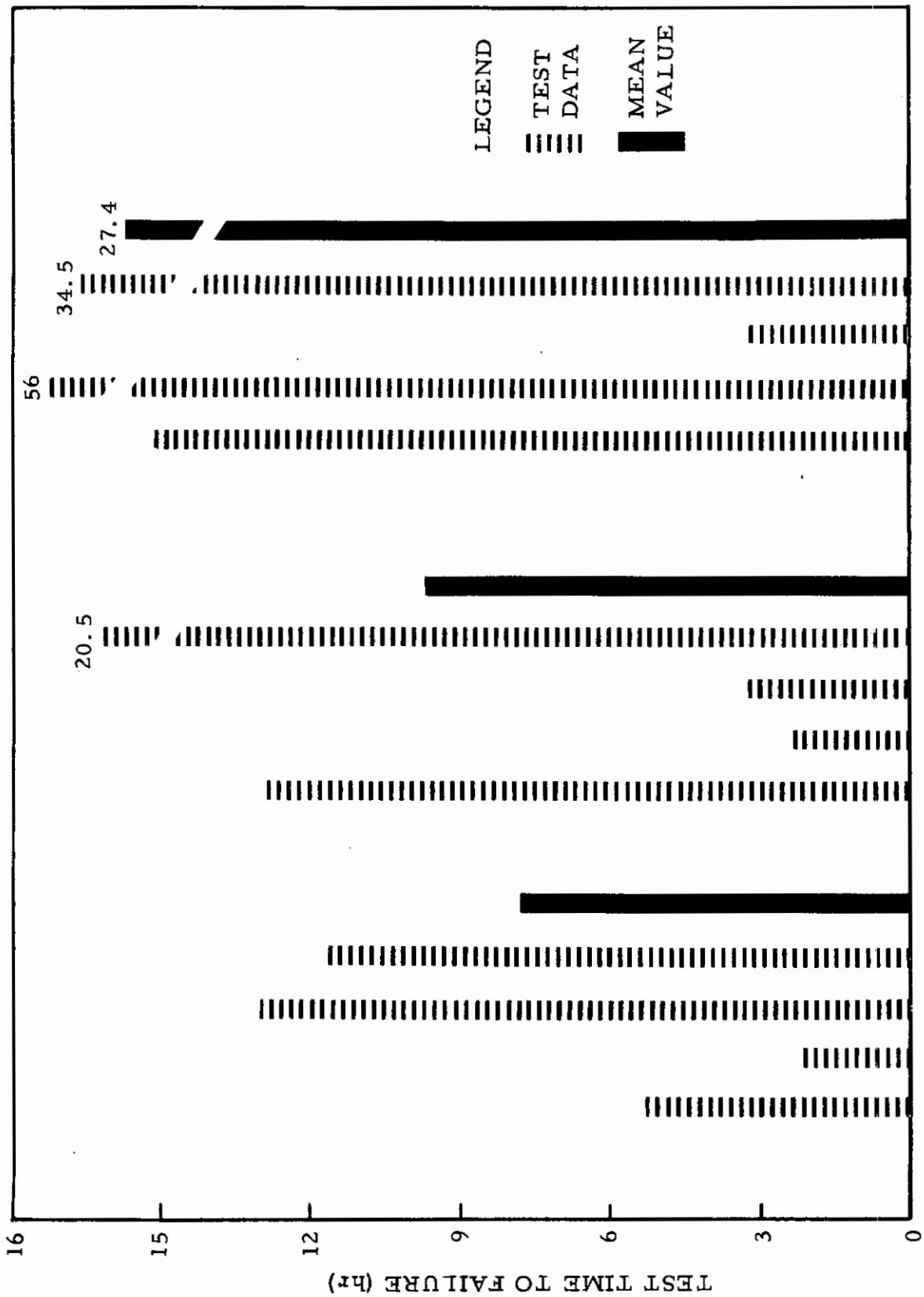


Figure 32. Oxidation Testing: Mean and Distribution for 2400°F Oxidation Test Results for Samples Prepared at High Substrate Loading Level in Coating Oxidation Sample Runs (Coated Refractory Fastener: Coated 1-in. Threaded Stud)

B. METALLOGRAPHY

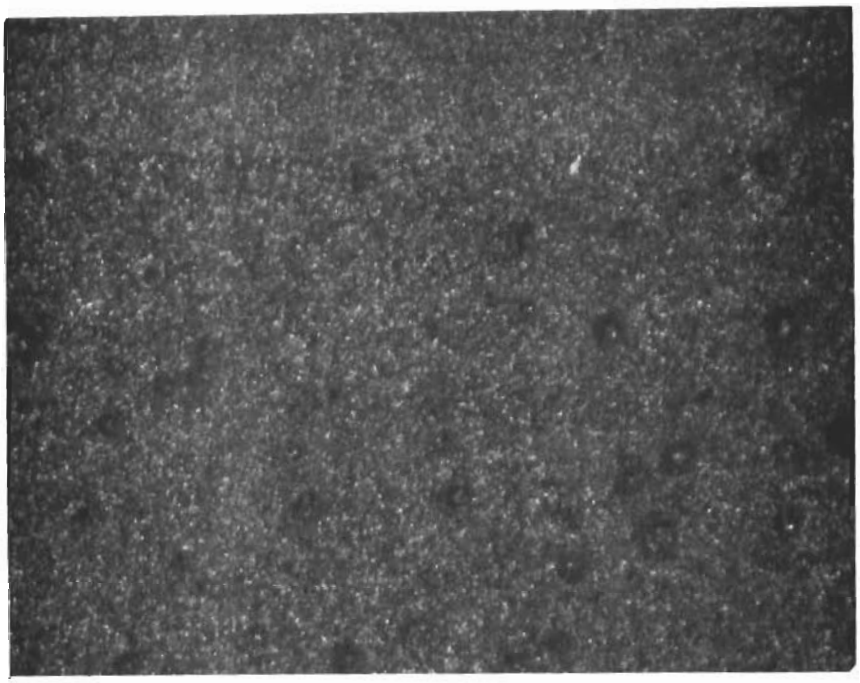
Photographs showing representative surfaces of coating deposits for samples prepared in gas feed geometry study and first statistical series are presented in Figure 33. Both flat panel and round rod substrates are illustrated in the figure.

Figure 34 presents photographs of mounted cross sections to show coating and substrate for representative second statistical series samples. Round rod substrates of columbium composition were utilized in the second statistical series.

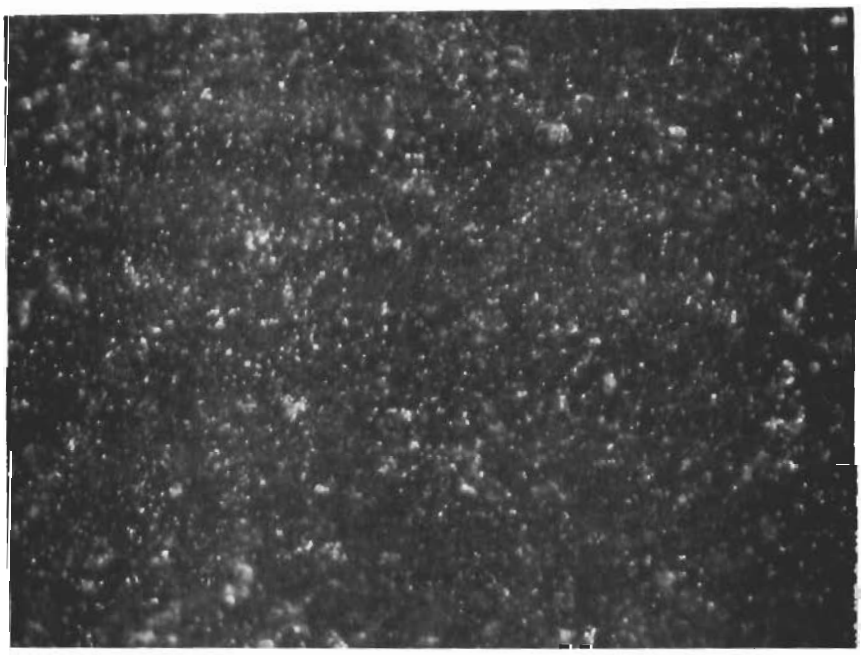
For threaded substrates — 1-in. threaded stud refractory fasteners of columbium alloy composition Cb 752 — photograph of mounted cross sections is shown in Figure 35 for deposit phase run sample. Coverage by the coating is illustrated in the figure for the threaded substrate.

For additional metallography, the structure of the Cb 752 alloy before and after coating is shown in Figure 36 for 1-in. threaded stud substrate. A nitric acid-hydrofluoric acid-glycerin solution was used as etchant in bringing out structure showing grain size and boundary. Figure 36a shows the structure before coating. Figures 36b and 36c depict the structure after coating.

Photographs showing surface of Cb 752 alloy before and after coating are presented in Figure 37. Figures 37a and 37b show the columbium alloy as received and after etching prior to coating. The surface, after coating, is shown in Figures 37c and 37d for representative samples prepared in coating oxidation samples runs.

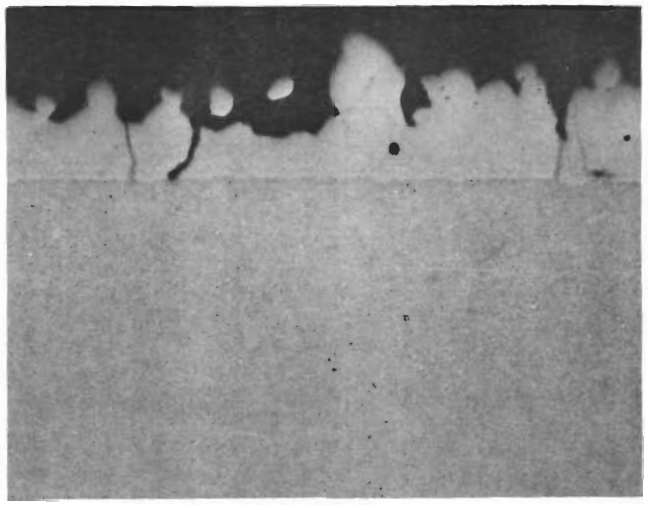


(a) CLY-90-68 (Flat Panel Substrate)

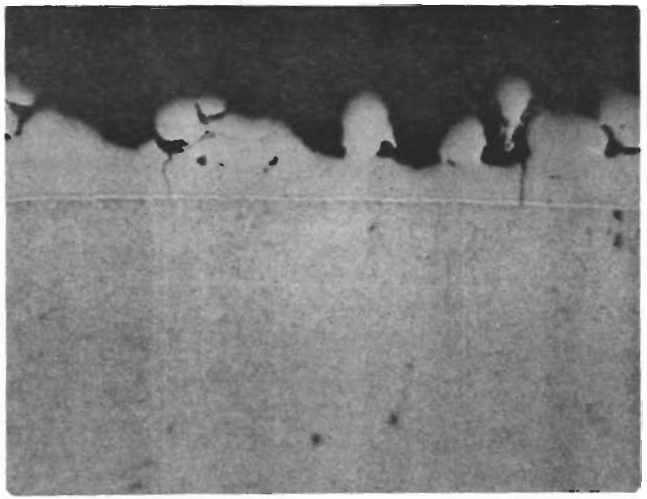


(b) CLY-93-68 (Round Rod Substrate)

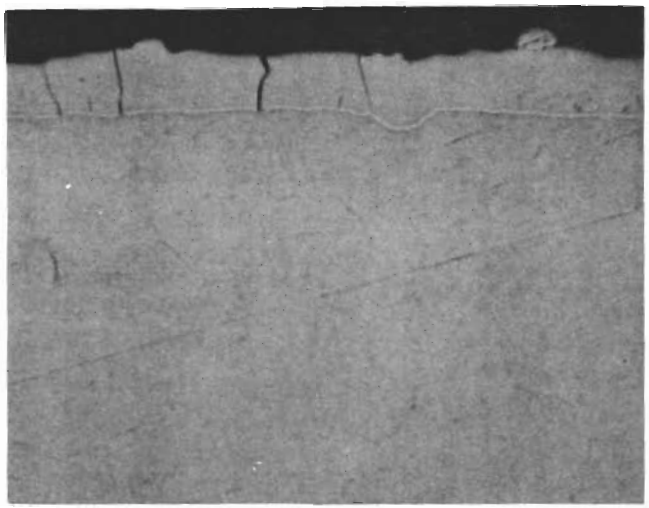
Figure 33. Metallography: Photographs Showing Representative Surface of Coating Deposit from Gas Feed Geometry Study and First Statistical Series (250X)



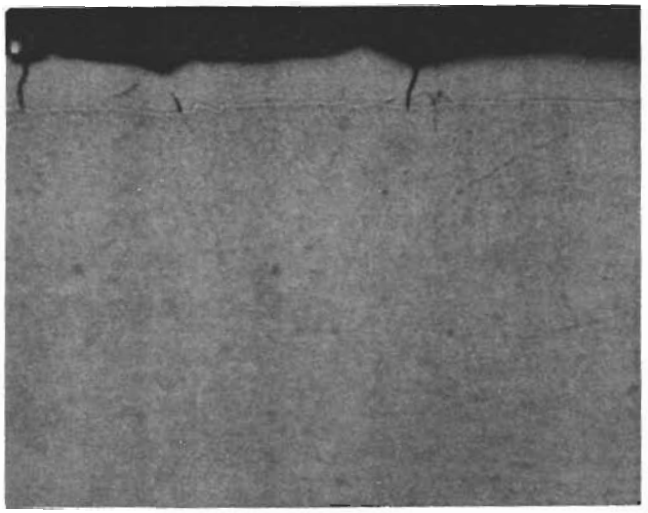
(a) CLY-113-68



(b) CLY-114-68



(c) CLY-115-68



(d) CLY-116-68

Figure 34. Metallography: Photographs of Cross Section Showing Coating and Substrate Resulting from Second Statistical Series (X500)

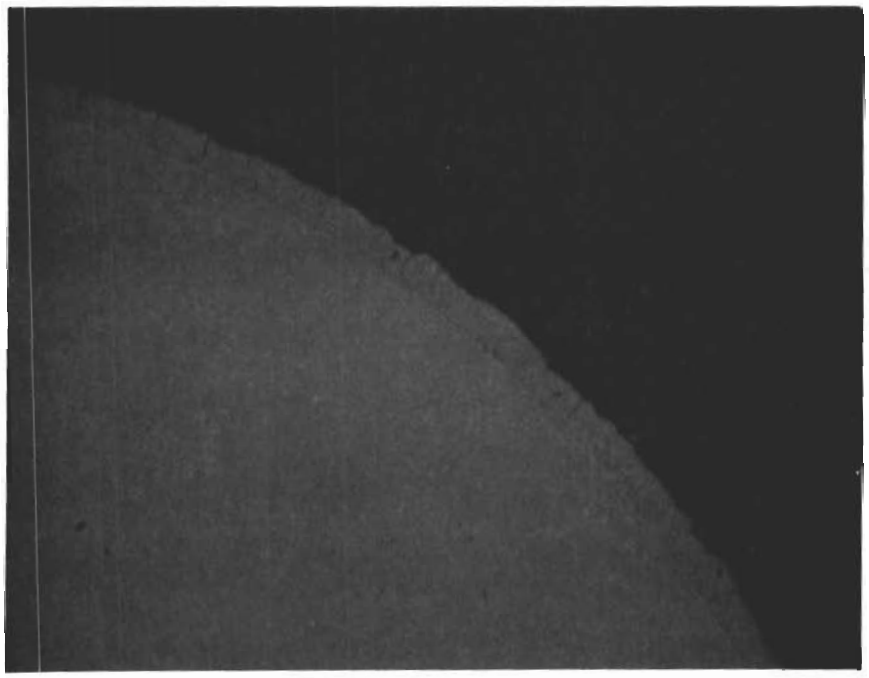
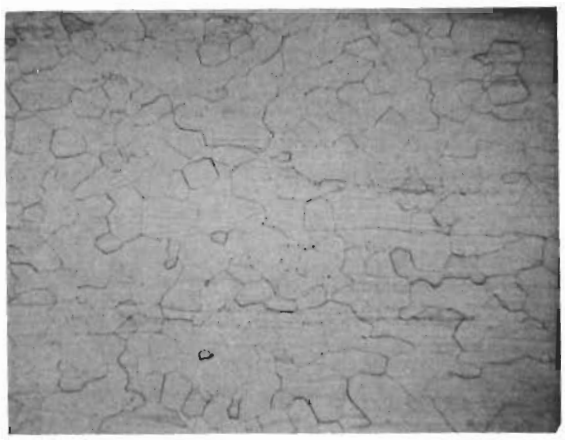
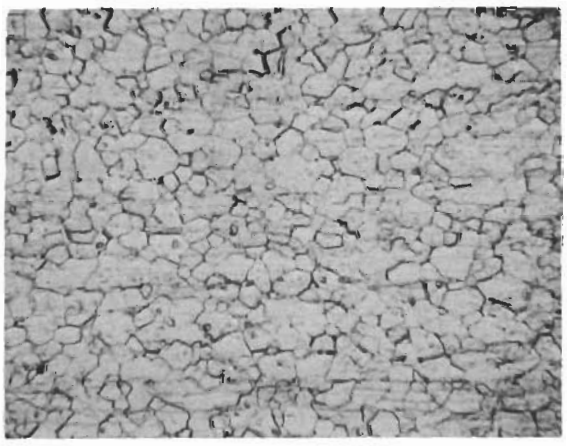


Figure 35. Metallography: Photograph of Mounted Cross Section for Deposit Phase Run Sample Showing Coating Coverage of Threaded Substrate (50X)



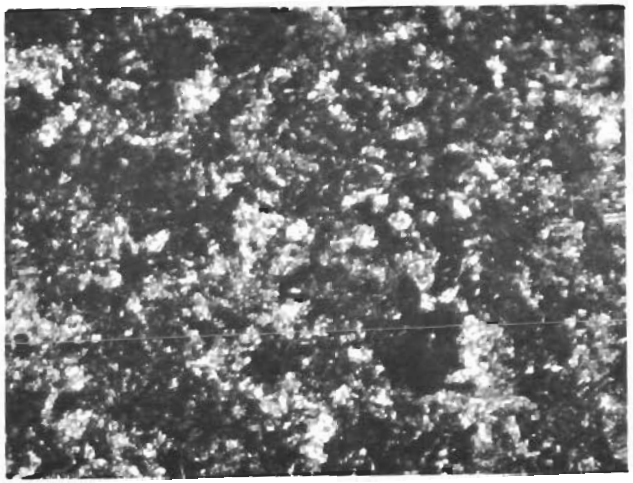
(a) Before Coating, as Received

(b) After Coating (CLY-138-69)

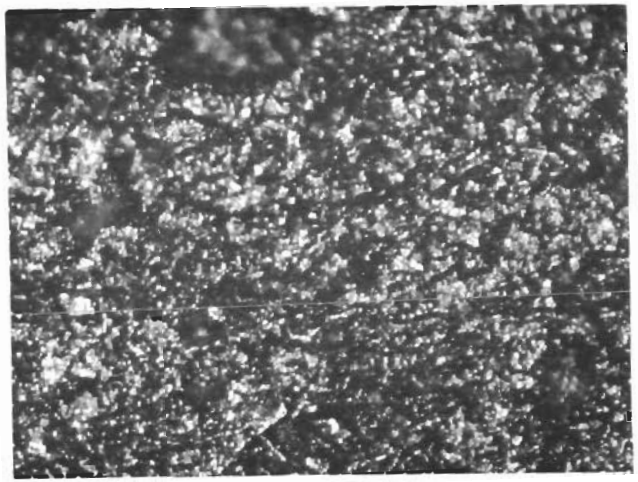


(c) After Coating (CLY-139-69)

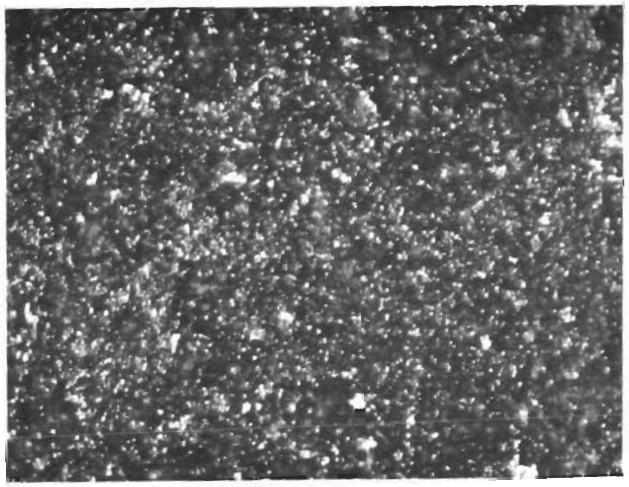
Figure 36. Metallography: Structure of Cb 752 Alloy Substrate Before and After Coating (1-Inch Threaded Stud, 500X, Etchant: 1 Part HNO_3, 1 Part HF and 1 Part Glycerin)



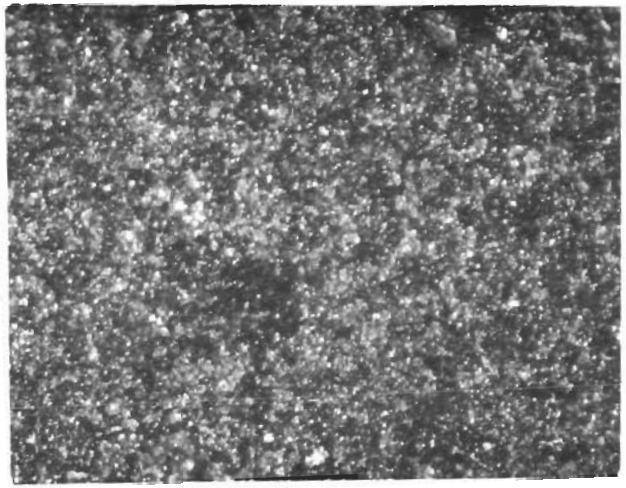
(a) As Received (Cb 752 Alloy)



(b) After Etching (Cb 752 Alloy)



(c) After Coating (CLY-151-68)



(d) After Coating (CLY-154-68)

Figure 37. Metallography: Surface of Cb 752 Alloy Before and After Coating in Coating Oxidation Sample Run (250X)

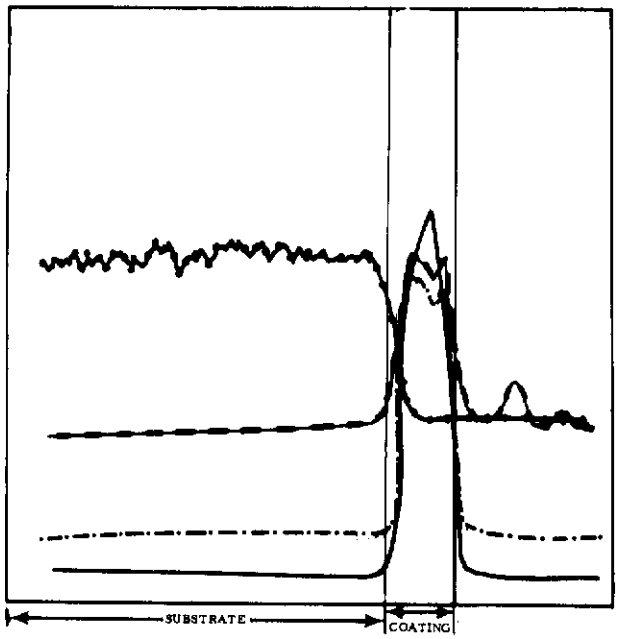
C. ELECTRON MICROPROBE

For "coating composition," electron microprobe traces showing chromium, titanium and silicon concentrations in the coating deposit are presented in Figure 38 for representative samples prepared in gas feed geometry study and first statistical series. In the figure, the microprobe trace height is for each component concentration in the coating. The traces for both flat panel and round rod substrates disclose that Cr, Ti and Si components are contained in the coating with negligible siliciding of substrate.

For representative second statistical series samples, coating compositions are illustrated with the electron microprobe traces shown in Figure 39. It is again noted in the figure that the respective components comprise the coating deposit with minimal siliciding of substrate. On the basis of relative constant level component traces across the coating (i.e., from coating-substrate interface to coating surface), the traces further reveal fairly constant component concentrations for Cr, Ti and Si in the coating deposit.

Coating compositions from electron microprobe traces for chromium, titanium and silicon are shown in Figure 40 for samples from coating oxidation sample runs. The graphical plots in the figure disclose the respective chromium, titanium and silicon concentration in the coating from coating-substrate interface to coating surface. The coating composition shown in Figure 40a is for the sample providing high oxidation resistance at 2200°F test temperatures. Figure 40b displays coating composition for sample with high oxidation resistance at 2400°F testing from coating oxidation samples with reactor loading of ten substrates.

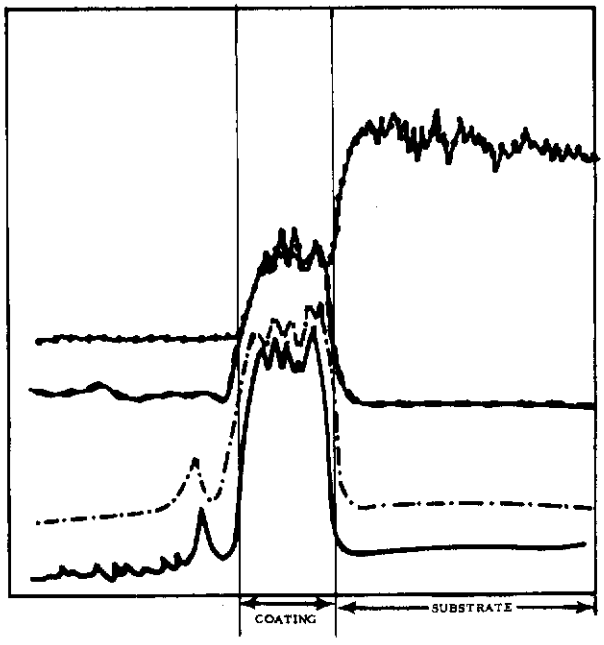
Coating compositions for all samples prepared in initial coating oxidation sample runs are presented in Table XXXII. The average component concentrations for chromium, titanium and silicon in the table apply for coating at the base of the 1-in. threaded stud substrate.



(a) CLY-90-68 (Flat Panel Substrate)

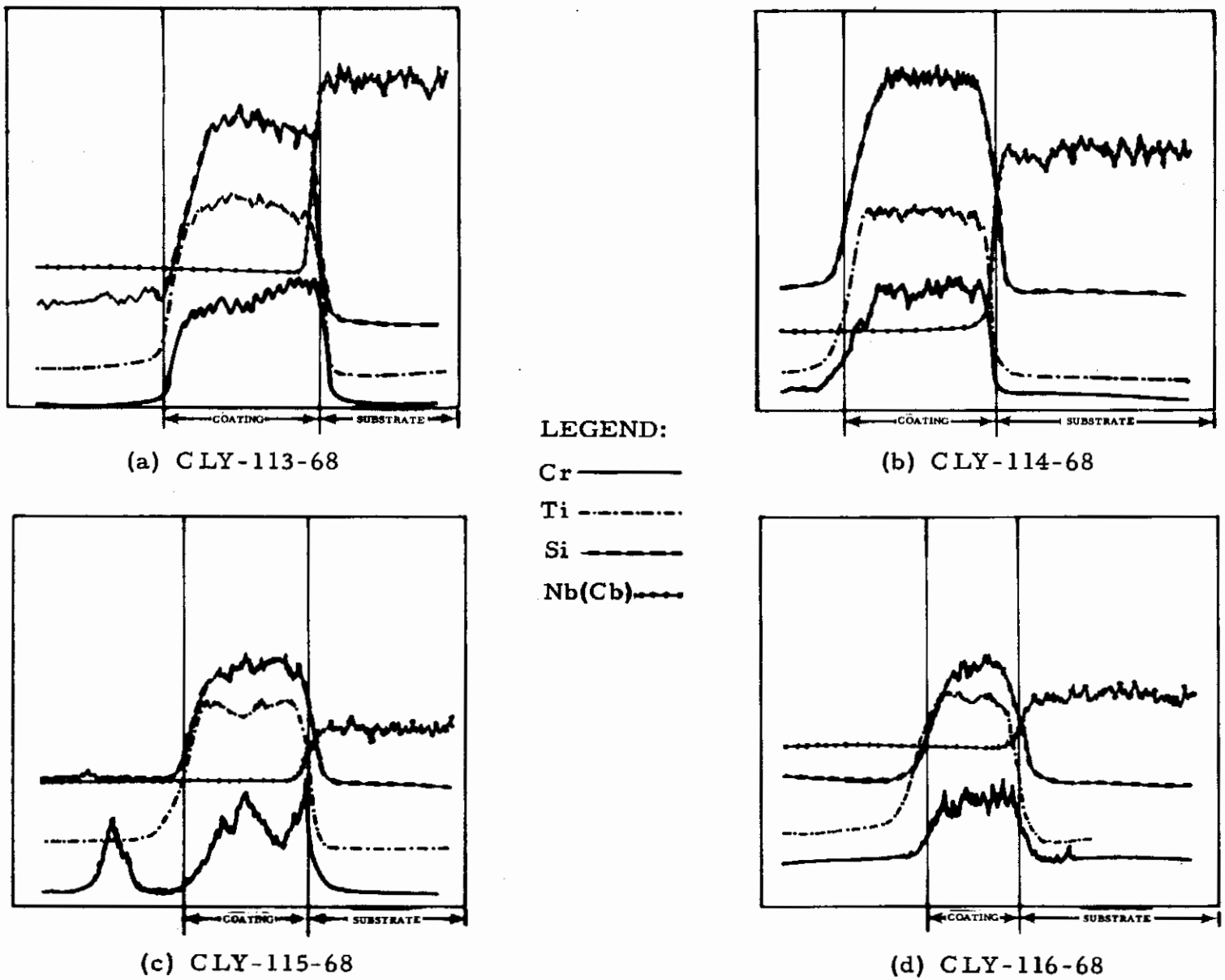
LEGEND:

Cr ——————
Ti -·-·-·-·-
Si ——————
Nb(Cb)——



(b) CLY-93-68 (Round Substrate)

Figure 38. Electron Microprobe: Analysis of Coating Deposit from Gas Feed Geometry Study



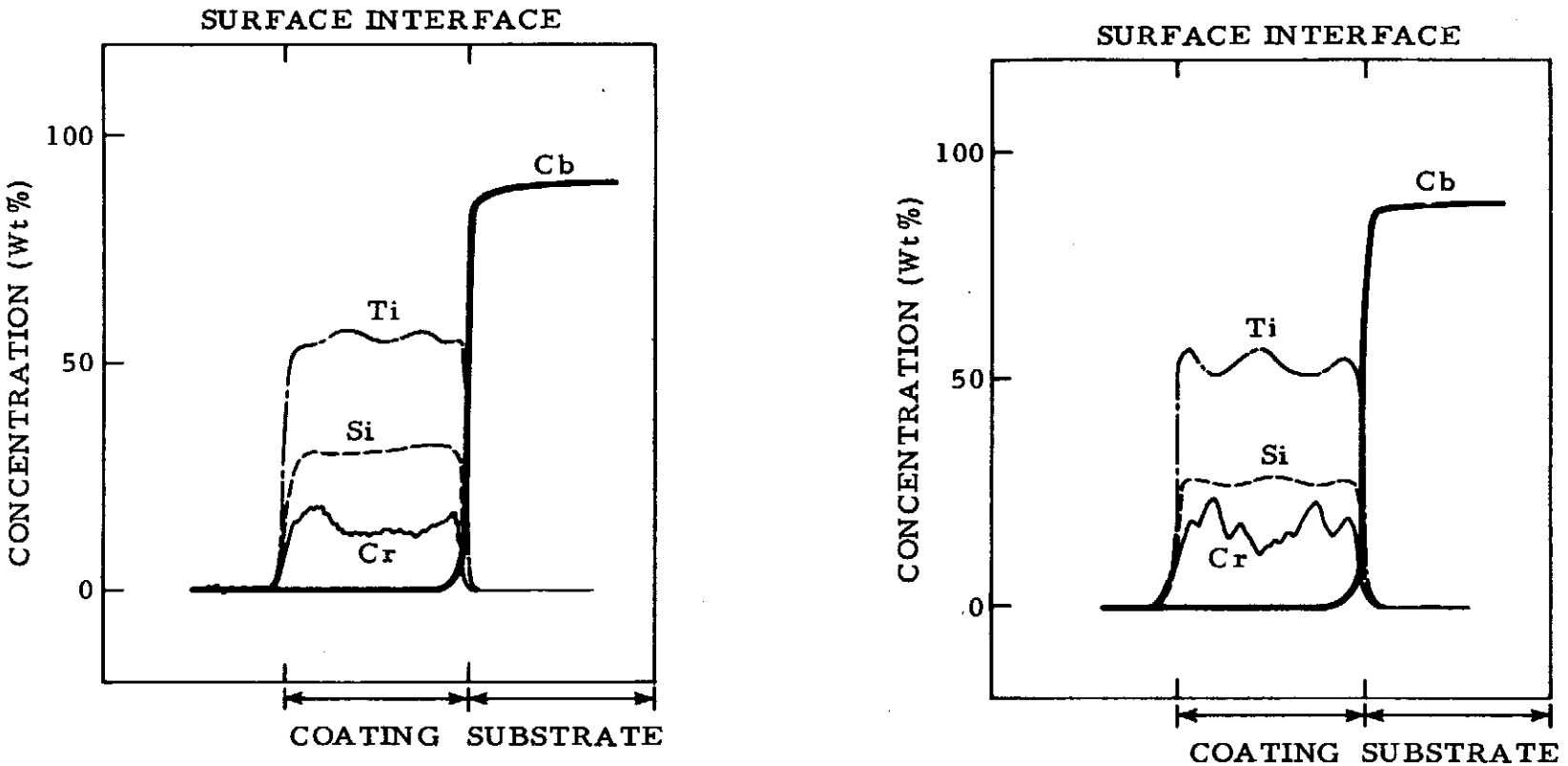
(a) CLY-113-68

(b) CLY-114-68

(c) CLY-115-68

(d) CLY-116-68

Figure 39. Electron Microprobe: Analysis of Coating Deposit from Second Statistical Series



(a) CLY-151-68

(b) CLY-154-68

Figure 40. Electron Microprobe: Coating Composition of Samples from Coating Oxidation Sample Runs (1-in. threaded stud)

Table XXXII

COATING COMPOSITION FROM ELECTRON MICROPROBE ANALYSIS OF SAMPLES FROM INITIAL COATING OXIDATION SAMPLE RUNS

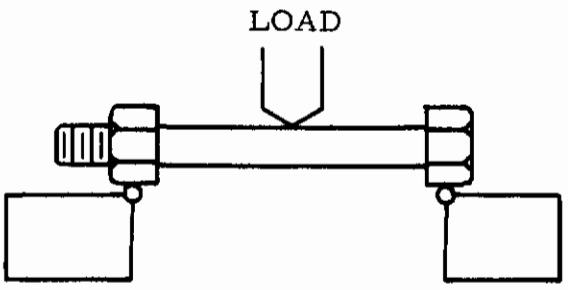
Run Number	Coating Composition: Average Component Concentration (wt %)		
	Cr	Ti	Si
1	8.7	61.0	30.3
2	11.5	53.7	34.8
3	8.7	61.3	30.0
4	11.9	55.6	32.5
5	19.3	52.5	28.2
6	17.5	54.3	28.2
7	14.5	55.2	30.3
8	18.4	51.0	30.6

Other Conditions:

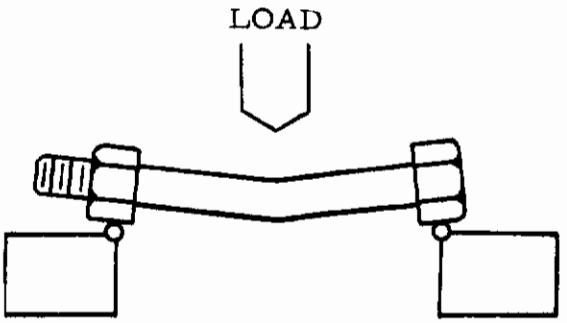
- Average component concentration is based on average electron microprobe analysis for each component in coating at base of threaded substrate.
- Run number refers to run in statistical plan for initial coating oxidation sample runs.

D. STRAIN EFFECT TEST

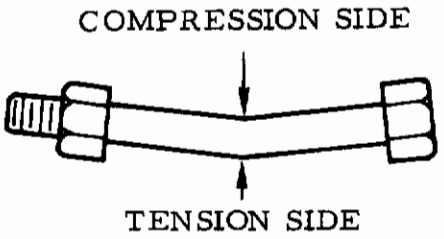
Progress was achieved in "strain effect test-evaluate" strained samples which involved applying strain on the sample and testing for oxidation performance of the strained sample. Application of strain on sample at two strain levels was made by equipment shown in Figure 41. Figures 41a and 41b illustrate the sample shape before and after strain. The compression and tension sides of the strained sample are depicted in Figure 41c. In most of the samples, a several hundred pound load was applied to deform coated sample and obtain strain on one quarter inch diameter samples. The resulting displacement from original shape was approximately ten mils for the high strain level and five mils for the low strain level.



(a) Before Strain



(b) After Strain



(c) After Strain

Figure 41. Strain Effect Test: Equipment Sketch for Applying Strain to Sample at High and Low Strain Levels (1 1/2-in. Hex Head Bolt)

Figure 42 presents oxidation performance results of the strained samples. The figure applies for 2400°F coating oxidation resistance for samples with and without strain (i.e., no strain, high strain level and low strain level). The undarkened graphical colums in the figure represent test data for samples without strain. The darkened graphical columns correspond to samples at high and low strain levels. Based on data shown in the figure for testing of twelve coated samples, completion of strain effect test-evaluate strained samples suggests that oxidation performance of the strained samples is within the scope of results for unstrained samples.

E. CYCLIC OXIDATION

Cyclic oxidation testing of samples — coated 1 1/2-in. hex head bolt refractory fasteners of columbium alloy composition Cb 752 — prepared in duplicate best coating runs was made at test temperatures of 2200°F, 2400°F, and 2600°F. The mean and distribution for cyclic 2400°F oxidation test results are graphically shown in Figure 43 for the 1 1/2-in. hex head bolt substrates which were coated with the fabricated reaction chamber (i.e., Reaction Chamber D). The first two runs in the figure (i.e., CLY-160-69 and CLY-161-69) were made at process conditions which provided best 2400°F coating oxidation resistance for 1-in. threaded stud substrates which were coated with the small reaction chamber (i.e., Reaction Chamber C). Comparison of the test results at high substrate reactor loading of ten (mean time: 27.4 hr. protection for 1-in. threaded stud versus 2 hr. protection for 1 1/2-in. hex head bolt as shown in Figure 43) indicate that change of substrate and reactor influences coating oxidation performance. Further, the comparison of mean test time to failure on successive runs in the figure indicates improvement of coating oxidation performance.

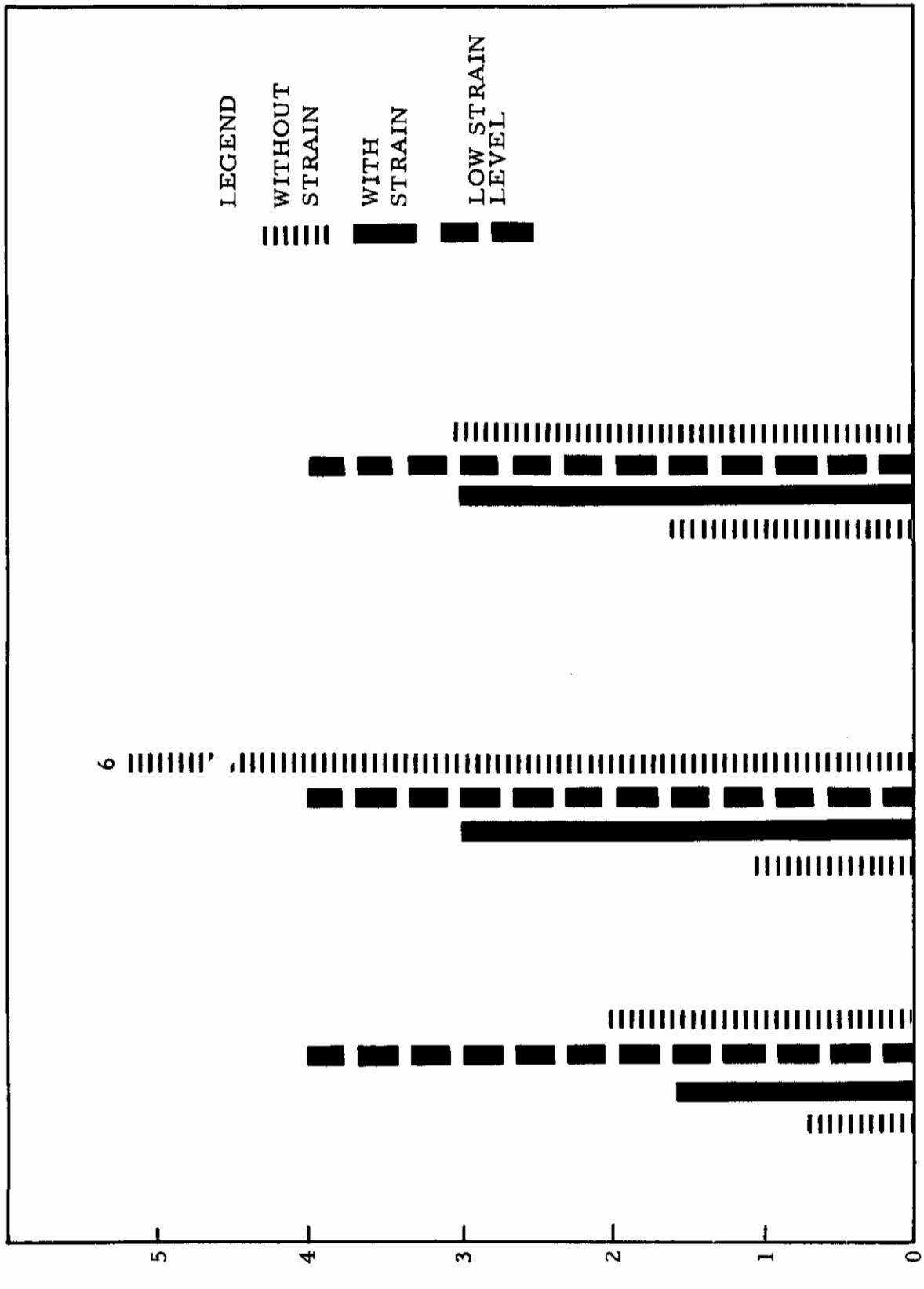


Figure 42. Strain Effect Test: 2400°F Oxidation Test Results for Samples at No Strain, High Strain Level and Low Strain Level (1 1/2-in. Hex Head Bolts)

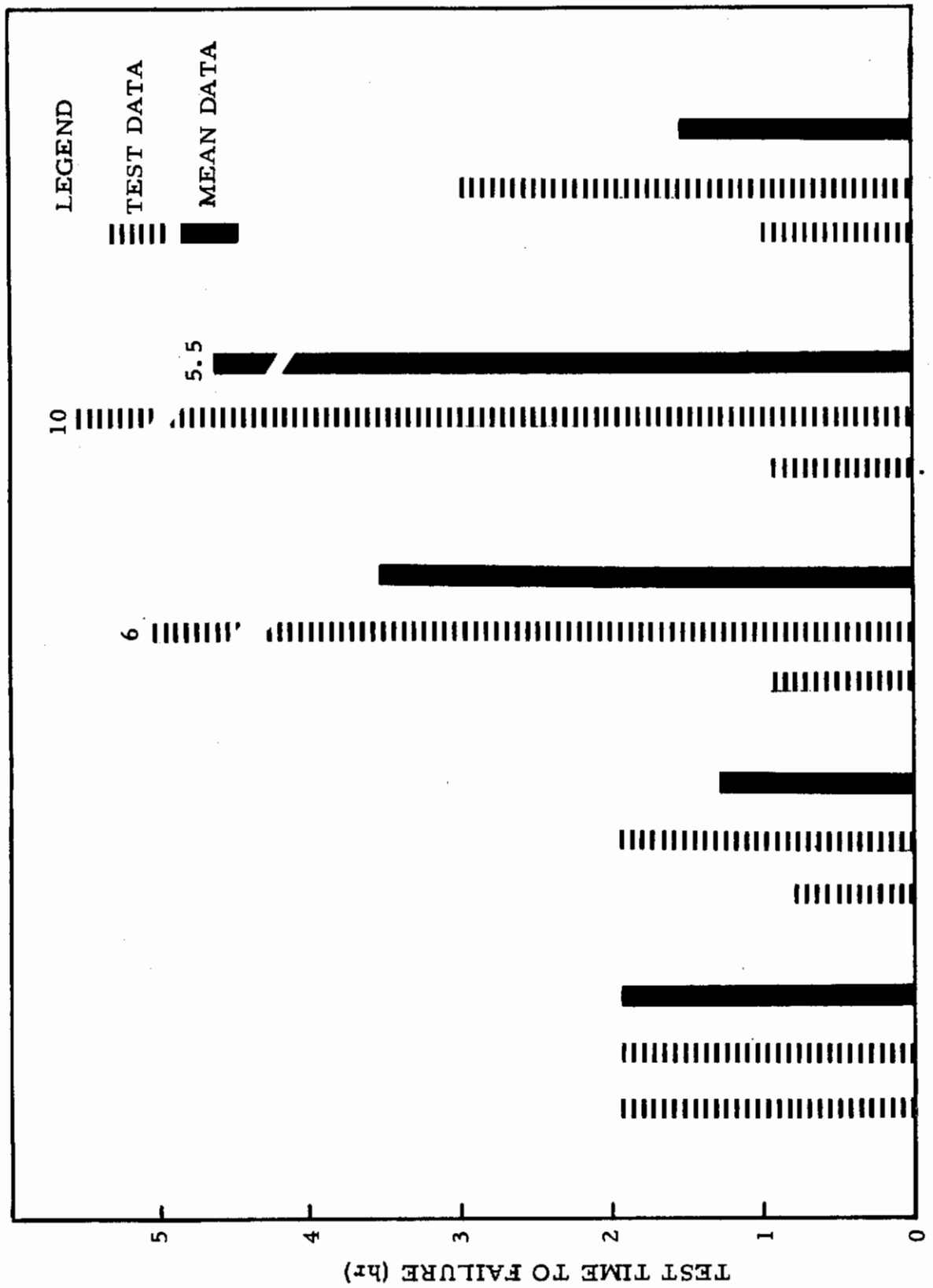


Figure 43. Cyclic Oxidation: Mean and Distribution for 2400°F Oxidation Test Results for Samples Prepared in Duplicate Best Coating Runs (1 1/2-in. Hex Head Bolts)

Figure 44 displays the mean and distribution of 2400°F oxidation test results for different shaped substrates coated in subsequent representative "product fastener" run. These results – especially the relative test time to failure for 1 1/2-in. round rod and 1 1/2-in hex head bolt substrates – were used as the base for the next experiments for coating oxidation property improvements.

Oxidation test results are shown in Figure 45 for representative cyclic oxidation runs in which round rod substrates were prepared at the reactor loading level of twenty substrates in the deposition run. Based on three different runs, the figure discloses coating protection of the round rod substrate from 2400°F oxidation for a test time exceeding thirty-five hours. Additional cyclic oxidation runs for coating oxidation property improvement were conducted. Figure 46 contains the oxidation test results for the additional runs. The figure reveals that for three coated samples (i.e., samples from three different runs) the coating protects the base substrate from 2400°F oxidation for test time exceeding eightly hours. This test time to failure of eighty plus hours was a considerable improvement over the previous thirty-five plus hours of protection.

Figure 47 presents 2600°F oxidation test results for representative cyclic oxidation runs in which round rod substrates were coated.

For production demonstration batches (i.e., coating of refractory fasteners – hex head bolts and hex nuts – at increased loading), four batches were selected from the process demonstration runs for use in the external testing. Cyclic oxidation results for the batches – A, B, C and E – are presented in Figures 48 and 49 for 2400°F and 2200°F test temperatures. The graphical results apply for both refractory fastener bolt and nut shapes (i.e., in testing, the CVD coated hex head bolt was attached to hex-nut as shown). Failure in most cases (for both test temperatures) involved small pin hole oxidation breaks in nut and thread regions. In general, the test time to failure in 2400°F oxidation environment exceeds twenty hours. It is noted that the twenty plus hour coating protection of the substrate applies for refractory fasteners coated at the increased current coating capability of coating thirty to fifty substrates per deposition run.

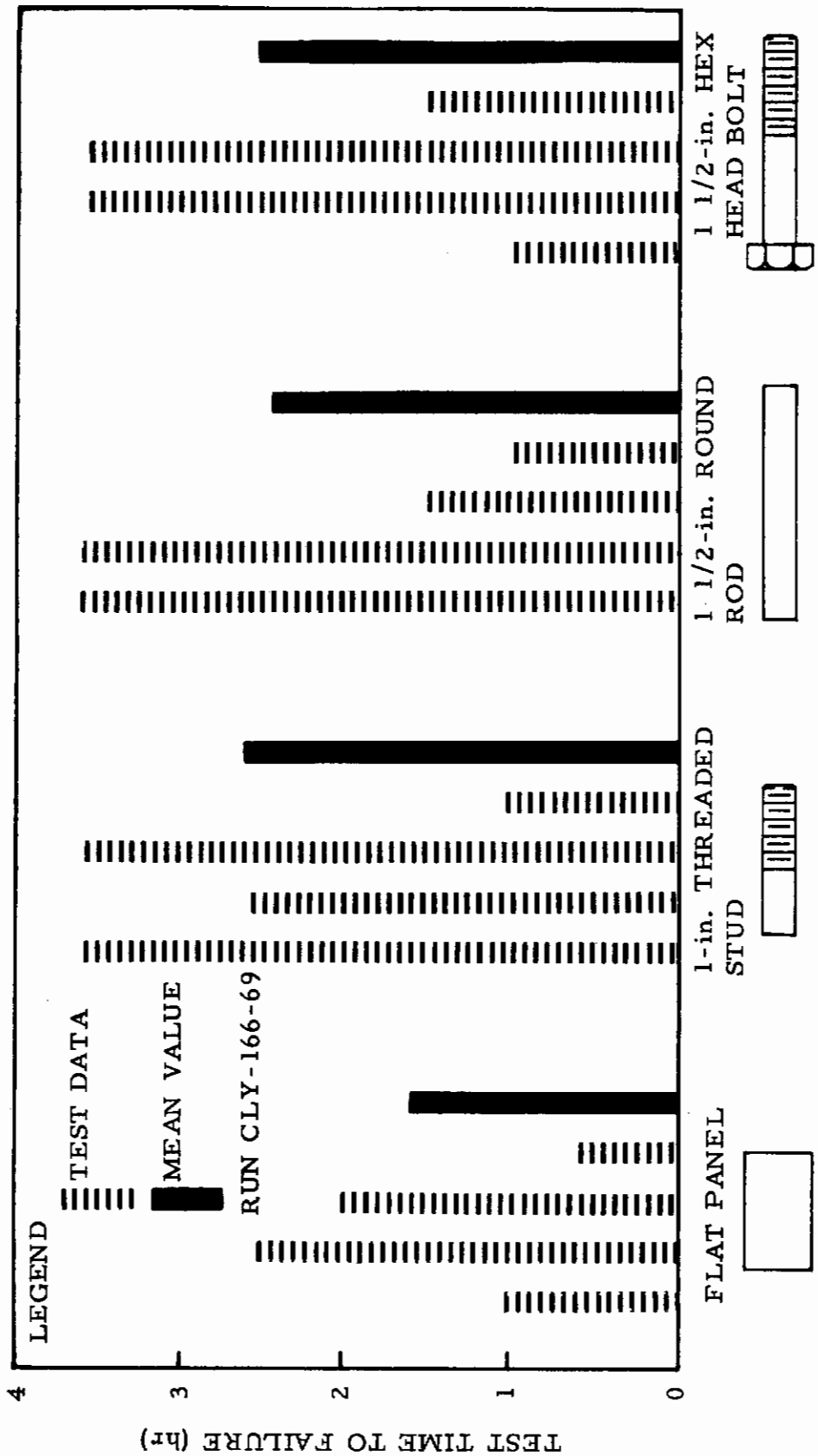
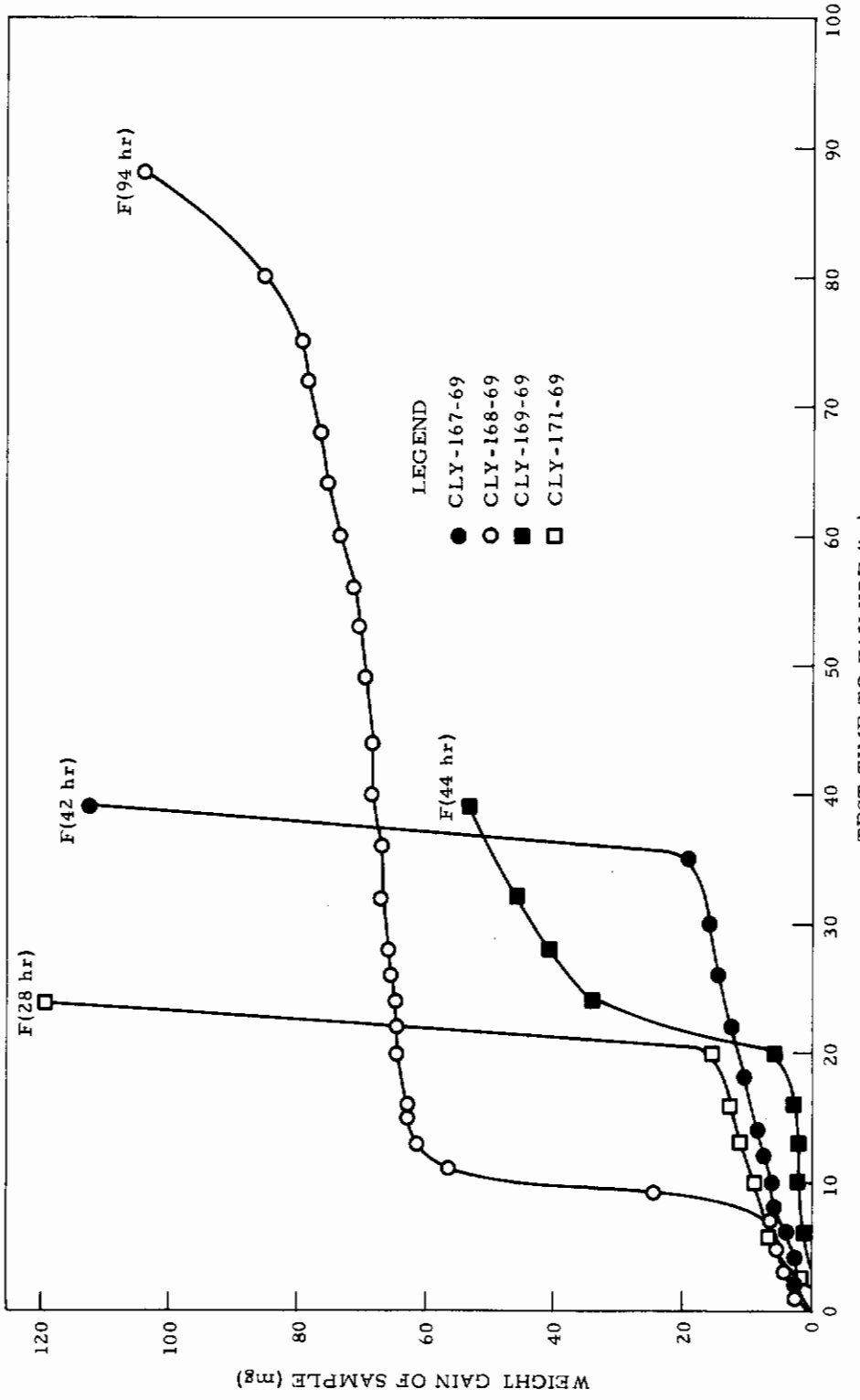
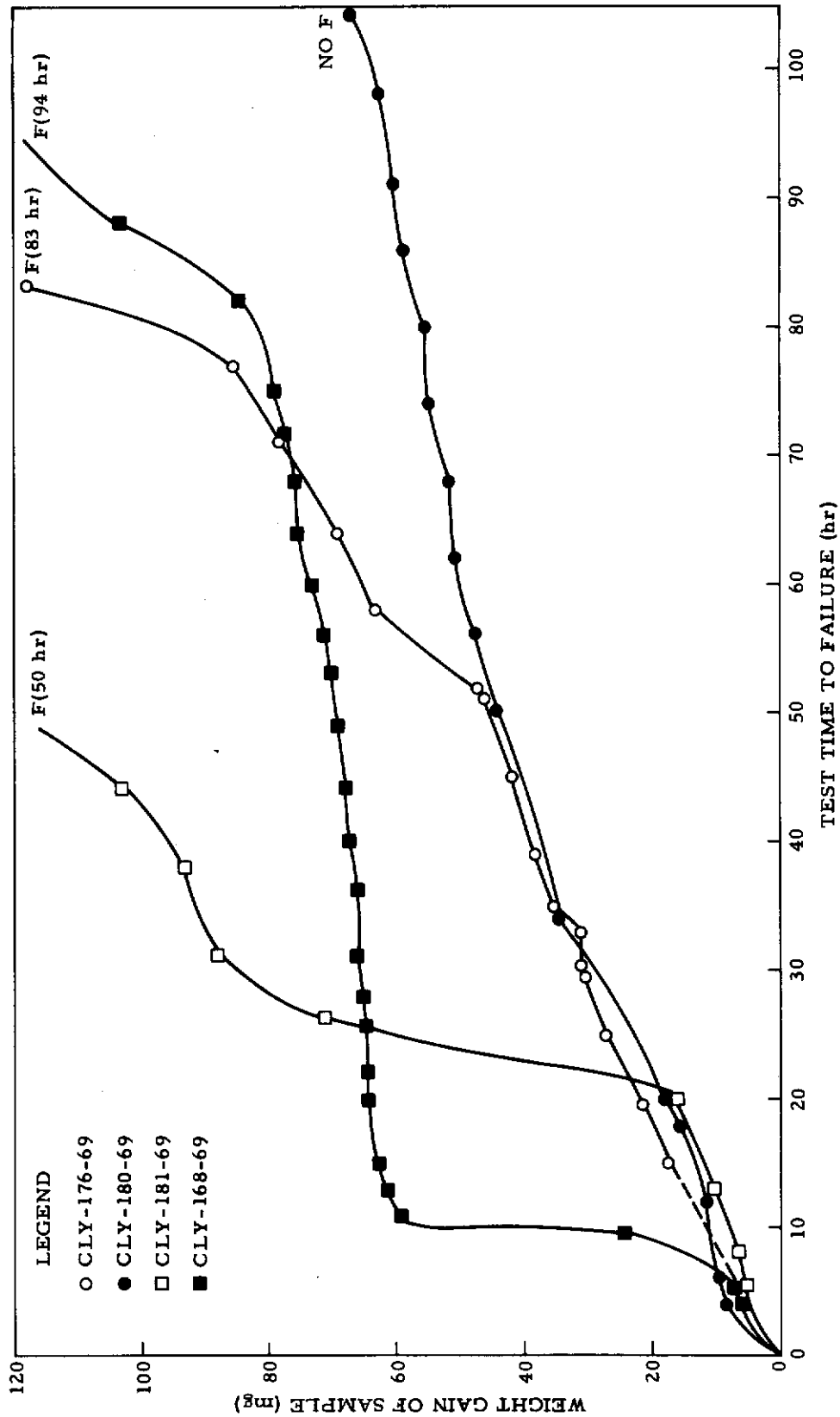


Figure 44. Cyclic Oxidation: Mean and Distribution for 2400°F Oxidation Test Results for Differently Shaped Substrated Coated in Representative Produce Fastener Run



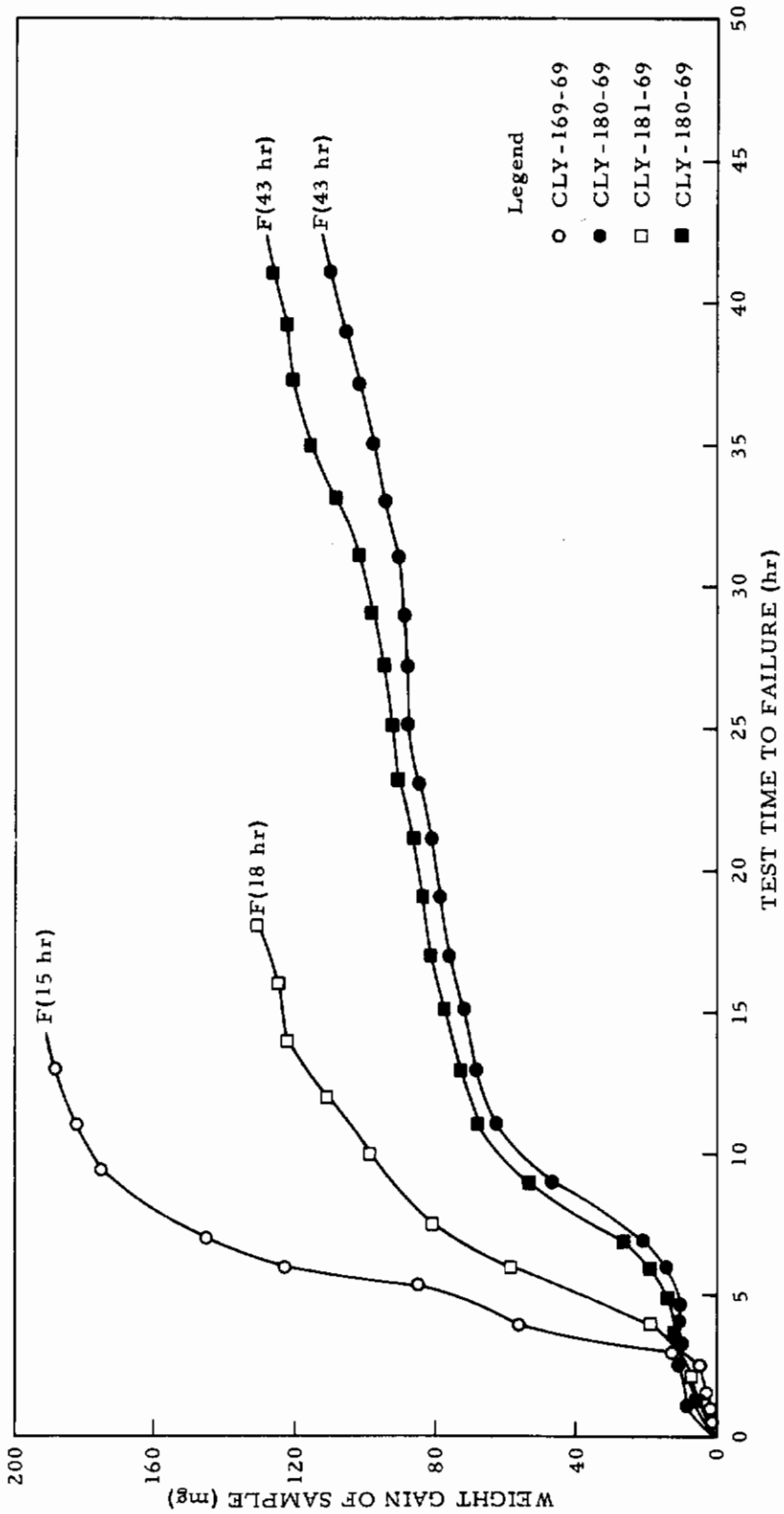
1 1/2-in. ROUND ROD SUBSTRATE

Figure 45. Cyclic Oxidation: 2400°F Oxidation Test Results for Representative Cyclic Oxidation Runs



1 1/2-in. ROUND ROD SUBSTRATE

Figure 46. Cyclic Oxidation: Additional 2400°F Oxidation Test Results for Representative Cyclic Oxidation Runs



1 1/2-in. ROUND ROD SUBSTRATE

Figure 47. Cyclic Oxidation: 2600°F Oxidation Test Results for Representative Cyclic Oxidation Runs

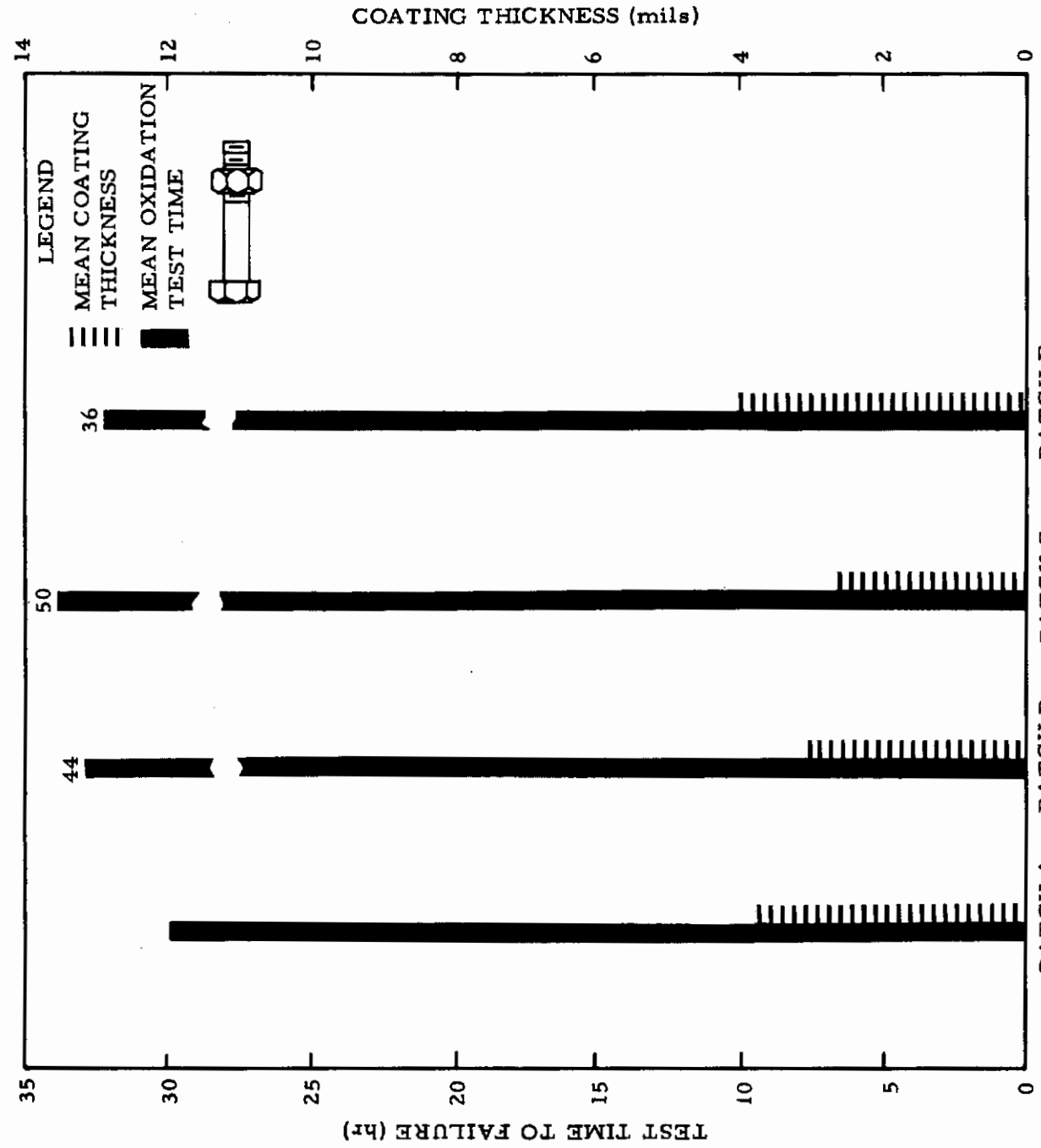


Figure 48. Cyclic Oxidation: 2400°F Cyclic Oxidation Results for Refractory Fasteners Coated at Current Coating Capability

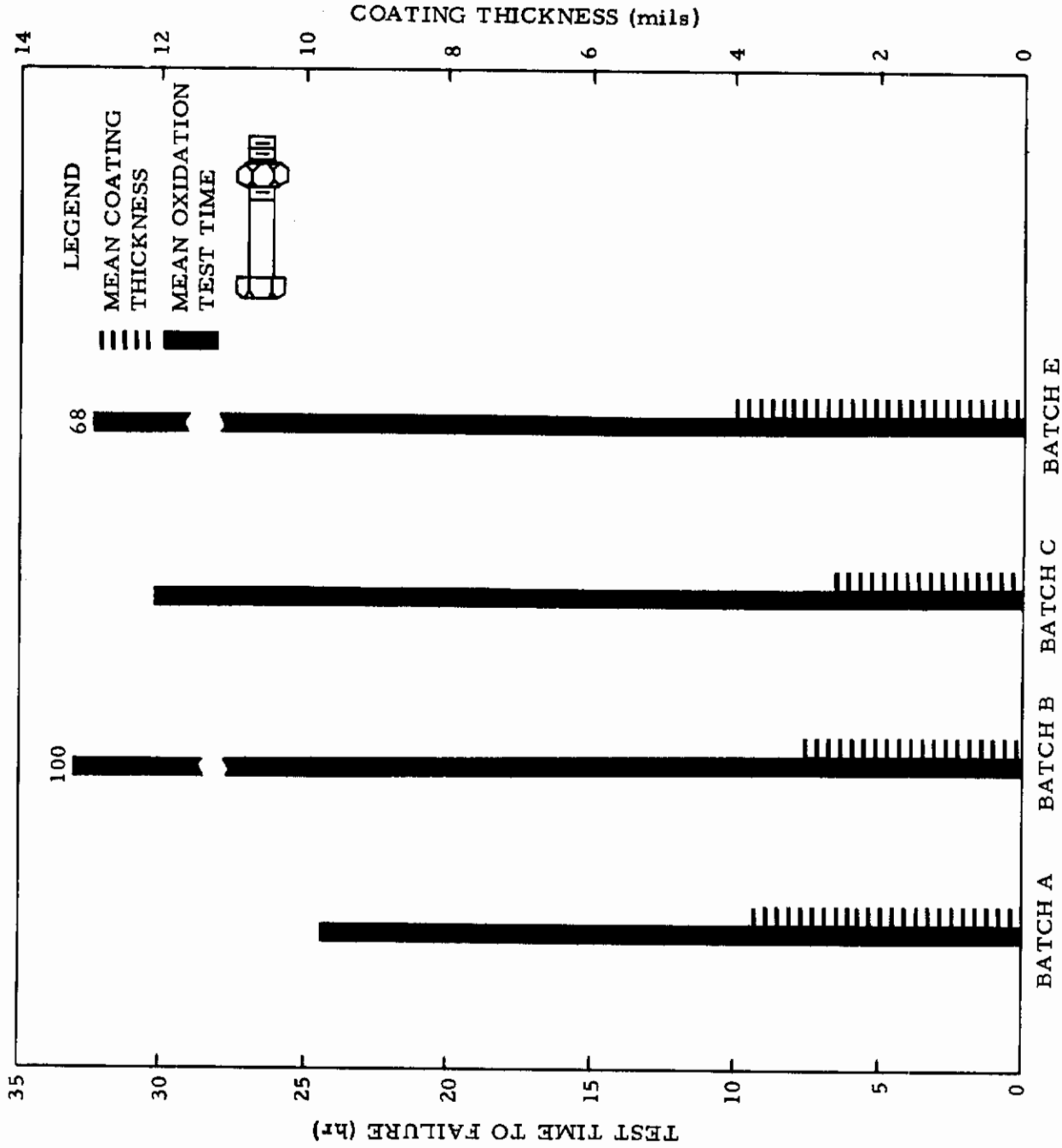


Figure 49. Cyclic Oxidation: 2200°F Cyclic Oxidation Results for Refractory Fasteners Coated at Current Coating Capability

F. MECHANICAL TESTS — EXTERNAL TEST — COMPARE TO STATE-OF-ART

Mechanical tests and external tests involved mechanical property testing and an independent evaluation of the coated refractory fasteners. Specific mechanical testing included ultimate and shear strengths in the respective temperature ranges of 80-2600°F and 80-2400°F. This testing was conducted by Standard Pressed Steel Co. (See tables in Appendix LV) on Cb 752 refractory fasteners which were coated at the increased current capability of coating thirty to fifty substrates per run with the processing equipment.

Ultimate tensile strength results including post-heat treatment coated samples at the various temperature levels are presented in Table XXXIII for fasteners from production demonstration batches. The tensile strength versus temperature is shown in Figure 50. The results indicate low tensile strength at room temperature but good tensile strength in the higher temperature ranges beginning at 600°F and extending into the 2000°F plus temperature. The room temperature tensile strength is significantly improved with post-heat treatment as shown for random production samples.

Table XXXIV gives the shear strength of coated refractory fasteners from the same production demonstration batches. Figure 51 depicts the shear strength versus temperature plot. Two of the shown batches exhibit low room temperature shear strength with better strength in the 600°F temperature range. With post-heat treatment, the shear strength at room temperature is appreciably enhanced as illustrated by the positive dotted lines.

Relaxation and reusability test results are shown in Tables XXXV and XXXVI for the refractory fasteners coated in production demonstration batches. For reusability, the tabulated results disclose slight and negligible coating damage at 2000°F test temperature.

Table XXXIII

ULTIMATE TENSILE STRENGTH OF COATED REFRACTORY FASTENERS FROM PRODUCTION DEMONSTRATION BATCHES*

Test Temp. °F	Batch B		Batch E		Batch A		Batch D	
	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)
	1800		1670		1050		1640	
80	1350	49,500	1430	48,700	1000	32,200	1420	48,100
80**	2400		2400		2400		2400	
	2800	84,800**	2800	84,800**	2800	84,800**	2800	84,800**
	2900		2900		2900		2900	
600	2015		1960		2065		1855	
	2080	64,300	2110	63,900	2090	65,300	1955	59,800
2000	1390		1430		1390		1200	
	1320	42,500	1410	44,600	1500	45,400	1150	36,900
2400	835		760		760		763	
	860	26,600	746	23,600	826	24,800	680	22,700
2600	635		635		670		595	
	638	20,000	640	20,000	690	21,400	637	19,400

*Tests conducted by Standard Pressed Steel Co. (SPS)

**With post-heat treatment of coated fasteners. Coated samples selected at random from production demonstration runs.

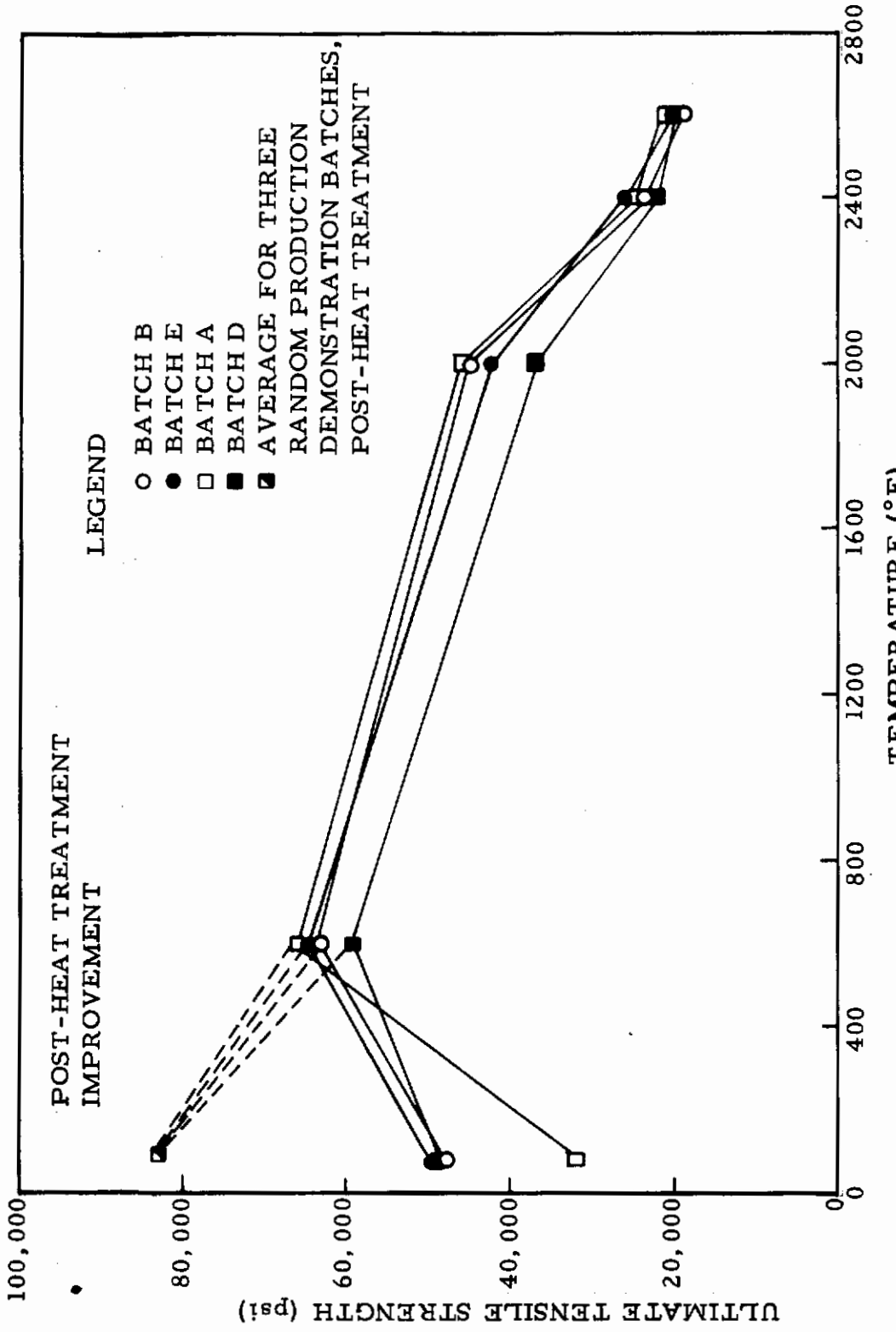


Figure 50. Mechanical Tests: Ultimate Tensile Strength versus Temperature for Production Demonstration Batches

Table XXXIV

SHEAR STRENGTH OF COATED REFRACTORY FASTENERS FROM PRODUCTION DEMONSTRATION BATCHES*

Test Temp. °F	Batch B		Batch E		Batch A		Batch D	
	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)
80	3250		3400		2540		5320	
	5450	41,900	2600	28,900	2310	23,400	5300	51,100
80**	6400		6400		6400		6400	
	6450	65,700**	6450	65,700**	6450	65,700**	6450	65,700**
	6460		6460		6460		6460	
600	4275		4320		4375		4275	
	4275	41,200	4240	41,300	4375	41,800	4180	40,800
2000	3335	32,100	3125	30,100	3065	29,500	3080	29,700
2400	2125	20,500	2205	21,300	2220	21,400	2050	19,800

*Tests conducted by Standard Pressed Steel Co. (SPS)

**With post-heat treatment of coated fasteners. Coated samples selected at random from production demonstration runs.

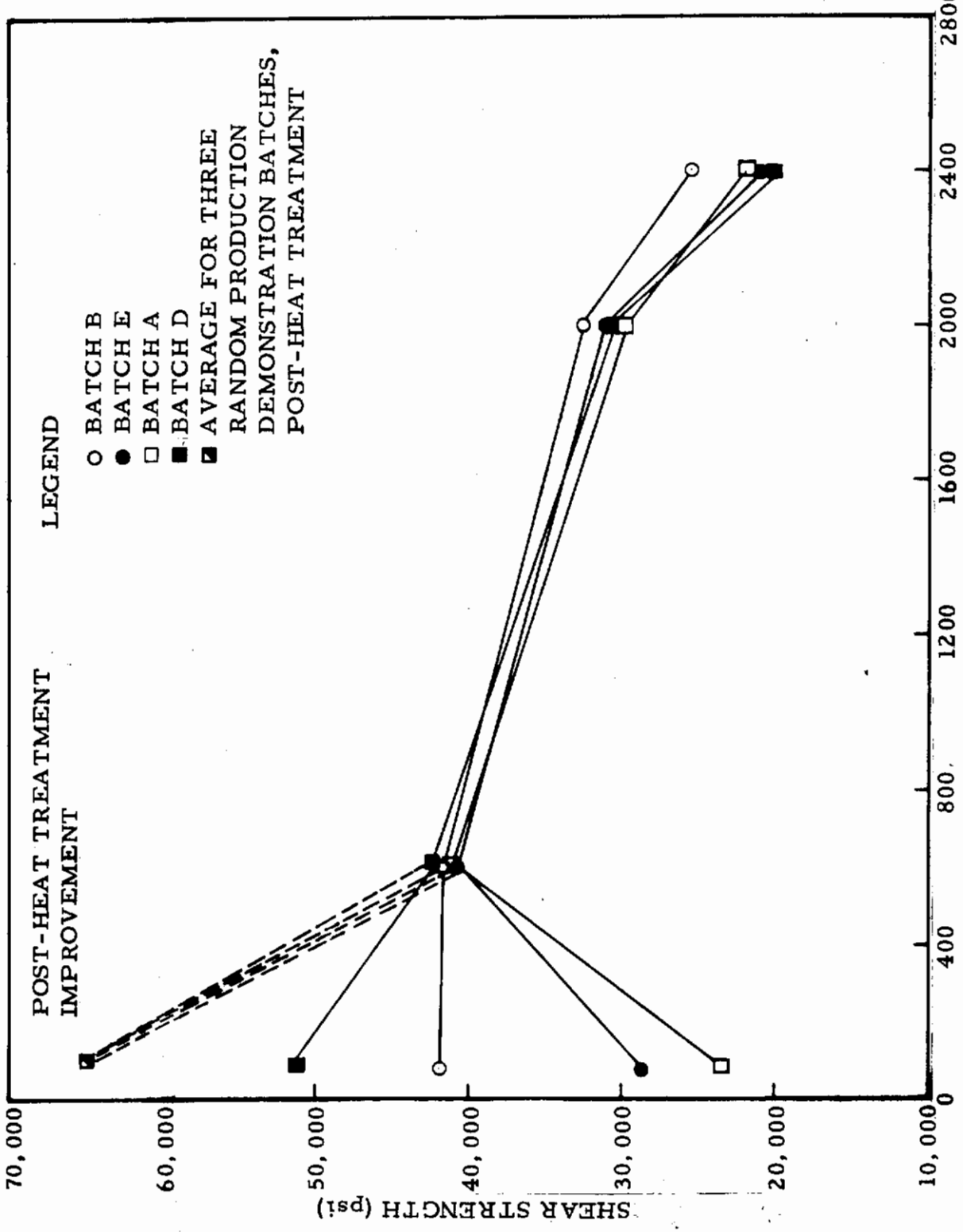


Figure 51. Mechanical Tests: Shear Strength versus Temperature for Production Demonstration Batches

Table XXXV

RELAXATION TEST RESULTS FOR COATED REFRACTORY FASTENERS FROM PRODUCTION DEMONSTRATION BATCHES *

Batch Type	Temperature °F	Length After Soak (Seated)	Length After Soak (Unseated)	Change in Length	Residual Load, psi
A	2000	1.6755	1.6752	0.0003	3750
B	2000	Broke Loading			
D	2000	1.6650	1.6648	0.0002	2500
E	2000	1.6764	1.6761	0.0003	3750
A	2400	Broke Loading			
B	2400	1.6855	1.6854	0.0001	1250
D	2400	1.6638	1.6637	0.0001	1250
E	2400	1.6809	1.6808	0.0001	1250

TEST CONDITIONS

Hex head bolts preloaded to 15,000 psi and exposed to elevated temperatures as shown for two hours.

*Tests conducted by Standard Pressed Steel Co. (SPS)

Table XXXVI

REUSABILITY RESULTS FOR COATED REFRACTORY FASTENERS FROM PRODUCTION DEMONSTRATION BATCHES *

Batch Type	Difficulty of Nut Removal		Coating Damage
	Starting	Turning	
	Test Temperature — 2000°F		
A	Very high breakaway	hard (wrench required)	slight
A	high breakaway	easy (finger loose)	Nil
B	high breakaway	easy (finger loose)	Nil
B	Very high breakaway	easy (finger loose)	Severe
D	high breakaway	easy (finger loose)	slight
D	Very high breakaway	hard (wrench required)	slight
E	high breakaway	easy (finger loose)	Nil
E	finger loose	easy (finger loose)	Nil
	Test Temperature — 2400°F		
A		no movement	
A		no movement	
B	Very high breakaway	hard (wrench required)	severe
B		no movement	
D		no movement	
D		no movement	
E		no movement	
E		no movement	

TEST CONDITIONS

Bolt, nut removal of parts tensile tested at 2000°F and 2400°F

*Tests conducted by Standard Pressed Steel Co. (SPS)

With respect to state-of-art, it is recognized that the coating oxidation protection of a substrate exposed to high temperature oxidation environment is influenced by many factors (substrate material, shape, temperature, exposure time, coating thickness, coating process, etc.). For columbium alloys, several of these factors are mentioned and discussed in a fairly recent literature review.[3]

A cursory state-of-art comparison for cyclic oxidation and mechanical properties is presented in Table XXXVII. The tabulation is based on limited literature screening. The tabulation involves several of the many factors influencing oxidation protection, i.e., substrate material, substrate shape, coating thickness, temperature and cyclic oxidation life. For cyclic oxidation, the data discloses thirty plus hour protection of hex head bolt substrate exposed to 2400°F oxidation environment for both this program and the other source presenting data for the same refractory fastener shape. For mechanical properties, room temperature tensile and shear strengths for this program are quite good for the post-heat treatment samples. In general, the remaining tabulated data suggests a favorable state-of-art comparison (i.e., comparable cyclic oxidation life and tensile shear strengths for shown temperature range).

Completion of this program activity disclosed the mechanical and cyclic oxidation state-of-art properties of coated Cb 752 refractory fasteners from production demonstration batches. For mechanical properties, tensile and shear strengths were favorable in temperature range of 80°F to above 2000°F. For cyclic oxidation, cursory literature screening revealed favorable state-of-art comparison based on this program and two independent literature sources.

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[3] Maisel, L., Metal Finishing, pg 76, January, 1968.

Table XXXVII

COMPARE TO STATE-OF-ART: CURSORY STATE-OF-ART COMPARISON ON CYCLIC OXIDATION AND ON MECHANICAL PROPERTIES

Cyclic Oxidation				
Identification	Substrate Alloy/Shape	Coating Thickness (mils)	Oxidation Temperature (°F)	Cyclic Oxidation Life (hrs)
This Program	Cb 752/Round Rod	3-3.5	2400 2600	90 43
	Cb 752/Hex Head Bolt and Nut	2.5-3	2200 2400 2600	100-no failure 44-50 0.5
	Cb 752/Hex Head Bolt	2.5-3	2400	38
Literature Review[1]	Cb 752/-	3	2000 2650	22 2
SPS Report[2]	Cb 752/Hex Head Bolt	—	2200 2400 2600	71 32 9

REFERENCES

1. Maisel, L., Metal Finishing, pgs. 76-81, note table on pg. 79, January, 1968
2. Roach, T.A. and E.F. Gowen, Jr., Standard Pressed Steel Co. (SPS), "Structural Fasteners for Extreme Elevated Temperatures," note figure on pg. 111, September, 1966

Table XXXVII (Contd)

Mechanical Properties					
Identification	Substrate Alloy/Shape	Coating Thickness (mils)	Temperature (°F)	Mechanical Properties	
				Tensile Strength (psi)	Shear Strength (psi)
This Program	Cb 752/Hex Head Bolt and Nut	2.5-3	80	84,800*	65,700*
			600	65,300	41,800
			2000	45,400	29,500
			2400	24,800	21,400
			2600	21,400	—
SPS Report[1]	Cb 752/Hex Head Bolt and Nut	—	80	82,000	62,000
			600	60,000	42,000
			2000	44,000	30,000
			2400	29,000	20,000
			2600	22,000	—

REFERENCES

1. Roach, T.A. and E.F. Gowen, Jr., Standard Pressed Steel Co. (SPS), "Structural Fasteners for Extreme Elevated Temperatures," pgs 169 and 171, September, 1966.

*With post-heat treatment of coated fasteners.

SECTION VII

EQUIPMENT MODIFICATION, DESIGN, CONSTRUCTION AND INSTALLATION FOR TUNGSTEN-TUNGSTEN SILICIDE COATING

Phase III which involved tungsten-tungsten silicide ($W-WSi_2$) coating on tantalum was started with equipment modification, design, construction and installation. The equipment from Phases I and II was modified when applicable. Design, construction and installation of additional materials and equipment was made including procurement of a special flow control system for the reactive tungsten hexafluoride (WF_6). The assembled equipment for the fluoride route to the deposition is shown in Figure 52. In the process flow diagram, a Hastings mass flow meter is used for flow control of the reactive tungsten hexaflouride (WF_6). A Fisher-Porter rotameter is utilized for flow control of the hydrogen required in tungsten deposition reaction. The figure further discloses the following equipment required for the tungsten-tungsten silicide ($W-WS_2$) coating: (a) H_2 purifier, (b) inert gas bubbler flow control for silicon tetrachloride ($SiCl_4$) bubbler, (c) inert gas purifier, (d) furnace containing rotating reaction chamber, (e) temperature control unit, (f) rotating reaction chamber and (g) motor – fine control system for rotation speed control of the reaction chamber.

The equipment modified, designed, constructed and installed in this program activity served as a base for the start-up coating experiments (i.e., coating preparation studies) for the fluoride route to tungsten deposition.

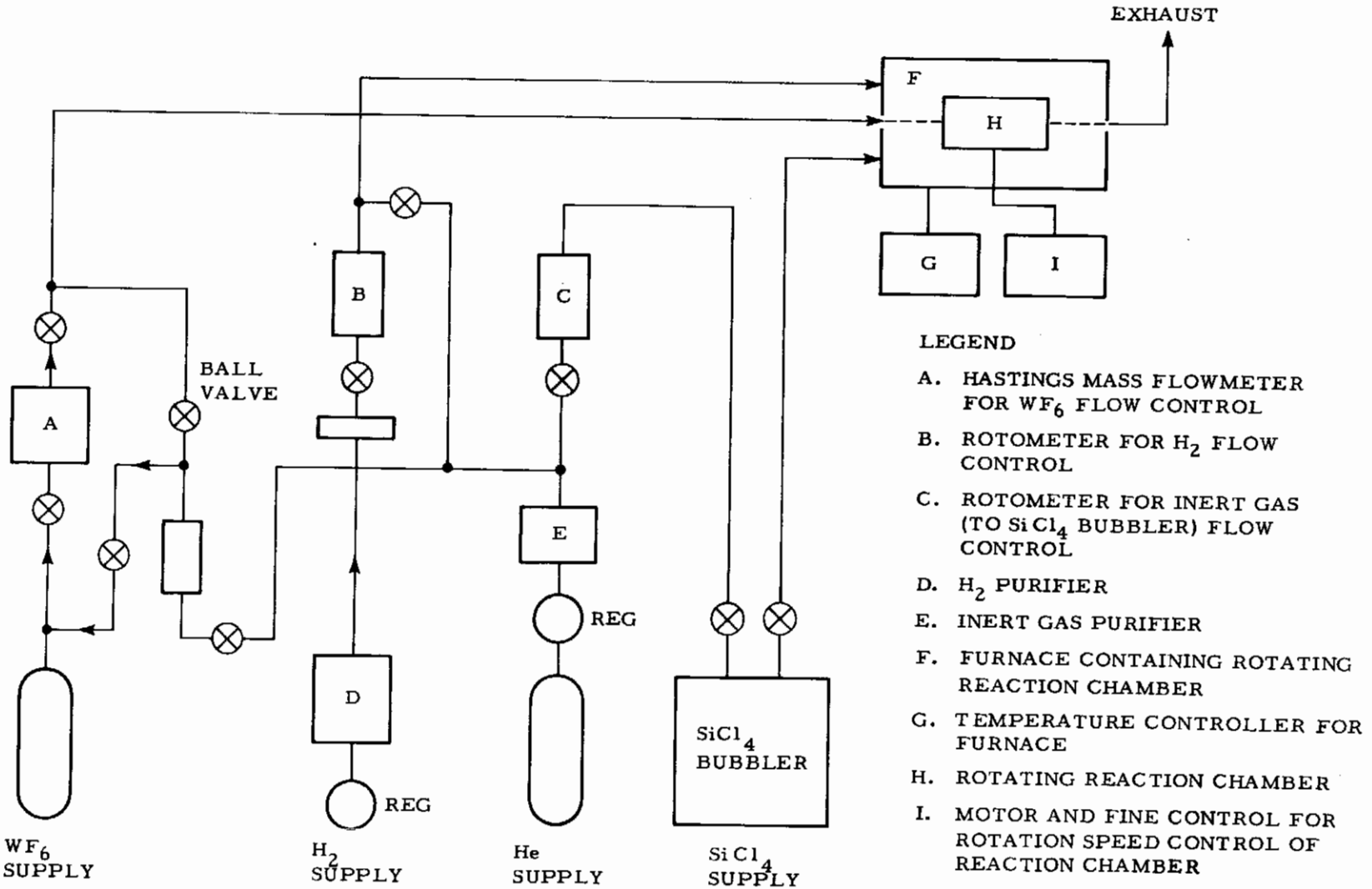


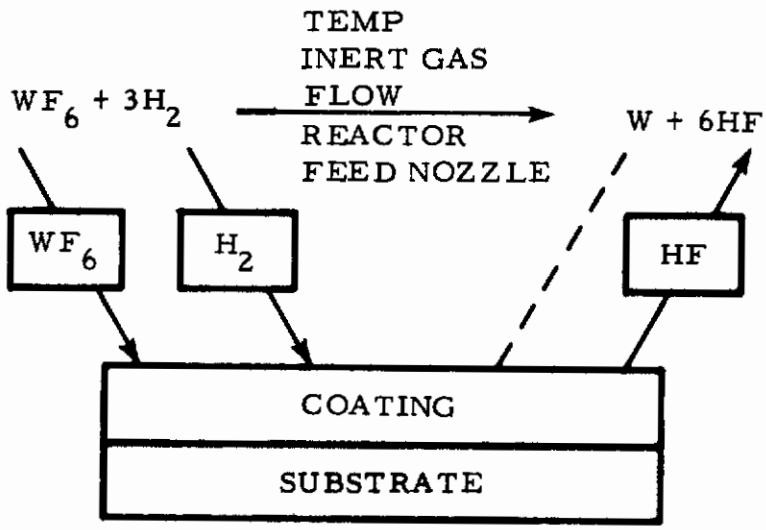
Figure 52. Process Flow Diagram for Fluoride Route to Tungsten-Tungsten Silicide Coating

SECTION VIII
COATING PREPARATION STUDIES

In coating preparation studies, fluoride and chloride routes were investigated for the tungsten-tungsten silicide coating of tantalum. This was accomplished in a concentrated effort to resolve technical difficulties and problems. Modified equipment from the Cr-Ti-Si coating work was utilized for the chloride route. Similar equipment was designed, constructed and installed as shown in Figure 52 for the fluoride route. In accelerated process variable screening, partial success was achieved for the chloride route based on deposition of silver gray tungsten coating in gas feed nozzle and reactor wall regions. For the fluoride route, improved partial success was demonstrated based on silver gray tungsten coating of tantalum T222 substrates with uniform coating coverage of the round rod small parts.

A. FLUORIDE ROUTE

The fluoride route for the tungsten-tungsten silicide deposition was based on simplified CVD reaction chemistry shown below for the tungsten (W) deposition:



The key process variables influencing the tungsten deposition include reaction temperature, reactant concentrations (tungsten fluoride, hydrogen, inert gas), flow rate of gases, reactor design and gas feed nozzle design for introducing the reaction gases into the reaction chamber.

Initial start-up of coating preparation runs for the fluoride route was made in the equipment modified and assembled as shown in Figure 52. Observations made in the initial runs are recorded in Table XXXVIII. In the first run for tungsten deposition, satisfactory operation of temperature control, rotation speed control and other equipment units was demonstrated. Constant reaction temperature was achieved throughout the deposition run. The coating deposit achieved on the substrate was analyzed by X-ray scan. The X-ray scan indicated that the coating deposit was tungsten on basis of deposit peaks matching tungsten ASTM reference peaks. In subsequent runs, reaction chamber breakage and other technical problems were experienced.

Process conditions, results and observations for the fluoride route are given in Tables XXXIX and XL for the process variable screening. Prior to conducting the tabulated deposition runs, initial experiments were conducted with the reactor and gas feed nozzle designs of previous Table XXXVIII. These experiments disclosed some fluoride etching of the quartz material of construction. For the other ten plus deposition runs shown in these last two tables, the hydrogen gas feed nozzle plugged in the first run. From subsequent runs, a gas feed nozzle design was selected which did not plug after several hours of operation. Reactor problems including reaction chamber cracking was experienced. The next tungsten deposition runs were conducted with a metal cage reactor having improved strength qualities. This reactor was then selected on the basis of several runs without any cracking and breakage of the reaction chamber. In conducting these experiments, some success for tungsten deposition in the fluoride route was achieved and several silver gray coatings were obtained. Additional runs were conducted in a concentrated effort to resolve the technical difficulties and problems.

Table XXXVIII

COATING PREPARATION STUDIES: INITIAL RUNS FOR FLUORIDE ROUTE

Run Number	Process Conditions	Observations
CLY3-1-69	• 650°C • WF_6 flow diluted with He • WF_6 = 0.012 ℓ/min • $H_2 \cong$ 0.048 ℓ/min	• Coating deposit achieved on substrate, coating submitted for X-ray analysis • Hydrogen flow not sufficient, need to increase • Fine needle valve needed for better WF_6 flow control
CLY3-2-69	• 650-700°C • WF_6 flow diluted with He • WF_6 = 0.15-0.20 ℓ/min • H_2 = 0.10-0.20 ℓ/min	• Both tungstem and tungsten-silicide deposition reactions conducted in equipment • Some coating deposit obtained on round rod substrates • Reaction chamber broke during run due to reactor support, large reactor size or substrate binding with gas feed inlet nozzles
CLY3-3-69	• 650-750°C • WF_6 flow diluted with He • $WF_6 \sim$ 0.045 ℓ/min • $H_2 \sim$ 0.3-0.6 ℓ/min	• Tungsten and tungsten-silicide deposition reactions conducted • Large metal reaction chamber utilized • Several different substrates used • Stainless 316 tubing-coating deposit obtained • Quartz tubing - some etching and reduction in size, some deposit and apparent diffusion • T222 alloy-coating appeared to be bonded • T121 – come coating, some bonding problem • Coated hex head bolt — come coating
CLY3-4-69	• 650°C • WF_6 flow diluted with He • $WF_6 \sim$ 0.015 ℓ/min • $H_2 \sim$ 0.10 ℓ/min	• Some coating deposit on reaction chamber • Insufficient coating inside reaction chamber chamber on substrates • Reaction chamber did not break, suggesting previous breakage due to substrate binding with gas feed inlet nozzles.

Table XXXIX

COATING PREPARATION STUDIES: PROCESS CONDITIONS AND RESULTS FOR FLUORIDE ROUTE

Run Number	WF_6 Flow (ℓ/min)	H_2 Flow (ℓ. min)	Inert Gas Dilution of H_2 (He, ℓ/min)	Inert Gas Flow (He, ℓ/min)		SiH_4 Flow (ℓ/min)	Total Flow Measured (ℓ/min)	Reaction Temp. (°C)	Deposition Time (min)	Rotation Speed (rpm)	Reactor Loading via Quantity of Substrates
				$SiCl_4$ Bubbler	Dilution						
CLY3-5-69	.030	.200	1.0	—	—	—	1.230	650	120P.	10-20	1
CLY3-6-69	.030	.400	1.0	.060	—	—	2.030	650	15P.	11	2
CLY3-7-69	.030	.400	1.0	.060	—	—	2.030	650	15P.	11	2
CLY3-17-69	.018	.077	.872	—	—	—	.967	650	180	10-20	2
CLY3-18-69	.018	.077	.872	.060	—	—	1.027	650	240	10-20	2
CLY3-19-69	.018	.077	.872	—	.100	—	1.067	650	180	10-20	2
CLY3-20-69	.018	.077	.872	—	.100	—	1.067	650	180	10-20	1
CLY3-21-69	.018	.190	.872	.060	.100	—	1.240	650	120	10-20	2
CLY3-22-69	.018	.190	.872	.060	.100	—	1.240	820	120	10-20	2
CLY3-23-69	.018	.190	.872	—	—	.050	1.040	400	60	10-20	2
CLY3-24-69	.018	.077	.872	—	.100	—	1.067	650	180	10-20	2

OTHER RUN CONDITIONS

- Equipment utilized as shown in Figure 52
- In CLY3-17-69, diluant introduced with WF_6 and $SiCl_4$

Table XL

COATING PREPARATION STUDIES:
OBSERVATIONS FOR FLUORIDE ROUTE

Run Number	Observation
CLY3-5-69	• Silver colored coating inside reaction chamber • H_2 feed nozzle plugged
CLY3-6-69	• Introduced H_2 thru larger feed nozzle • H_2 feed nozzle did not plug • Other feed nozzle with WF_6 and $SiCl_4$ did plug after short operation period.
CLY3-7-69	• Increased flow with diluent gas thru nozzle feeding WF_6 and $SiCl_4$ • Feed nozzle plugged after longer operation period
CLY3-17-69	• Conducted deposition run with hand fabricated new nozzle with separate feed entries for WF_6, $SiCl_4$ and H_2. • Feed nozzle did not plug after three hour operation with WF_6 and H_2 • Substrates experienced weight gain indicating coating deposit
CLY3-18-69	• Conducted deposition run with welded new feed nozzle having separate feed entries for each reactant. • Feed nozzle did not plug after four operation including one hour operation with $SiCl_4$. • Graphite reactor cracked during deposition run.
CLY3-19-69	• Conducted deposition run with metal cage reactor having improved strength qualities. • Metal cage reactor did not crack in deposition run. • Silver gray coating deposit achieved in run.
CLY3-20-69	• Conducted second deposition run with metal cage reactor. • Reactor condition satisfactory without cracking after three hour operation for W deposition.

Table XL (Contd)

Run Number	Observation
CLY3-21-69	• Conducted WSi_x deposition run for two hours with metal cage reactor and feed nozzle having separate entry for each reactant. • After two hour operation feed nozzle did not plug including $SiCl_4$ entry.
CLY3-22-69	• Conducted WSi_x deposition at higher reaction temperature using $SiCl_4$. • Dark powder obtained as reaction product.
CLY3-23-69	• Conducted WSi_x deposition run using SiH_4. • After short operation period at 400°C reaction temperature, the SiH_4 feed flow started dropping and continued dropping due to partial plugging.
CLY3-24-69	• Conducted WSi_x deposition run using $SiCl_4$. • No pluggage after three hour operation. • Dark powder obtained as reaction product.

In the additional runs for the fluoride route to tungsten deposition, some substrate damage was experienced in the first several runs which were conducted with the metal cage reactor discussed previously. After conducting the next several runs without substrate damage (using a graphite reactor), the graphite reactor was selected for use in subsequent deposition runs. Several tungsten silicide depositions were conducted in the subsequent runs. A silver gray coating deposit was obtained on the T222 substrate in the experiments. Emission spec analysis for two of the tungsten silicide deposition runs disclosed very little silicon content in the coating (i.e., coating composition: Si = 1-100 ppm, W = 99+%).

Subsequent runs for the fluoride route were conducted for tungsten deposition with partial success, i.e., some silver gray coatings were deposited on T222 substrates in these runs. A photograph showing the surface and uniform coverage of this silver gray coating is presented in Figure 53.

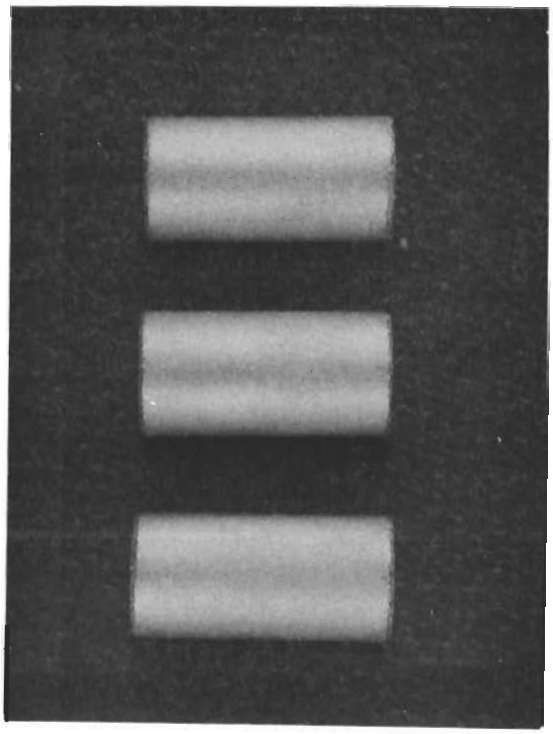
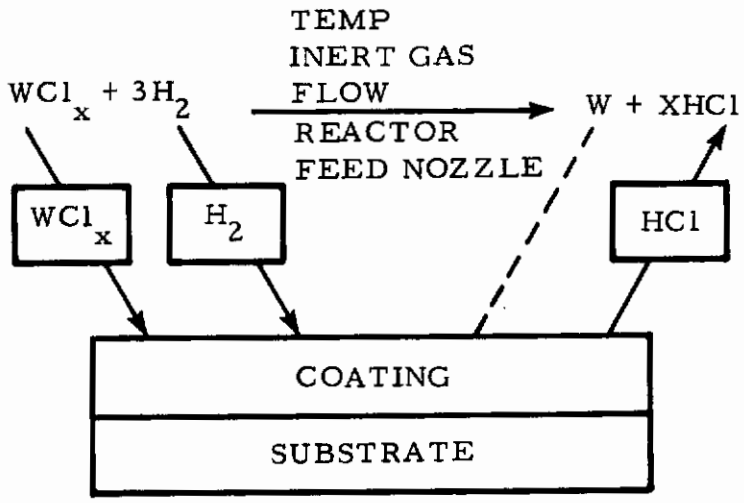


Figure 53. Coating Preparation Studies: Tungsten Coating Deposit on T222 Substrate for Fluoride Route (CLY3-36-69)

B. CHLORIDE ROUTE

The chloride route involved the following simplified CVD reaction chemistry for tungsten (W) deposition:



For initial runs, the tungsten chloride (WCl_x) was generated by passing gas phase chlorine over tungsten chips. The important process variables as shown above for the chloride route are reaction temperature, reactant concentrations (tungsten chloride, hydrogen, inert gas), flow rate, reactor design and gas feed nozzle design.

In initial process variable screening, Table XLI contains process conditions and results for the chloride route. The table discloses that more than eleven deposition runs were conducted. In each run, the tungsten chips experienced a weight loss indicating generation of tungsten chloride feed by passage of chlorine over the chips. With respect to tungsten deposition in the runs, some cursory coatings were obtained in the immediate region of chip holder exhaust for the gas feed nozzle design.

Table XLI

COATING PREPARATION STUDIES: INITIAL PROCESS CONDITIONS AND RESULTS FOR CHLORIDE ROUTE

Run Number	WCl_x Feed			H_2 Feed		Inert Gas Flows Ar, (ℓ/min)		Total Flow Measured (ℓ/min)	Reaction Temp. (°C)	Deposition Time (min)	Rotation Speed (rpm)	Reactor Loading via Quantity of Substrates
	Approx. Cl_2 Flow (ℓ/min)	W Chips Wt. Loss (gm)	Inert Gas Dilution (Ar, ℓ/min)	H_2 Feed (ℓ/min)	Inert Gas Dilution (Ar, ℓ/min)	$SiCl_4$ Bubbler	Dilution					
CLY3-8-69	1.0	12.481	—	6.0	—	—	—	7.0	1050	10	11	2
CLY3-9-69	1.0	47.0042	—	6.0	—	.060	1.0	9.060	1050	60	11	2
CLY3-10-69	.2	43.8058	—	6.0	—	.060	2.0	8.260	1050	45	11	2
CLY3-11-69	.1	Yes	3.0	6.0	6.0	—	1.0	16.1	1040	45	11	2
CLY3-12-69	2.0	Yes	3.0	6.0	6.0	—	1.0	18.0	640	45	11	2
CLY3-13-69	5.0	18.3820	3.0	6.0	6.0	—	2.5	22.5	830	45	11	2
CLY3-14-69	5.0	50.7787	3.0	6.0	6.0	—	2.5	22.5	1000	45	11	2
CLY3-15-69	.040	2.1356	4.5	5.0	0.5	0.5	—	10.540	1010	45	11	2
CLY3-16-69	.040	0.0448	—	5.0	0.5	0.5	—	6.040	700	45	11	2
CLY3.1-17-69	.035	1.4153	—	6.0	—	5.0	—	11.035	800	45	11	2
CLY3.1-18-69	.035	1.6970	4.5	6.0	—	—	5.0	15.535	1005	45	11	2
CLY3.1-19-69	.040	0.7486	5.0	—	5.0	5.0	—	15.040	1005	45	11	2

Further process variable screening for the chloride route was completed including specific screening of process variables of reaction temperature, reactant concentrations (including hydrogen, tungsten chloride and inert gas dilution), flow rate and gas feed nozzle design. Detailed specifics including process conditions and results are presented in the appendix. For this cursory screening with tungsten chloride feed generation by passing gas phase chlorine over tungsten chips, silver gray coating deposits were achieved and reproduced in the immediate region of the gas feed nozzle design. But such coating deposits could not be achieved on the substrates because of technical problems. The effort was then switched to the chloride route with tungsten hexachloride (i.e., tungsten chloride feed generation with inert gas passage over the tungsten hexachloride).

Approximately fifteen deposition runs were conducted — process variable screening for the chloride route with tungsten hexachloride. Reaction temperature, reactant concentrations, reactor design and gas feed nozzle design were cursorily screened. In some of the runs, coating deposits were possibly suggested by the substrates experiencing slight weight gains (usually several mg). In those runs with reactor design screening, some silver gray coating was obtained on the reactor walls. Additional specifics — process conditions and observations — are given in the appendix.

Completion of the program activity of coating preparation disclosed partial success with tungsten deposition on T222 substrates via the fluoride route. The concentrated and accelerated work effort further disclosed that the technical problems — associated with the tungsten and tungsten silicide depositions in program activities of coating preparation, oxidation test and mechanical tests — could not be resolved in the short Phase III contract time even with the inclusion of additional resources.

SECTION IX

CONCLUSIONS

The following conclusions were made as a result of work completed in this program for continued development of CVD coating refractory processes and practical production equipment for applying these coatings to large quantities of small parts:

1. The trideposition reaction with hydrogen reduction of gas phase silicon, titanium and chromium chloride feeds was demonstrated as a CVD chemistry base for depositing chromium-titanium-silicon (Cr-Ti-Si) coating on columbium with the processing equipment.

2. Coating rate increases for the trideposition reaction can be achieved with the following important process variables: gas feed geometry; reaction temperature; silicon chloride concentration; flow rate; dual chamber prereduction; titanium tetrachloride concentration; hydrogen concentration and argon dilution level of the hydrogen gas feed.

3. Statistical analyses (i.e., T- and F-tests) confirmed the process variable influence for coating rate improvement at a 95% confidence level for coating 1/4-in. dia. round rod substrates of columbium with the developed CVD-barrel coating technology.

4. Acceptable coating deposits may be achieved on threaded substrates — 1-in. threaded stud refractory fasteners of columbium alloy Cb 752 composition — with the processing equipment.

5. Other refractory fastener shapes including 1 1/2-in. long hex head bolts of Cb 752 may be CVD coated at high reactor loading of ten substrates per run.

6. Application of the technology for coating additional shapes – bolts, studs, rods and flat panels – in one run was demonstrated with the potential production equipment at loading of twenty substrates.

7. Three refractory fastener shapes – hex head bolts, threaded studs and hex nuts of Cb 752 composition – may be CVD coated at a loading level of thirty substrates per run (i.e., ten of each shape) with uniform coating coverage.

8. From production demonstration batches, specific refractory fasteners – 1 1/2-in. long hex head bolts and complimenting 1/4-in. dia. hex nuts – may be coated with reproducibility at increased loading of coating thirty to fifty substrates per run. Based on a total of more than twenty demonstration runs, this current coating capability illustrates that the developed technology is within the scope of potential production equipment.

9. The uniform coating coverage achieved on refractory fasteners permits attachment of the coated hex bolt to coated hex nut. This suggests that the CVD coated components are amenable for use in this phase of their original application.

10. For coating oxidation properties, eighty plus hours of coating protection in 2400°F oxidation environment can be obtained for 1 1/2-in. round rods that are CVD coated in the apparent optimum region at high loading level with the practical equipment.

11. Coating of 1 1/2-in. hex head bolt refractory fasteners in apparent optimum region provides several fold coating oxidation property improvement. Results of twenty plus hours protection compared to uncoated fastener failure with severe oxidation after only one-half hour maybe achieved at high loading level (coating twenty to thirty substrates per run).

12. From production demonstration batches, CVD coating of specific refractory fasteners — hex head bolts and complimenting hex nuts — provides twenty plus hours coating protection of the substrate from high temperature oxidation (2400°F). This applies for refractory fasteners coated with the developed technology at the increased current coating capability (i.e., coating thirty to fifty substrates per run) with the potential production equipment.

13. For mechanical properties of the production demonstration batches, room temperature tensile and shear strengths are significantly enhanced with post-heat treatment. Mechanical properties in general are favorable in the wide temperature range of 80°F to above 2000°F. For cyclic oxidation, cursory literature screening revealed favorable state-of-art comparison based on this program and two independent literature sources.

14. From electron microprobe analysis, the component traces reveal that columbium alloy substrates including refractory fasteners may be CVD coated with the technology to provide a Cr-Ti-Si coating with minimal siliciding of the substrate.

15. For tungsten-tungsten silicide ($W-WSi_2$) coating, a silver gray tungsten (W) coating may be CVD deposited — via the fluoride route — on tantalum alloy T222 round rod substrates with uniform coverage.

16. This program has demonstrated that the developed CVD-barrel coating technology is a reproducible process for Cr-Ti-Si coating of refractory fasteners within scope of potential production equipment.

SECTION X
RECOMMENDATIONS

The CVD-barrel coating technology was shown in this program to be a reproducible process for Cr-Ti-Si coating of columbium allow refractory fasteners within the scope of potential production equipment for applying such coatings to large quantities of small parts. To continue the process development for further practical extension, the following additional works is needed:

1. Process development of equipment to permit tungsten-tungsten silicide coating of small samples in batches of several samples per run.

2. Additional development of tungsten-tungsten silicide coating of tantalum alloy and evaluation of coating properties such as oxidation performance, coating-substrate interaction and reliability.

3. Optimization studies for tungsten-tungsten silicide coating of tantalum alloys including coating procedures and process parameters.

SECTION XI

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300 College Park Avenue
Dayton, Ohio 45409

Vitro Laboratories
Attn: Mr. M. Ortner
Chemistry & Arc Research Dept.
200 Pleasant Valley Way
West Orange, New Jersey 07050

Westinghouse Electric Corporation
Astronuclear Laboratory
P.O. Box 10864
Pittsburgh, Pennsylvania 15236

Whittaker Corporation
Research & Development/San Diego
Attn: Library
3540 Aero Court
San Diego, California 92123

APPENDIXES

APPENDIX I

OPTIMIZE PARAMETERS: RESULTS FOR GAS FEED GEOMETRY STUDY AND FIRST STATISTICAL SERIES

Run Number	Inert Gas Flows (ℓ/min)				Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Flow (ℓ/min)		Inert Gas	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Weight Gain of Metal Substrate				Substrate Identification	Reaction Chamber	Gas Feed Geometry
	$SiCl_4$		$TiCl_4$				H_2	Inert Diluent						1	2	3	Avg.			
	Bubbler	Diluent	Bubbler	Diluent			Steam	Gas												
CLY-79-68	–	–	6.5	.50	–	–	–	3.5	Ar	10.5	–	–	11	Yes	Yes	Yes		Flat panel (2 cm x 1 cm)	A (7-in. quartz rocking bottle)	A
CLY-80-68	.090	.25	6.5	.50	–	–	–	3.5	Ar	10.84	–	–	11	Yes	Yes	Yes		Flat panel (2 cm x 1 cm)	A (7-in. quartz rocking bottle)	A
CLY-81-68	.090	.25	6.5	.50	–	–	–	4.5	Ar	11.84	–	–	11	Yes	Yes	Yes		Flat panel (2 cm x 1 cm)	A (7-in. quartz rocking bottle)	A
CLY-82-68	.090	.25	6.5	.50	–	–	–	5.0	Ar	12.34	–	–	11	Yes	Yes	Yes		Flat panel (2 cm x 1 cm)	A (7-in. quartz rotating bottle)	A
CLY-83-68[1]	.045	.25	3.25	.50	1.197	–	3.0	.65	Ar	7.695	25	≈1250	11	–	–	–	–	Flat panel (2 cm x 1 cm)	B (specialty reaction chamber)	B
CLY-84-68[2]	.180	.25	6.5	.50	14.370	–	6.0	.65	Ar	14.08	180	1230	11	16.5	20.6	30.2	22.4	Flat panel (2 cm x 1 cm)	A (specialty reaction chamber)	B
CLY-85-68	.090	.25	6.5	.50	7.026	–	6.0	.65	Ar	13.99	120	1230	11	20.9	21.9	22.4	21.7	Flat panel (2 cm x 1 cm)	A (specialty reaction chamber)	B
CLY-86-68	.090	.25	6.5	.50	12.815	–	6.0	.65	Ar	13.99	240	1230	11	41.4	40.5	47.5	43.1	Flat panel (2 cm x 1 cm)	A (specialty reaction chamber)	B
CLY-87-68	.18	.16	6.5	.50	5.548	–	6.0	.65	Ar	13.99	120	1230	11	22.2	28.9	25.1	25.4	Flat panel (2 cm x 1 cm)	A (specialty reaction chamber)	B
CLY-88-68	.0225	.25	1.63	.23	.5072[4]	–	1.50	.23	Ar	3.863	120	1170	11	16.7	12.8	13.1	14.2	Flat panel (2 cm x 1 cm)	C (small reaction chamber)	B
CLY-89-68	.0225	.25	1.63	.23	.6488	–	1.50	.23	Ar	3.863	120	1115-1170[3]	11	26.4	26.8	29.9	27.7	Flat panel (2 cm x 1 cm)	C (small reaction chamber)	C
CLY-90-68	.045	.50	3.26	.46	.7312	–	3.0	.46	Ar	7.725	120	1170	11	24.7	32.2	39.1	32.0	Flat panel (2 cm x 1 cm)	C (small reaction chamber)	C
CLY-91-68	.045	.50	3.26	.46	.9703	–	3.0	.46	Ar	7.725	120	1170	11	22.1	22.0	29.1	24.4	Flat panel (2 cm x 1 cm)	C (small reaction chamber)	D
CLY-92-68	.0225	.25	1.63	.23	.5095	–	1.50	.23	Ar	3.863	120	1170	11	31.4	36.0	42.3	36.5	Flat panel (2 cm x 1 cm)	C (small reaction chamber)	D
CLY-93-68	.0225	.25	1.63	.23	.7521	–	1.50	.23	Ar	3.863	120	1115	11	45.2	47.6	51.7	48.2	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-94-68	.045	.50	3.26	.46	.4565	–	3.0	.46	Ar	7.725	120	1115	11	77.9	70.3	63.6	70.6	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-95-68	.0225	.5225	3.26	.46	.2685	–	3.0	.46	Ar	7.725	120	1115	11	47.8	46.6	46.3	46.9	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-96-68	.045	4.365	3.26	.46	1.0504	–	3.0	.46	Ar	11.59	120	1115	11	47.4	44.0	41.5	44.3	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-97-68	.0225	4.3875	3.26	.46	1.9738	–	3.0	.46	Ar	11.59	120	1115	11	72.4	71.7	70.3	71.1	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-98-68	.045	.50	3.26	.46	1.0589	–	3.0	4.325	Ar	7.725	120	1115	11	98.7	95.5	95.6	96.6	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-99-68	.0225	4.387	3.26	.46	2.841	–	3.0	.46	Ar	11.59	120	1015	11	22.9	22.6	33.5	26.3	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-100-68	.045	.50	3.26	.46	.6337	–	3.0	.46	Ar	7.725	120	1015	11	44.4	45.8	43.2	44.5	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-101-68	.0225	.5225	3.26	.46	.3930	–	3.0	.46	Ar	7.725	120	1015	11	45.5	43.0	43.8	44.1	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-102-68	.0225	4.365	3.26	.46	1.9364	–	3.0	.46	Ar	11.59	120	1015	11	73.5	73.9	72.3	73.2	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-103-68	.045	4.365	3.26	.46	2.6272	–	3.0	.46	Ar	11.59	120	1115	11	85.0	82.6	82.5	83.3	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-104-68	.0338	2.6	3.26	.46	2.5929	–	3.0	.46	Ar	9.66	120	1115	11	80.6	80.5	81.4	80.8	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-105-68	.0225	4.3875	3.26	.46	.8924	–	3.0	.46	Ar	11.59	120	1015	11	56.1	56.1	57.5	56.4	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D
CLY-106-68	.0225	.5225	3.26	.46	.8680	–	3.0	.46	Ar	7.725	120	1015	11	52.7	52.9	51.6	52.4	Round rod (1 in. x 1/4 in.)	C (small reaction chamber)	D

OTHER RUN CONDITIONS AND OBSERVATIONS:

1. In CLY-83-68, with the small specialty reactor, $TiCl_4$ bubbler and feed gas plug problems were experienced.
2. Some trouble experienced with hydrogen regulator in CLY-84-68.
3. High reaction temperature based on identical furnace temperature in preceding run and in subsequent run.
4. Approximate measured weight loss of Cr chips due to experimental difficulties.

APPENDIX II

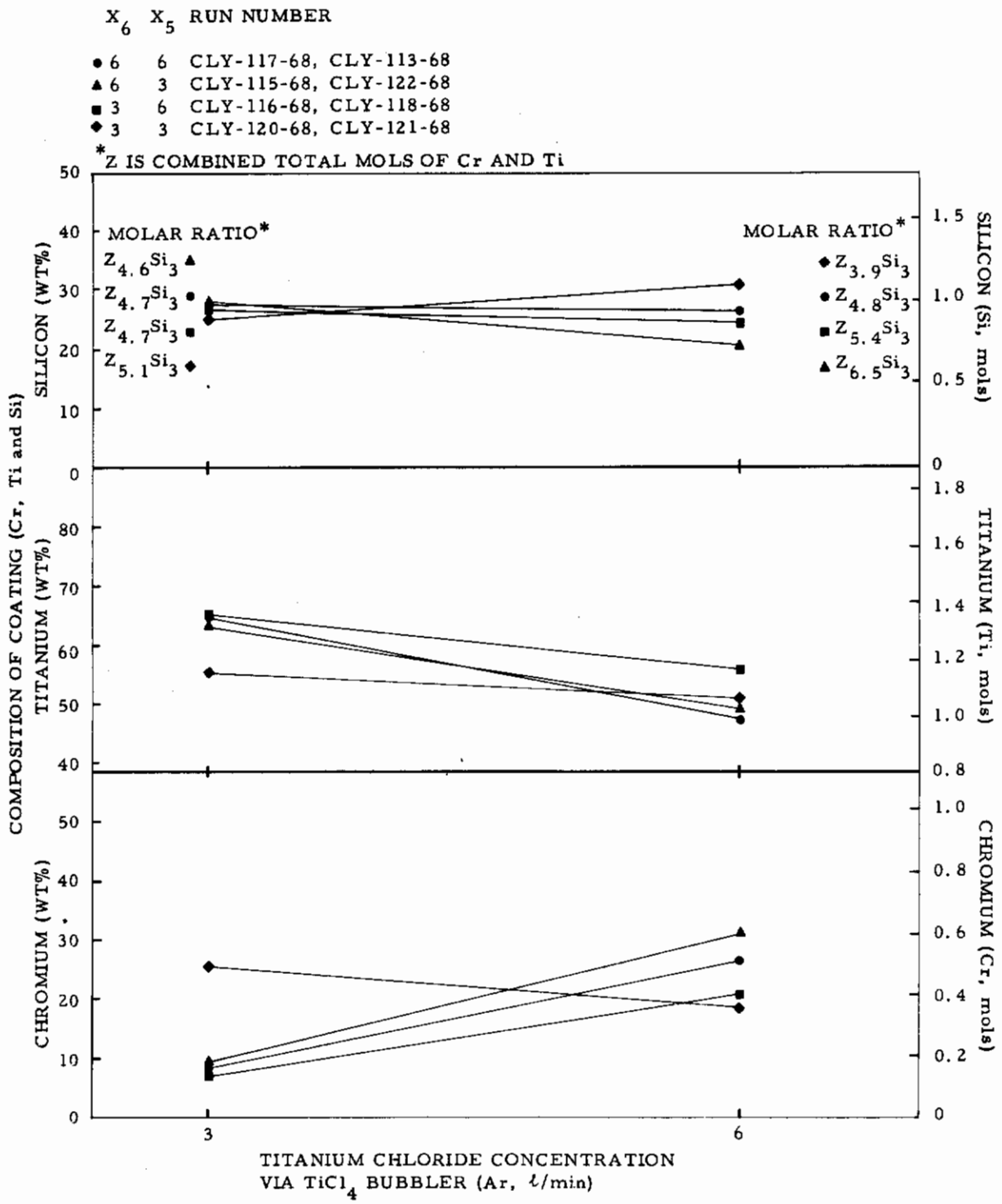
OPTIMIZE PARAMETERS: PROCESS CONDITIONS FOR INITIAL DUAL CHAMBER RUNS AND SECOND STATISTICAL SERIES EXPERIMENTS

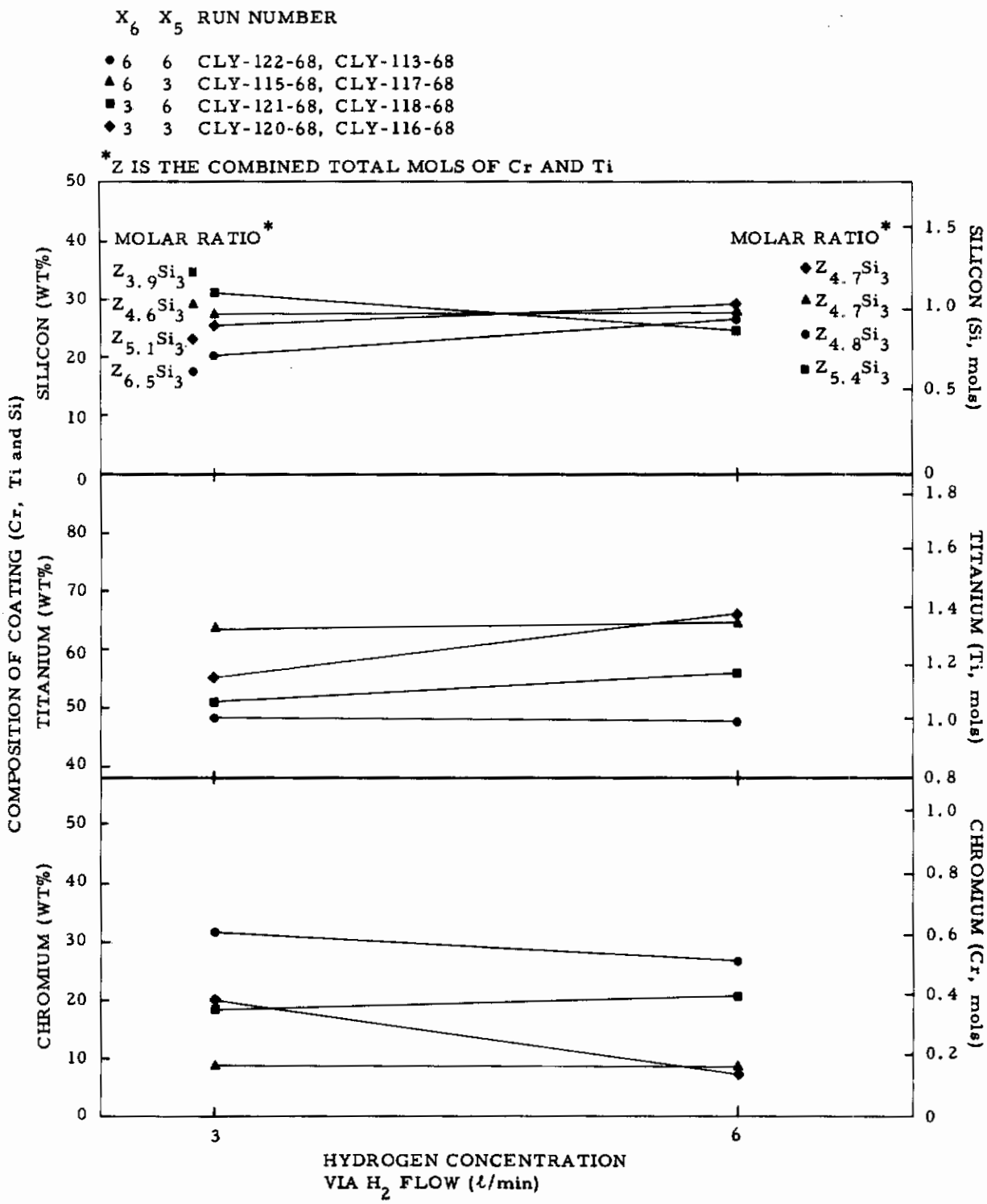
Run Number	Inert Gas Flows (ℓ/min)				Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Flow (ℓ/min)		Inert Gas	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Weight Gain of Metal Substrate			
	$SiCl_4$		$TiCl_4$				H_2 Stream	Inert Diluent Gas						1	2	3	Avg.
	Bubbler	Diluent	Bubbler	Diluent													
CLY-107-68	.045	.50	3.26	.46	2.321	—	3.0	4.325	Ar	11.59	120	1115	11	97.9	95.6	92.6	95.5
CLY-108-68	.045	.50	3.26	.46	1.3516	2.014	3.0	4.325	Ar	11.59	120	1115	11	108.6	114.3	115.9	112.9
CLY-109-68	.0675	.75	4.9	.69	2.3387	3.0892	4.5	6.5	Ar	17.41	120	1115	11	122.4	124.1	120.9	122 5
CLY-110-68	.050	6.95	2.0	.50	.8828	1.3697	2.0	2.5	Ar	14.0	120	1115	11	63.1	66.8	65.3	65.1
CLY-111-68	.050	6.95	3.0	.50	.0941	1.5943	2.0	2.5	Ar	15.0	120	1115	11	85.0	79.6	84.8	83.1
CLY-112-68	.060	9.44	3.0	.50	.9226	2.1376	3.0	3,0	Ar	19.0	120	1120	11	143.6	144.7	146.1	144 8
CLY-113-68	.060	.44	6.0	.50	2.2027	4.1638	6.0	6.0	Ar	19.0	120	1120	11	100.1	96.9	102.3	99.7
CLY-114-68	.060	6.44	6.0	.50	1.4091	2.9862	3.0	3.0	Ar	19.0	120	1120	11	94.7	95.6	103.4	97 9
CLY-115-68	.060	6.44	3.0	.50	.9562	2.3823	3.0	6.0	Ar	19.0	120	1120	11	68.9	69.5	68.9	69 1
CLY-116-68	.060	6.44	3.0	.50	.8068	2.1923	6.0	3.0	Ar	19.0	120	1120	11	65.2	57.7	60.4	61.1
CLY-117-68	.060	3.44	3.0	.50	.7397	3.1878	6.0	6.0	Ar	19.0	120	1120	11	75.4	76.8	70.0	74.1
CLY-118-68	.060	3.44	6.0	.50	1.1649	3.5597	6.0	3.0	Ar	19.0	120	1120	11	71.6	68.5	63.9	68 0
CLY-119-68	.060	3.44	6.0	.50	.9141	2.8608	3.0	6.0	Ar	19.0	120	1120	11	58.0	65.2	60.0	61.1
CLY-120-68	.060	9.44	3.0	.50	.7646	3.7923	3.0	3.0	Ar	19.0	120	1120	11	56.0	59.1	53.7	56.3
CLY-121-68	.060	6.44	6.0	.50	1.7982	2.3728	3.0	3.0	Ar	19.0	120	1120	11	61.4	67.1	63.9	64.1
CLY-122-68	.060	3.44	6.0	.50	3.338*	2.947	3.0	6.0	Ar	19.0	120	1120	11	81.3	69.7	73.9	74.9
CLY-123-68	.060	9.44	3.0	.50	2.5487	3.2112	3.0	3.0	Ar	19.0	120	1120	11	55.3	63.1	56.7	58.4

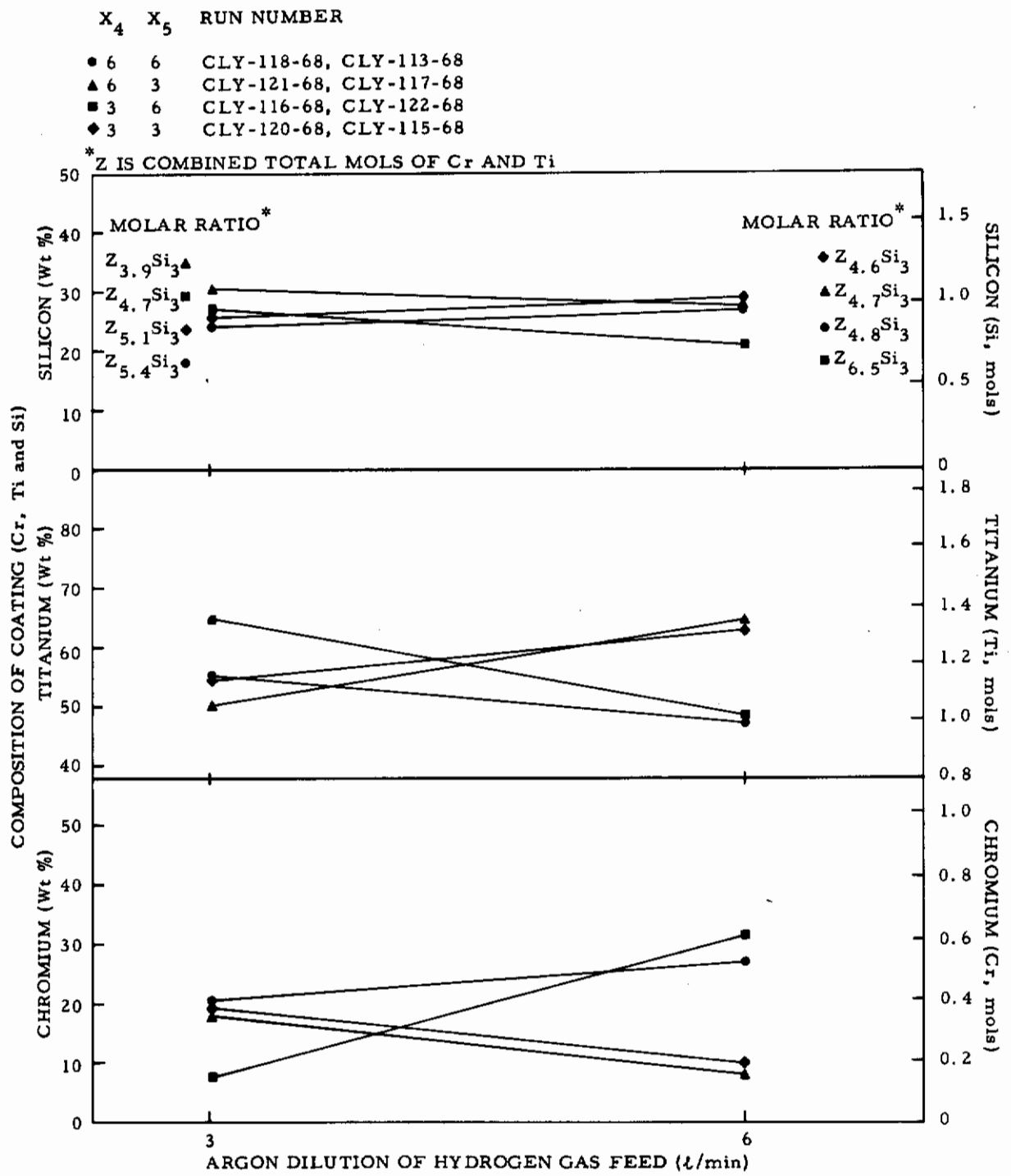
OTHER RUN CONDITIONS:

- Substrate Identification: Round rod (1 in. by 1/4 in.)
- Reaction Chamber: C(small reaction chamber)
- Gas Feed Geometry: D
- $TiCl_4$ bubbler filled prior to CLY-112-68 and used through CLY-121-68
- Same $SiCl_4$ bubbler used in CLY-112-68 through CLY-122-68
- Large $TiCl_4$ bubbler installed prior to CLY-122-68
- Large $SiCl_4$ bubbler installed prior to CLY-123-68

*Possible loss of Cr chips in reaction chamber.







APPENDIX III

ANALYSIS: MULTIPLE REGRESSION ANALYSIS TAB RUN-FIRST STATISTICAL SERIES

MULTIPLE REGRESSION.....DEP.

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1065.00000	53.45224	0.46819	0.00110	0.00037	2.99380
2	0.03375	0.01203	0.46819	4.88889	1.63300	2.99380
3	9.66000	2.06326	0.68101	0.04145	0.00952	4.35462
DEPENDENT						
4	0.51000	0.12558				

INTERCEPT	-1.22691
MULTIPLE CORRELATION	0.94983
STD. ERROR OF ESTIMATE	0.05196

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	3	0.09960	0.03320	12.29613
DEVIATION FROM REGRESSION	4	0.01080	0.00270	
TOTAL	7	0.11040		

APPENDIX IV

ANALYSIS: MULTIPLE REGRESSION TAB RUN-SECOND STATISTICAL SERIES

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	4.50000	1.60357	0.46486	0.03192	0.01344	2.37469
2	4.50000	1.60357	0.39203	0.02692	0.01344	2.00268
3	4.50000	1.60357	0.69061	0.04742	0.01344	3.52794
DEPENDENT 4	0.59137	0.11010				

INTERCEPT	0.11325
MULTIPLE CORRELATION	0.92017
STD. ERROR OF ESTIMATE	0.05702

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	3	0.07185	0.02395	7.36542
DEVIATION FROM REGRESSION	4	0.01301	0.00325	
TOTAL	7	0.08485		

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	0.61900	0.65500	-0.03600
2	0.46900	0.43200	0.03700
3	0.53500	0.52775	0.00725
4	0.57600	0.57425	0.00175
5	0.83100	0.75075	0.08025
6	0.56700	0.60850	-0.04150
7	0.62400	0.67000	-0.04600
8	0.51000	0.51275	-0.00275

APPENDIX V

ANALYSIS: FACTORIAL ANALYSIS OF VARIANCE TAB RUN-FIRST STATISTICAL SERIES

THREE WAY FACTORIAL ANALYSIS OF VARIANCE - 1 REPLICATION

VARIABLE	LEVELS
1	2
2	2
3	2

INPUT DATA

LEVEL OF VARIABLE 1	LEVEL OF VARIABLE 2	LEVEL OF VARIABLE 3	OBSERVATION
1	1	1	0.3700
1	1	2	0.4700
1	2	1	0.3700
1	2	2	0.6100
2	1	1	0.3900
2	1	2	0.5900
2	2	1	0.5900
2	2	2	0.6900

ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE
1	1	0.24202347E-01	0.24202347E-01	0.89659061E 01
2	1	0.24202347E-01	0.24202347E-01	0.89659061E 01
3	1	0.51200867E-01	0.51200867E-01	0.18967667E 02
12	1	0.31986237E-02	0.31986237E-02	0.11849489E 01
13	1	0.20027161E-03	0.20027161E-03	0.74191809E-01
23	1	0.19836426E-03	0.19836426E-03	0.73485196E-01
RESIDUAL	1	0.72002411E-02	0.72002411E-02	
TOTAL	7	0.11040306E 00		

APPENDIX VI

ANALYSIS: FACTORIAL ANALYSIS OF VARIANCE TAB RUN-SECOND STATISTICAL SERIES

THREE WAY FACTORIAL ANALYSIS OF VARIANCE - 1 REPLICATION

VARIABLE	LEVELS
1	2
2	2
3	2

INPUT DATA

LEVEL OF VARIABLE 1	LEVEL OF VARIABLE 2	LEVEL OF VARIABLE 3	OBSERVATION
1	1	1	0.4690
1	1	2	0.5760
1	2	1	0.5100
1	2	2	0.6190
2	1	1	0.5350
2	1	2	0.6240
2	2	1	0.5670
2	2	2	0.8310

ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE
1	1	0.18335342E-01	0.18335342E-01	0.56389494E 01
2	1	0.13040543E-01	0.13040543E-01	0.40105581E 01
3	1	0.40472031E-01	0.40472031E-01	0.12446986E 02
12	1	0.30059814E-02	0.30059814E-02	0.92447573E 00
13	1	0.23460388E-02	0.23460388E-02	0.72151339E 00
23	1	0.39157867E-02	0.39157867E-02	0.12042818E 01
RESIDUAL	1	0.37384033E-02	0.37384033E-02	
TOTAL	7	0.84854126E-01		

APPENDIX VII

DEPOSIT PHASES: CHEMICAL COMPOSITION OF COLUMBIUM ALLOY THREADED SUBSTRATES

Element Identification	Composition
Cb (Columbium)	87.89
W (Tungsten)	9.85
Zr (Zirconium)	2.26
N_2 (Nitrogen)	trace (.0076)
H_2 (Hydrogen)	trace (.0004)
Total	100.00

Note: The chemical composition of the columbium alloy used to fabricate the threaded substrates was furnished by the fastener supplier (Standard Press Steel; Jenkintown, Penn.).

APPENDIX VIII

DEPOSIT PHASES: TABULATED PROCESS CONDITIONS FOR DEPOSIT PHASE RUNS

Run Number	Inert Gas Flows (ℓ/min) $SiCl_4$ Bubbler	$SiCl_4$ Diluent	$TiCl_4$ Bubbler	$TiCl_4$ Diluent	Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Stream	Inert Diluent Gas	Inert Gas	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quantity of Substrates	Weight Gain of Metal Substrate (mg) 1	2	3	Avg.	Dual Chamber Identification	Substrate Identification	Reaction Chamber	Gas Feed Geometry	Cr and Ti Chips Charge
CLY-124-68	.040	3.46	3.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	142.5	148.6	148.9	146.6	Chamber A	Threaded Substrate	C	D	S_1
CLY-125-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	162.5	161.5	170.1	164.7	Chamber A	Threaded Substrate	C	D	S_1
CLY-126-68	.040	0.46	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	159.7	174.3	168.1	167.4	Chamber A	Threaded Substrate	C	D	S_1
CLY-127-68	.080	3.42	3.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	108.6	97.1	91.4	98.7	Chamber B	Threaded Substrate	C	D	S_2
CLY-128-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	187.3	176.3	162.9	182.2	Chamber B	Threaded Substrate	C	D	S_2
CLY-129-68	.040	0.46	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	152.4	166.2	177.3	165.3	Chamber B	Threaded Substrate	C	D	S_2
CLY-130-68	.040	3.46	3.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	134.1	135.3	133.6	134.3	Chamber B	Threaded Substrate	C	D	S_2
CLY-131-68	.080	3.42	3.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	139.2	136.4	136.6	137.4	Chamber B	Threaded Substrate	C	D	S_2
CLY-132-68	.120	0.38	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	319.2	312.0	332.4	321.2	Chamber B	Threaded Substrate	C	D	S_3
CLY-133-68	.120	3.38	3.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	258.1	288.1	270.7	272.3	Chamber B	Threaded Substrate	C	D	S_3
CLY-134-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1080	11	10	10 substrates			97.8	Chamber B	Round Rod Substrate	C_1	D	S_3
CLY-135-68	.120	0.38	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	209.4	219.6	222.3	217.1	Chamber B	Round Rod Substrate	C_1	D	S_3
CLY-136-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	10	10 substrates			128.8	Chamber B	Threaded Substrate	C	D	S_4
CLY-137-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	7	7 substrates			164.8	Chamber B	Threaded Substrate	C	D	S_4
CLY-138-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	163.3	169.5	166.4	185.7	Chamber B	Threaded Substrate	C	D	S_4
CLY-139-68	.080	0.42	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	12 substrates			99.4	Chamber B	Threaded Substrate	C	D	S_5
CLY-140-68	.060	0.44	6.0	.50	Yes	Yes	6.0	6.0	Ar	19	180	1100	11	3	163.3	169.5	166.4	166.4	Chamber B	Threaded Substrate	C	D	S_5
CLY-141-68	.060	6.44	3.0	.50	Yes	Yes	3.0	6.0	Ar	19	180	1100	11	3	256.0	246.2	245.2	249.1	Chamber B	Threaded Substrate	C	D	S_5
CLY-142-68	Reactor broke		—	—	—	—	—	—	—	—	—	—	—	3	—	—	—	—	Chamber B	Threaded Substrate	C	D	S_6
CLY-143-68	.060	3.44	6.0	.50	Yes	Yes	3.0	6.0	Ar	19	180	1100	11	3	173.1	170.1	182.4	175.2	Chamber B	Threaded Substrate	C_1	D	S_7
CLY-144-68	.060	5.44	4.0	.50	Yes	Yes	3.0	6.0	Ar	19	180	1100	11	3	205.2	200.9	206.7	204.3	Chamber B	Threaded Substrate	C_1	D	S_7
CLY-145-68	.060	4.44	5.0	.50	Yes	Yes	3.0	6.0	Ar	19	180	1100	11	3	191.7	192.5	185.7	189.9	Chamber B	Threaded Substrate	C_1	D	S_7
CLY-146-68	Experimental difficulties encountered				—	—	—	—	—	—	—	—	—	5	—	—	—	—	Chamber B	Threaded Substrate	C_1	D	S_8

OTHER RUN CONDITIONS

- Threaded substrate (dimension: 1 in. x 1/4-in. with 1/2 in. of 1/4 - 20 refractory threads one end, material: Cb 752 alloy)
- Round Rod Substrate (dimension: 1 in. x 1/4-in., material: Cb)
- Substrate weight gain for CLY-134-68 (average: 97.8, each; 91.8, 98.8, 98.6, 91.7, 85.3, 101.2, 104.0, 99.2, 113.4, and 94.4)
- Substrate weight gain for CLY-136-68 (average: 128.8, each; 138.7, 137.4, 124.9, 123.2, 132.6, 130.0, 125.6, 131.2, 130.6, and 113.5)
- Substrate weight gain for CLY-137-68 (average: 164.8; each; 162.6, 163.8, 170.1, 169.6, 160.1, 157.6, and 139.7)
- Substrate weight gain for CLY-139-68 (average: 99.4, each; 100.2, 109.4, 104.9, 101.3, 98.8, 96.3, 96.0, 97.0, 96.3, 96.0, 92.5, and 103.5)

APPENDIX IX

COATING OXIDATION SAMPLES: PROCESS CONDITIONS AND RESULTS FOR COATING OXIDATION SAMPLE RUNS

Run Number	Inert Gas Flows (ℓ/min)				Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	Hydrogen Gas Feed (ℓ/min)		Inert Gas Identification	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quantity of Substrate	Coating Deposit: Average Weight Gain of Substrate (mg)	Substrate Identification	Reaction Chamber Identification	Gas Feed Geometry Identification	Dual Chamber Identification	Cr and Ti Chips Charge
	$SiCl_4$		$TiCl_4$				H_2 Feed	Inert Diluent Gas												
	Bubbler	Diluent	Bubbler	Diluent																
CLY-147-68	.040	4.46	4.0	.50	Yes	Yes	4.0	4.0	Ar	17	180	1100	11	6	128.5	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-148-68	.040	4.46	4.0	.50	Yes	Yes	4.0	4.0	Ar	17	180	1000	11	6	92.1	Threaded Substrate	C_2	D	Chamber B	Used
CLY-149-68	.040	6.46	4.0	.50	Yes	Yes	6.0	4.0	Ar	21	180	1100	11	10	165.5	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-150-68	.040	.46	6.0	.50	Yes	Yes	4.0	6.0	Ar	17	180	1100	11	10	109.7	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-151-68	.040	2.46	6.0	.50	Yes	Yes	6.0	6.0	Ar	21	180	1000	11	6	111.1	Threaded Substrate	C_2	D	Chamber B	Used
CLY-152-68	.080	.42	4.0	.50	Yes	Yes	6.0	6.0	Ar	17	180	1100	11	6	218.5	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-153-68	.080	6.42	4.0	.50	Yes	Yes	4.0	6.0	Ar	21	180	1000	11	10	82.0	Threaded Substrate	C_2	D	Chamber B	Used
CLY-154-68	.080	.42	6.0	.50	Yes	Yes	6.0	4.0	Ar	17	180	1000	11	10	141.7	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-155-68	.080	6.42	6.0	.50	Yes	Yes	4.0	4.0	Ar	21	180	1100	11	6	209.8	Threaded Substrate	C_2	D	Chamber B	Used
CLY-156-68	.080	5.42	4.5	.50	Yes	Yes	4.0	3.5	Ar	18	180	1025	11	10	134.9	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-157-68	.100	7.40	4.0	.50	Yes	Yes	3.0	2.0	Ar	17	180	1000	11	10	106.9	Threaded Substrate	C_2	D	Chamber B	Used
CLY-158-68	.110	8.39	3.75	.50	Yes	Yes	2.5	1.25	Ar	16.5	180	988	11	10	94.3	Threaded Substrate	C_2	D	Chamber B	Fresh
CLY-159-68	.100	7.40	4.0	.50	Yes	Yes	3.0	2.0	Ar	17	252	1000	11	10	142.5	Threaded Substrate	C_2	D	Chamber B	Used

OTHER RUN CONDITIONS

- Threaded substrate (dimension: 1 in. x 1/4-in. with 1/2 in. of 1/4 - 20 refractory threads one end, material: Cb 752 alloy)
- For Cr and Ti chips charge column in table, fresh refers to new clean charge of Cr and Ti chips for present run.

Run Number	Quantity of Substrate	Coating Deposit: Weight Gain of Substrate (mg)											Substrate Identification
		1	2	3	4	5	6	7	8	9	10	Avg.	
CLY-147-68	6	131.7	132.8	138.2	115.2	129.3	124.0	—	—	—	—	128.5	Threaded Substrate
CLY-148-68	6	92.9	93.6	92.4	91.2	91.5	91.0	—	—	—	—	92.1	Threaded Substrate
CLY-149-68	10	162.0	163.0	168.5	168.4	166.0	164.8	165.5	165.9	166.6	164.5	165.5	Threaded Substrate
CLY-150-68	10	111.2	109.6	113.5	112.2	111.8	108.0	106.4	109.1	109.1	107.0	109.7	Threaded Substrate
CLY-151-68	6	114.5	115.2	106.9	111.9	106.6	112.0	—	—	—	—	111.1	Threaded Substrate
CLY-152-68	6	220.5	189.5	242.9	216.8	223.8	217.7	—	—	—	—	218.5	Threaded Substrate
CLY-153-68	10	59.8	90.2	80.1	56.2	90.0	91.2	89.5	91.8	90.7	80.7	82.0	Threaded Substrate
CLY-154-68	10	147.1	138.8	134.1	145.4	134.4	136.6	142.0	144.1	147.0	147.9	141.7	Threaded Substrate
CLY-155-68	6	205.0	207.8	210.7	210.3	200.4	224.5	—	—	—	—	209.8	Threaded Substrate
CLY-156-68	10	136.6	130.5	133.2	127.3	134.2	134.9	135.7	132.2	135.5	139.3	134.9	Threaded Substrate
CLY-157-68	10	117.0	104.9	101.7	103.4	108.4	103.4	107.3	106.6	110.3	106.0	106.9	Threaded Substrate
CLY-158-68	10	93.4	93.1	93.6	95.1	93.4	94.3	94.7	96.7	95.7	98.4	94.3	Threaded Substrate
CLY-159-68	10	137.9	136.8	134.9	139.0	143.0	138.4	139.9	142.3	141.1	140.4	139.4	Threaded Substrate

APPENDIX X

ANALYSIS OF TESTS: CURSORY MULTIPLE REGRESSION ANALYSIS FOR 2200°F AND 2400°F COATING OXIDATION RESISTANCE CORRELATIONS

Variable	Regression Coefficient		Computed Absolute T Value		T Value for Confidence Level	
	2200°F	2400°F	2200°F	2400°F	95%	90%
X_8-Coating Thickness (mils)	-14.8	11.8	2.46	0.813	2.36	1.90
X_9-Coating Cr Concentration (wt%)	0.699	-0.324	1.63×10^{-3}	0.31×10^{-3}	2.36	1.90
X_{10}-Coating Ti Concentration (wt%)	2.60	-2.41	6.06×10^{-3}	2.34×10^{-3}	2.36	1.90
X_{11}-Coating Si Concentration (wt%)	-0.923	-1.07	2.15×10^{-3}	1.04×10^{-3}	2.36	1.90
Intercept	-92.39	156.7				
Standard Error of Estimate	4.26	10.3				
Multiple Correlation Coefficient	0.899	0.650				

- Y_3 and $Y_4 = aX_8 + bX_a + cX_{10} + dX_{11}$ + Intercept
- a, b, c and d = Regression coefficient
- Y_3 and Y_4 = Coating oxidation Resistance at 2200°F and 2400°F via Average Test Time Before Failure (hr)
- Correlation based on samples at two coating thickness levels from coating oxidation sample runs
- 1-in. Threaded Stud Substrate
- Reaction Chamber C (small reaction chamber)
- Gas Feed Geometry D

APPENDIX XI

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-2200°F OXIDATION RESISTANCE CORRELATION FOR COATING BASED ON SAMPLES FROM TWO COATING THICKNESS LEVELS

MULTIPLE REGRESSION.....OXID

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1.77500	0.40089	0.08407	-14.84648	6.03899	-2.45844
2	13.71249	3.41234	-0.21699	0.69873	428.82715	0.00163
3	55.32495	3.20880	0.60449	2.60067	428.82764	0.00606
4	30.96249	2.58398	-0.46411	-0.92272	428.82666	-0.00215
DEPENDENT 5	6.15000	6.35812				

INTERCEPT	-92.39082
MULTIPLE CORRELATION	0.89854
STD. ERROR OF ESTIMATE	4.26264

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	4	228.46912	57.11728	3.14347
DEVIATION FROM REGRESSION	3	54.51038	18.17012	
TOTAL	7	282.97949		

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	11.80000	10.82382	0.97618
2	9.80000	9.74762	0.05238
3	0.50000	4.49060	-3.99060
4	0.50000	-1.75777	2.25777
5	17.29999	13.50742	3.79257
6	2.00000	3.11244	-1.11244
7	0.50000	-0.54846	1.04846
8	6.80000	9.82538	-3.02538

APPENDIX XII

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-2400°F OXIDATION RESISTANCE CORRELATION FOR COATING BASED ON SAMPLES FROM TWO COATING THICKNESS LEVELS

MULTIPLE REGRESSION.....OXID

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1.77500	0.40089	0.13444	11.83229	14.54653	0.81341
2	13.71249	3.41234	0.57958	-0.32405	1032.94482	-0.00031
3	55.32495	3.20880	-0.37744	-2.41223	1032.94629	-0.00234
4	30.96249	2.58398	-0.29667	-1.06983	1032.94385	-0.00104
DEPENDENT 5	6.63750	8.84613				

INTERCEPT 156.65955

MULTIPLE CORRELATION 0.65009

STD. ERROR OF ESTIMATE 10.26771

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	4	231.49986	57.87495	0.54896
DEVIATION FROM REGRESSION	3	316.27783	105.42593	
TOTAL	7	547.77759		

APPENDIX XII (CONTD)

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	6.50000	10.15958	-3.65958
2	2.00000	0.47940	1.52060
3	6.80000	2.20959	4.59040
4	6.80000	8.81717	-2.01717
5	1.00000	-0.68454	1.68454
6	27.50000	15.27510	12.22490
7	2.00000	9.44312	-7.44312
8	0.50000	7.39967	-6.89967

APPENDIX XIII

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-2200°F OXIDATION RESISTANCE CORRELATION FOR COATING BASED ON ALL SAMPLES FROM COATING OXIDATION SAMPLE RUNS

MULTIPLE REGRESSION.....CX2200

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1.87500	0.65937	-0.14217	-6.32253	16.86595	-0.37487
2	13.56666	3.48851	0.01440	-5.18444	3074.93872	-0.00169
3	55.29163	3.37947	0.03638	-5.31827	3074.93872	-0.00173
4	31.14162	2.37581	-0.07289	-6.09004	3074.93774	-0.00198
DEPENDENT 5	15.26666	28.93753				

INTERCEPT 581.16602

MULTIPLE CORRELATION 0.15516

STD. ERROR OF ESTIMATE 35.81267

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	4	233.35121	58.33780	0.04549
DEVIATION FROM REGRESSION	7	8977.83594	1282.54785	
TOTAL	11	9211.18359		

MULTIPLE REGRESSION.....0X2200

SELECTION..... 1

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	2.00000	20.79619	-18.79619
2	17.29999	12.80843	4.49156
3	11.80000	20.67409	-8.87409
4	103.50000	19.67558	83.82442
5	26.50000	5.05284	21.44716
6	9.80000	16.99738	-7.19738
7	2.00000	16.00758	-14.00758
8	2.00000	9.21768	-7.21768
9	0.50000	13.55283	-13.05283
10	0.50000	15.44144	-14.94144
11	0.50000	16.36810	-15.86810
12	6.80000	16.59550	-9.79551

APPENDIX XIV

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-2400°F OXIDATION RESISTANCE CORRELATION FOR COATING BASED ON ALL SAMPLES FROM COATING OXIDATION SAMPLE RUNS

MULTIPLE REGRESSION.....CX2400

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1.67500	0.65937	0.22513	2.54672	7.16075	0.35565
2	13.56666	3.48851	0.56348	-0.77730	1305.52173	-0.00060
3	55.29163	3.37947	-0.43612	-2.67461	1305.52173	-0.00205
4	31.14162	2.37581	-0.20703	-3.04360	1305.52124	-0.00233
DEPENDENT 5	11.55000	14.46201				

INTERCEPT	259.98633
MULTIPLE CORRELATION	0.54459
STD. ERROR OF ESTIMATE	15.20493

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	4	682.31885	170.57971	0.73783
DEVIATION FROM REGRESSION	7	1618.33008	231.19000	
TOTAL	11	2300.64893		

MULTIPLE REGRESSION.....0X2400

SELECTION..... 1

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	0.50000	0.39827	0.10173
2	1.00000	3.81958	-2.81958
3	6.50000	22.55800	-16.05800
4	42.00000	12.16656	29.83344
5	9.00000	9.14354	-0.14354
6	2.00000	6.67639	-4.67639
7	27.50000	20.92535	6.57465
8	34.00000	23.78493	10.21507
9	2.00000	8.92128	-6.92128
10	6.80000	11.80615	-5.00615
11	6.80000	5.45193	1.34806
12	0.50000	12.94275	-12.44275

APPENDIX XV

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-CORRELATION FOR 2200°F COATING OXIDATION RESISTANCE AS FUNCTION OF PROCESS VARIABLES, BASED ON ALL SAMPLES FROM COATING OXIDATION SAMPLE RUNS

MULTIPLE REGRESSION.....PR220C

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1034.41650	49.13332	-0.03444	-0.23865	0.21622	-1.10372
2	0.07250	0.02598	-0.46542	-140.64786	503.80737	-0.27917
3	18.37500	1.96706	0.44519	3.40009	5.40475	0.62909
4	4.68750	0.98353	0.36022	3.47523	10.80949	0.32150
5	4.37500	1.29904	0.53652	6.48795	10.07614	0.64389
6	4.06250	1.69535	0.50536	2.57562	8.71785	0.29544
7	8.66667	1.96946	-0.46535	-3.94254	5.32204	-0.74080
DEPENDENT 8	15.26666	28.93752				

INTERCEPT 188.88246

MULTIPLE CORRELATION 0.75917

STD. ERROR OF ESTIMATE 31.23470

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	7	5308.75781	758.29360	0.77736
DEVIATION FROM REGRESSION	4	3902.42578	975.60645	
TOTAL	11	9211.18359		

APPENDIX XV (CONTD)

MULTIPLE REGRESSION.....PR2200

SELECTION..... 1

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	2.00000	28.90628	-26.90628
2	17.29999	15.84744	1.45255
3	11.80000	1.37286	10.42714
4	103.50000	67.58426	35.91574
5	26.50000	17.54254	8.95746
6	9.80000	26.26184	-16.46184
7	2.00000	27.43658	-25.43658
8	2.00000	19.96622	-17.96622
9	0.50000	5.39383	-4.89383
10	0.50000	-6.94194	7.44194
11	0.50000	-13.22913	13.72913
12	6.80000	-6.94194	13.74194

APPENDIX XVI

ANALYSIS OF TESTS: MULTIPLE REGRESSION TAB RUN-CORRELATION FOR 2400°F COATING OXIDATION RESISTANCE AS FUNCTION OF PROCESS VARIABLES, BASED ON ALL SAMPLES FROM COATING OXIDATION SAMPLE RUNS

MULTIPLE REGRESSION.....PR240C

SELECTION..... 1

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
1	1034.41650	49.13332	0.03176	-0.06385	0.03542	-1.80259
2	0.07250	0.02598	-0.14771	191.70824	82.52715	2.32297
3	18.37500	1.96706	0.39634	1.96333	0.88533	2.21762
4	4.66750	0.98353	0.79260	11.67665	1.77067	6.59449
5	4.37500	1.29904	0.43321	3.54084	1.65054	2.14526
6	4.06250	1.69535	0.28127	-1.96999	1.42804	-1.37950
7	8.66667	1.96546	-0.50175	-2.99027	0.87179	-3.43005
DEPENDENT 8	11.55000	14.46202				

INTERCEPT -8.68819

MULTIPLE CORRELATION 0.97698

STD. ERROR OF ESTIMATE 5.11646

ANALYSIS OF VARIANCE FOR THE REGRESSION

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
ATTRIBUTABLE TO REGRESSION	7	2195.93726	313.70532	11.98347
DEVIATION FROM REGRESSION	4	104.71265	26.17816	
TOTAL	11	2300.64990		

APPENDIX XVI (CONTD)

MULTIPLE REGRESSION.....PR24CC

SELECTION..... 1

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	0.50000	3.55899	-3.05899
2	1.00000	0.14828	0.85172
3	6.50000	4.62660	1.87340
4	42.00000	37.90733	4.09267
5	9.00000	7.98441	1.01559
6	2.00000	3.17960	-1.17960
7	27.50000	29.70122	-2.20122
8	34.00000	36.04933	-2.04933
9	2.00000	6.45674	-4.45674
10	6.80000	3.49950	3.30050
11	6.80000	1.98898	4.81102
12	0.50000	3.49950	-2.99950

APPENDIX XVII

CYCLIC OXIDATION OPTIMIZATION: PROCESS CONDITIONS AND RESULTS FOR CYCLIC OXIDATION RUNS

Run Number	Inert Gas Flows (ℓ/min) $SiCl_4$ Bubbler	$SiCl_4$ Diluent	$TiCl_4$ Bubbler	$TiCl_4$ Diluent	Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Gas Flow (ℓ/min) H_2 Feed	H_2 Inert Diluent Gas	Inert Gas Identification	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quantity of Substrates	Coating Deposits Average Weight Gain of Substrate (mg)	Substrate Identification	Reaction Chamber Identification	Gas Feed Geometry Identification	Dual Chamber Identification	Cr and Ti Chips Charge
CLY-160-68	.08	.42	6.0	.5	Yes	Yes	6.0	4.0	Ar	17.0	240	1000	11	10	176.4	D	D	D	Chamber B	Fresh
CLY-161-69	.04	2.46	6.0	.5	Yes	Yes	6.0	6.0	Ar	21.0	300	1000	11	10	147.2	D	D	D	Chamber B	Fresh
CLY-162-69	.078	2.822	8.6	.5	Yes	Yes	6.5	3.5	Ar	21.0	300	1000	11	10	297.3	D	D	D	Chamber B	Fresh
CLY-163-69	.096	2.204	12.2	.5	Yes	Yes	8.0	2.0	Ar	25.0	300	960	11	10	306.8	D	D	D	Chamber B	Fresh
CLY-164-69	.120	1.38	15.0	.5	Yes	Yes	10.0	0	Ar	28.75	60	900	11	10	81.39	D	D	D	Chamber B	Fresh
CLY-165-69	.120	1.38	17.0	.5	Yes	Yes	10.0	0	Ar	29.08	270	900	11	10	330.7	D	D	D	Chamber B	Fresh
CLY-166-69	.096	2.204	12.2	.5	Yes	Yes	8.0	2.0	Ar	25.0	420	960	11	20	132.7-194.2-51.4-84.3	A-B-D-C	A	D	Chamber B	Fresh
CLY-167-69	.108	1.79	14.6	.5	Yes	Yes	9.0	1.0	Ar	26.998	480	930	11	20	119.0-224.2	A-B	A	D	Chamber B	Fresh
CLY-168-69	.084	2.616	9.80	.5	Yes	Yes	7.0	3.0	Ar	23.0	480	990	11	20	226.2-112.3	A-B	A	D	Chamber B	Fresh
CLY-169-69	.120	1.38	17.0	.5	Yes	Yes	10.0	0	Ar	29.0	480	900	11	20	267.6-118.2	A-B	A	D	Chamber B	Fresh
CLY-170-69	.096	2.204	12.2	.5	Yes	Yes	8.0	2.0	Ar	25.0	480	960	11	20	160.9-73.7	A-B	A	D	Chamber B	Fresh
CLY-171-69	.132	.968	19.4	.5	Yes	Yes	11.0	0	Ar	32.0	480	870	11	20	193.2-108.2	A-B	A	D	Chamber B	Fresh
CLY-172-69	.072	3.028	7.4	.5	Yes	Yes	6.0	4.0	Ar	21.0	480	1020	11	20	358.2-111.0	A-B	A	D	Chamber B	Fresh
CLY-173-69	.072	3.028	7.4	.5	Yes	Yes	6.0	4.0	Ar	21.0	480	1020	11	20	157.3-134.2	A-B	A	D	Chamber B	Fresh
CLY-174-69	.084	2.616	9.80	.5	Yes	Yes	7.0	3.0	Ar	23.0	480	990	11	20	157.6-161.9	A-B	A	D	Chamber B	Fresh
CLY-175-69	.084	2.616	9.80	.5	Yes	Yes	7.0	3.0	Ar	23.0	480	990	11	10	689.0	D	A	D	Chamber B	Fresh
CLY-176-69	.084	2.616	9.80	.5	Yes	Yes	7.0	3.0	Ar	23.0	480	990	11	20	347.7-88.3	A-B	A	D	Chamber B	Fresh
CLY-177-69	.084	2.616	9.80	.5	Yes	Yes	7.0	3.0	Ar	23.0	480	990	11	30	528.2-118.6-147.6	D-E-C	A	D	Chamber B	Fresh

OTHER RUN CONDITIONS

- Substrate Identification
  - A. 1 1/2-in. Round Rod
  - B. Flat Panel (app. 1 in. X 1/2 in.)
  - C. 1-in. Threaded Stud
  - D. 1 1/2-in. Hex Head Bolt
  - E. Hex Nut

APPENDIX XVII (CONTD)

Run Number	Quantity of Substrate	Coating Deposit: Weight Gain of Substrate (mg)											Substrate Identification
		1	2	3	4	5	6	7	8	9	10	Avg.	
CLY-160-68	10	146.5	159.6	170.8	182.7	183.6	193.6	194.7	193.0	191.3	167.8	178.4	D
CLY-161-69	10	125.4	152.0	147.7	143.6	143.6	138.0	157.3	163.2	156.1	145.6	147.2	D
CLY-162-69	10	300.5	294.4	297.0	297.8	302.0	294.7	294.1	294.0	295.6	302.6	297.3	D
CLY-163-69	10	314.6	305.0	311.4	302.2	305.5	305.4	296.7	296.7	317.3	313.7	306.8	D
CLY-164-69	10	67.5	66.7	99.3	82.9	63.0	69.1	94.1	79.2	86.1	106.0	81.4	D
CLY-165-69	10	326.5	337.9	331.6	333.6	328.7	327.8	329.8	332.9	329.3	329.0	330.7	D
CLY-166-69	5	84.7	83.4	83.8	83.4	86.0	–	–	–	–	–	84.3	C
CLY-166-69	5	47.3	45.9	46.1	55.0	53.6	–	–	–	–	–	51.4	B
CLY-166-69	5	128.9	133.9	132.5	136.0	132.1	–	–	–	–	–	132.7	A
CLY-166-69	5	193.7	191.5	197.4	193.1	195.3	–	–	–	–	–	194.2	D
CLY-167-69	10	112.5	120.1	128.5	114.1	128.1	113.4	129.3	68.5	136.4	138.5	118.9	B
CLY-167-69	10	223.7	217.7	223.6	222.9	223.9	221.2	218.5	228.4	227.9	234.3	224.2	A
CLY-168-69	10	261.4	264.1	259.8	261.8	263.2	269.6	270.9	270.4	273.5	267.0	266.2	A
CLY-168-69	10	104.3	105.1	112.3	111.7	110.5	110.9	138.7	117.0	87.9	124.8	112.3	B
CLY-169-69	10	259.4	261.5	268.1	268.3	261.3	267.9	268.3	272.3	276.5	278.0	267.7	A
CLY-169-69	10	100.9	104.1	113.0	114.5	118.9	121.0	120.9	128.0	127.1	133.9	118.2	B
CLY-170-69	10	152.9	157.9	155.9	159.7	158.3	165.3	164.5	163.4	165.4	166.1	160.9	A
CLY-170-69	10	67.1	65.8	65.5	71.7	73.7	73.8	79.3	80.2	81.3	78.9	73.7	B
CLY-171-69	10	181.9	184.6	185.5	190.5	183.4	183.7	208.5	204.8	204.0	205.4	193.2	A
CLY-171-69	10	94.4	107.0	101.0	107.1	98.8	102.7	119.7	111.7	116.5	123.4	108.2	B
CLY-172-69	10	342.5	347.3	351.1	356.3	354.8	351.7	353.0	366.6	357.2	363.4	358.2	A
CLY-172-69	10	101.1	102.4	115.0	103.0	108.9	112.3	107.8	112.4	113.2	128.8	110.9	B
CLY-173-69	10	160.2	146.3	159.4	160.0	160.9	156.0	157.5	175.9	98.3	158.8	151.3	A
CLY-173-69	10	128.5	130.0	127.5	138.8	137.7	133.1	121.2	143.8	132.9	148.2	134.2	B
CLY-174-69	10	144.7	140.8	158.3	147.5	154.9	153.5	161.1	157.4	199.7	158.3	157.6	A
CLY-174-69	10	142.9	151.1	160.9	154.8	169.2	174.2	173.6	166.0	158.4	178.0	161.9	B
CLY-175-69	10	686.2	693.6	702.5	696.7	695.7	684.3	688.4	685.2	711.8	695.8	689.0	D
CLY-176-69	10	336.2	349.1	346.8	344.3	346.9	339.7	358.6	351.1	352.2	349.8	347.7	A
CLY-176-69	10	78.8	75.6	90.0	81.8	79.2	96.9	99.7	84.2	104.0	93.1	88.4	B
CLY-177-69	10	521.3	521.9	506.7	526.6	542.7	530.8	328.6	528.4	538.8	536.7	528.3	D
CLY-177-69	10	117.4	112.6	119.5	118.0	119.6	118.3	123.7	124.1	116.3	116.3	118.6	E
CLY-177-69	10	158.7	147.0	145.9	150.9	147.9	144.0	146.7	141.9	149.7	143.7	147.7	C
CLY-178-69	10	224.6	226.4	219.4	221.0	225.0	218.4	222.8	218.5	226.3	228.7	223.1	D
CLY-178-69	10	43.2	42.5	39.9	42.2	40.1	39.7	40.3	40.3	41.3	41.1	41.0	E
CLY-178-69	10	51.8	52.1	50.9	50.8	52.8	54.8	53.4	54.3	52.4	52.8	52.6	C

APPENDIX XVIII

CYCLIC OXIDATION OXIDATION: PROCESS CONDITIONS AND RESULTS FOR CYCLIC OXIDATION RUNS

Run Number	Inert Gas Flows (ℓ/min)				Weight Loss of Cr Chips (mg)	Weight Loss of Ti Chips (mg)	H_2 Gas Flows (ℓ/min)		Inert Gas Identification	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quality of Substrates	Coating Deposits Average Weight Gain of Substrate (mg)	Substrate Identification	Reaction Chamber Identification	Gas Feed Geometry Identification	Dual Chamber Identification	Cr and Ti Chips Charge
	$SiCl_4$		$TiCl_4$				H_2 Feed	Inert Diluent Gas												
	Bubbler	Diluent	Bubbler	Diluent																
CLY-178-69	.072	3.028	7.40	.5	Yes	Yes	6.0	4.0	Ar	21	210	1020	11	30	223.1-52.6-41.1	C-D-E	A	D	B	Fresh
CLY-179-69	.072	3.028	7.40	.5	Yes	Yes	6.0	4.0	Ar	21	390	1020	11	20	171.5-146.6-59.4	A-B-F	A	D	B	Fresh
CLY-180-69	.072	3.028	7.40	.5	Yes	Yes	6.0	4.0	Ar	21	540	1020	11	20	310.6-157.1-124.4	A-B-F	A	D	B	Fresh
CLY-181-69	.060	3.44	5.0	.5	Yes	Yes	5.0	5.0	Ar	19	600	1050	11	20	270.7-129.9-102.7	A-B-F	A	D	B	Fresh
CLY-182-69	.072	3.028	7.40	.5	Yes	Yes	6.0	4.0	Ar	21	360	1020	11	10	202.1	D	A	D	B	Fresh
CLY-183-69	.072	3.028	7.40	.5	Yes	Yes	6.0	4.0	Ar	21	480	1020	11	10	151.2-458.3	C-D	A	D	B	Fresh
CLY-184-69	.060	3.44	5.0	.5	Yes	Yes	5.0	5.0	Ar	19	480	1050	11	20	107.2-323.3	C-D	A	D	B	Fresh
CLY-185-69	.096	2.204	12.2	.5	Yes	Yes	8.0	2.0	Ar	25	480	960	11	20	111.3-302.8	C-D	A	D	B	Fresh

OTHER RUN CONDITIONS

- **Substrate Identification**

  A. 1 1/2-in. Round Rod
  B. Flat Panel (app. 1 in. x 1/2 in.)
  C. 1-in. Threaded Stud
  D. 1 1/2-in. Hex Head Bolt
  E. Hex Nut
  F. Spot Weld Flat Panel (app. 1-1/2 in. x 1/4-1/2 in.)

APPENDIX XVIII (CONTD)

Run Number	Quantity of Substrates	COATING DEPOSIT: WEIGHT GAIN OF SUBSTRATE (mg)											Substrate Identification
		1	2	3	4	5	6	7	8	9	10	Avg	
CLY-178-69	10	224.6	226.4	219.4	221.0	225.0	218.4	222.8	218.5	226.3	228.7	223.1	D
CLY-178-69	10	43.2	42.5	39.9	42.2	40.1	39.7	40.3	40.3	41.3	41.1	41.0	E
CLY-178-69	10	51.8	52.1	50.9	50.8	52.8	54.8	53.4	54.3	52.4	52.8	52.6	C
CLY-179-69	10	163.1	161.5	166.2	165.9	174.7	158.4	183.1	185.9	187.0	170.6	171.5	A
CLY-179-69	5	144.4	143.3	138.9	144.1	162.3	—	—	—	—	—	146.4	F
CLY-179-69	5	20.1	60.8	58.7	77.1	80.5	—	—	—	—	—	59.4	B
CLY-180-69	10	311.8	215.3	305.9	306.4	307.1	313.7	317.9	301.9	308.9	318.3	310.6	A
CLY-180-69	5	156.3	152.1	156.2	154.8	166.5	—	—	—	—	—	157.2	F
CLY-180-69	5	115.9	126.4	136.3	120.4	124.9	—	—	—	—	—	124.4	B
CLY-181-69	10	264.7	259.3	253.6	260.3	258.0	264.9	279.9	282.4	285.6	298.4	270.7	A
CLY-181-69	5	109.4	126.5	131.9	134.0	138.8	—	—	—	—	—	129.9	F
CLY-181-69	5	103.0	96.8	103.8	106.6	103.4	—	—	—	—	—	102.7	B
CLY-182-69	5	205.0	200.4	202.6	200.8	201.4	—	—	—	—	—	202.1	D
CLY-183-69	10	150.3	147.8	151.8	150.6	151.9	156.2	149.8	145.6	153.6	154.6	151.2	C
CLY-183-69	10	454.9	450.3	451.0	459.2	457.3	464.4	461.7	461.2	461.4	461.0	458.3	D
CLY-184-69	10	105.4	104.5	105.3	109.1	107.2	109.7	108.1	107.9	108.2	106.8	107.2	C
CLY-184-69	10	322.5	317.1	322.0	323.3	320.0	331.5	326.3	324.8	321.3	324.5	323.3	D
CLY-185-69	10	302.8	308.6	308.3	308.8	308.0	306.3	310.6	306.9	311.3	307.0	307.8	D
CLY-185-69	10	108.8	112.0	112.2	111.9	111.3	110.6	111.9	111.6	111.8	111.2	111.3	C

APPENDIX XIX

PRODUCTION DEMONSTRATION BATCHES: PROCESS CONDITIONS AND RESULTS

Run Number	Inert Gas Flows (ℓ/min) $TiCl_4$ Bubbler	$TiCl_4$ Diluent	$SiCl_4$ Bubbler	$SiCl_4$ Diluent	Weight Loss of Cr Chips	Weight Loss of Ti Chips	H_2 Gas Flows (ℓ/min) H_2 Feed	H_2 Inert Diluent Gas	Inert Gas Identification	Total Flow Measured (ℓ/min)	Deposition Time (min)	Reaction Temp. (°C)	Rotation Speed (rpm)	Quantity of Substrates	Coating Deposit Average Weight Gain of Substrate (mg)	Substrate Identification	Reaction Chamber Identification	Gas Feed Geometry Identification	Dual Chamber Identification	Cr and Ti Chips Charge
CLY-185-69	12.2	.5	.096	2.204	Yes	Yes	8.0	2.0	Ar	25	480	960	11.0	20	307.8-111.3	D-C	A	D	Chamber B	Fresh
CLY-186-69	8.5	↑	.078	2.922	↑	↑	6.5	3.5	↑	22	↕	1005	↑	10	492.4	D	↑	↑	↑	↑
CLY-187-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	40	307.9	↑	↑	↑	↑	↑
CLY-188-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	30	157.9	↑	↑	↑	↑	↑
CLY-189-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	480	↑	↑	20	268.8	↑	↑	↑	↑	↑
CLY-190-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	600	↑	↑	30	421.5-221.7	D-A	↑	↑	↑	↑
CLY-191-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	29	477.4-236.9	D-A	↑	↑	↑	↑
CLY-192-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	30	442.2	D	↑	↑	↑	↑
CLY-193-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	600	↑	↑	↑	285.9	↑	↑	↑	↑	↑
CLY-194-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	900	↑	↑	↑	481.5	↑	↑	↑	↑	↑
CLY-195-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	900	↑	11.0	↑	502.2	↑	↑	↑	↑	↑
CLY-196-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	480	↑	1.2	↑	305.2	↑	↑	↑	↑	↑
CLY-197-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	480	↑	.5	30	259.8	D	↑	↑	↑	↑
CLY-198-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	900	↑	↑	50	432.3-75.1	D-E	↑	↑	↑	↑
CLY-199-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	30	368.7	D	↑	↑	↑	↑
CLY-200-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	50	286.2-59.4	D-E	↑	↑	↑	↑
CLY-201-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	↑	280.3-66.5	D-E	↑	↑	↑	↑
CLY-202-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	↑	463.6-69.7	D-E	↑	↑	↑	↑
CLY-203-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	900	↑	↑	50	X-84.0	E	↑	↑	↑	↑
CLY-204-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	600	↑	↑	30	265.9	D	↑	↑	↑	↑
CLY-205-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	720	↑	↑	↑	358.0	D	↑	↑	↑	↑
CLY-206-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	720	↑	↑	45	299.5-63.8	D-E	↑	↑	↑	↑
CLY-207-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	240	↑	↑	45	—	D-E	↑	↑	↑	↑
CLY-208-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	720	↑	↑	—	—	—	↑	↑	↑	↑
CLY-209-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	45	212.0-45.7	D-E	↑	↑	↑	↑
CLY-210-69	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↕	↑	↑	45	376.9-62.1	D-E	↑	↑	↑	↑
CLY-211-69	8.5	.5	.078	2.922	Yes	Yes	6.5	3.5	Ar	22	720	1005	.5	52	493.1-116.4	D-E	A	D	Chamber B	Fresh

OTHER RUN CONDITIONS

- **Substrate Identification**
  - A. 1 1/2-in. Round Rod
  - B. Flat Panel (approximately 1 in. x 1/2 in.)
  - C. 1-in. Threaded Stud
  - D. 1 1/2-in. Hex Head Bolt
  - E. Hex Nut
- In run CLY-203-69, some problems experienced with bolts
- In Run CLY-207-69, reaction chamber broke
- In run CLY-208-69, new reaction chamber coated
- Batch A is CLY-202-69
- Batch B is CLY-205-69 (bolts) and CLY-203-69 (nuts)
- Batch C is CLY-206-69
- Batch D is CLY-210-69 with re-etched bolts and nuts from reaction chamber break run of CLY-207-69
- Batch E is CLY-211-69

APPENDIX XIX (CONTD)

Run Number	Quantity of Substrate	Coating Deposit: Weight Gain of Substrate (mg)																													Substrate Identification
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	Avg.	
CLY-186-69	10	478.3	485.0	516.7	481.4	488.8	496.2	Fillers	→	→	→	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	492.4	D
CLY-187-69	40	305.7	309.9	303.6	301.7	304.2	313.2	Fillers	→																			→	To 40			307.9	D
CLY-188-69	30	158.3	160.1	157.2	158.8	154.6	158.9	Fillers	→																						→	157.9	D
CLY-189-69	20	263.0	268.3	272.2	271.8	Fillers	→														→	—	—	—	—	—	—	—	—	—	—	268.8	D
CLY-190-69	27	424.8	427.3	412.0	416.1	430.7	419.3	Fillers	→																			→	—	—	—	421.5	D
CLY-190-69	3	212.9	225.3	226.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	221.7	A
CLY-191-69	26	478.8	475.0	474.4	485.9	467.5	482.1	Fillers	→																		→	—	—	—	—	477.4	D
CLY-191-69	3	231.9	244.2	234.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	236.9	A
CLY-192-69	30	438.1	448.1	443.4	448.4	Fillers	→																								→	444.2	D
CLY-193-69	30	292.4	290.0	271.5	290.0	Fillers	→																								→	285.9	D
CLY-194-69	30	483.0	478.9	481.0	475.8	481.1	489.6	Fillers	→																						→	481.5	D
CLY-195-69	30	505.4	505.0	493.9	503.9	498.9	505.9	Fillers	→																						→	502.2	D
CLY-196-69	30	308.2	307.4	300.7	304.8	305.0	Fillers	→																							→	305.2	D
CLY-197-69	30	240.8	243.4	251.5	258.5	279.7	277.0	Fillers	→																						→	259.8	D
CLY-198-69	30	307.4	335.8	330.2	323.6	Fillers	→																								→	324.2	D
CLY-198-69	20	81.7	75.8	83.6	72.7	66.2	70.6	Fillers	→												→	—	—	—	—	—	—	—	—	—	—	75.1	E
CLY-199-69	30	361.3	347.8	365.4	389.3	379.8	Fillers	→																							→	368.7	D
CLY-200-69	30	280.2	278.5	295.7	286.1	290.8	Fillers	→																							→	286.2	D
CLY-200-69	20	60.0	61.9	56.2	60.6	58.5	Fillers	→													→	—	—	—	—	—	—	—	—	—	—	59.4	E
CLY-201-69	30	280.4	283.3	270.8	283.5	283.6	Fillers	→																							→	280.3	D
CLY-201-69	20	63.9	66.0	66.8	69.6	66.5	Fillers	→													→	—	—	—	—	—	—	—	—	—	—	66.5	E
CLY-202-69	30	475.9	477.6	454.2	427.6	451.3	455.3	470.6	459.1	452.5	462.2	466.4	463.9	468.2	465.5	474.4	467.8	461.7	474.0	442.6	466.9	459.4	460.4	455.9	458.4	476.3	462.3	477.3	485.9	473.5	461.6	463.6	D
CLY-202-69	20	67.7	68.8	69.7	71.5	71.4	67.2	68.8	66.7	84.9	65.4	63.1	73.1	71.6	69.2	72.2	74.9	70.6	76.8	86.5	69.7	—	—	—	—	—	—	—	—	—	—	71.4	E
CLY-203-69	19	85.2	80.2	81.2	85.0	95.5	92.8	86.1	92.8	84.0	86.1	86.3	87.0	78.6	79.1	89.0	85.5	97.7	100.6	109.7	—	—	—	—	—	—	—	—	—	—	—	84.0	E
CLY-204-69	30	267.8	259.6	260.1	267.5	274.6	Fillers	→																							→	265.9	D
CLY-205-69	30	320.9	307.1	310.5	319.5	319.8	342.2	341.8	341.7	342.1	345.5	346.3	343.1	341.8	341.5	339.7	342.3	341.5	349.0	346.4	346.5	346.3	340.4	341.1	346.7	342.9	344.6	346.4	344.4	359.0	361.4	358.0	D
CLY-206-69	25	299.7	288.7	305.2	315.3	281.7	297.0	303.4	307.7	289.4	272.7	291.4	300.4	305.6	305.4	274.4	291.0	291.6	300.0	305.7	300.6	301.5	281.2	300.7	299.1	294.4	—	—	—	—	—	299.5	D
CLY-206-69	20	62.1	65.8	64.0	62.3	64.4	60.8	65.1	62.6	62.4	60.0	63.1	69.6	55.5	65.7	60.4	64.5	64.8	67.7	65.9	69.2	—	—	—	—	—	—	—	—	—	—	63.8	E
CLY-209-69	20	189.5	213.2	233.3	Fillers	→															→	—	—	—	—	—	—	—	—	—	—	212.0	D
CLY-209-69	25	45.1	47.3	46.2	44.9	45.5	46.5	Fillers	→																	→	—	—	—	—	—	45.7	E
CLY-210-69	25	318.3	350.0	373.2	366.1	389.5	378.5	382.0	350.0	364.7	390.5	378.4	317.9	405.0	376.2	371.0	368.8	372.2	377.6	380.4	376.5	395.0	383.0	415.4	426.4	414.6	—	—	—	—	—	376.9	D
CLY-210-69	20	62.2	60.9	58.3	51.6	52.9	56.3	59.2	59.2	67.8	58.4	62.6	57.5	63.0	61.9	62.0	63.0	62.2	60.3	62.2	63.9	—	—	—	—	—	—	—	—	—	—	62.1	E
CLY-211-69	28	498.8	468.7	493.0	497.4	452.3	449.2	442.5	522.0	528.3	535.0	540.2	535.7	481.9	469.8	494.1	498.0	485.5	443.7	464.4	454.1	455.1	459.9	476.9	470.7	510.3	546.9	549.6	601.5	—	—	493.1	D
CLY-211-69	24	98.9	108.5	107.6	107.9	108.1	107.3	111.3	111.1	111.5	113.7	96.7	107.8	106.0	106.8	109.2	115.5	114.3	116.8	117.6	114.8	116.1	122.6	140.6	111.8	—	—	—	—	—	—	116.5	E

APPENDIX XX

OXIDATION TESTING: OXIDATION TEST RESULTS FOR FIRST STATISTICAL SERIES SAMPLES

Run Number*	Oxidation Results: **Weight Gain of Sample (mg)							
	1 hr	3 hr	4 hr	5 hr	6 hr	19 hr	20.7 hr	21.5 hr
CLY-94-68 (6)	1.4	2.7	6.4	—	—	X	X	X
CLY-95-68 (3)	.7	1.9	4.9	—	—	X	X	X
CLY-96-68	3.2	3.8	8.3	—	—	X	X	X
CLY-97-68	3.0	4.6	X	X	X	X	X	X
CLY-98-68	2.3	2.3	4.4	—	—	X	X	X
CLY-99-68	4.6	X	X	X	X	X	X	X
CLY-100-68 (8)	4.9	X	X	X	X	X	X	X
CLY-101-68 (2)	2.8	X	X	X	X	X	X	X
CLY-102-68 (1)	7.8	X	X	X	X	X	X	X
CLY-103-68 (5)	5.2	12.1	15.8	—	—	—	X	X
CLY-104-68	X	X	X	X	X	X	X	X
CLY-105-68 (4)	.5	—	—	2.0	3.1	—	—	X
CLY-106-68	X	X	X	X	X	X	X	X
CLY-107-68	3.3	—	—	X	X	X	X	X

OTHER RUN CONDITIONS:

Oxidation Temperature: 2500°F

X Denotes visible breakdown, (i.e., visible oxidation of substrate).
— Denotes that weight gain of sample not determined at that specific time.
* Number in parenthesis corresponds to run number of first statistical series.
** Sample is round rod substrate (dimensions: 1 in. x 1/4 in., approximate surface area: 5.714 cm^2).

APPENDIX XXI

OXIDATION TESTING: OXIDATION TEST RESULTS FOR SAMPLES PREPARED IN SECOND STATISTICAL SERIES

Run Number*	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE** (mg)																													
	1	1.5	2	2.5	3	4	5	5.5	6	7.5	11	12.1	13.8	20	20.5	21.5	23	24	24.5	26	28	29	30	32.5	33.6	35.3	47.3	51.3	52.8
CLY-108-68	2.5	–	–		–	–	4.4	–	5.1	–	–	–	–	–	–	10.8	–	10.8	–	11.1	11.4	11.6	–	–	–	–	17.9	X	X
CLY-109-68	4.0	–	–		–	–	6.7	–	7.4	–	–	–	–	–	–	11.5	–	11.5	–	12.0	12.4	12.4	X	X	X	X	X	X	X
CLY-110-68	–	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-111-68	–	-1.3	–	–	–	–	–	–	–	–	–	–	–	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-112-68	–	–	.6	–	2.5	2.5	–	–	–	–	–	–	–	12.7	X	–	16.5	–	–	–	–	X	X	X	X	X	X	X	X
CLY-113-68(5)	–	–	–	4.9	–	–	–	5.7	–	–	–	–	–	–	10.5	–	–	–	12.6	–	–	–	13.5	15.8	17.3	19.9	–	26.3	X
CLY-114-68	–	–	–	4.3	–	–	–	5.1	–	–	–	–	–	–	8.5	–	–	–	11.6	–	–	–	12.2	14.3	15.6	19.6	–	X	X
CLY-115-68(4)	–	–	–	–	.2	–	–	–	–	.9	9.3	29.8	X	X	X	X	X	X	X	X	X	–	X	X	X	X	X	X	X
CLY-116-68(8)	-1.1	–	–	–	0	–	–	–	–	1.9	10.5	45.3	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-117-68(1)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-118-68(6)	–	–	4.9	–	–	13.6	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-119-68	–	–	5.3	–	–	6.8	–	8.5	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-120-68(2)	–	–	3.6	–	–	7.9	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-121-68(3)	–	–	4.5	–	–	6.6	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-122-68(7)	–	6.6	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-123-68	–	22.8	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Other Run Conditions

Oxidation Temperature: 2500°F

X Denotes visible breakdown (i.e., visible oxidation of the substate)

– Denotes weight gain of sample not determined at that specific time

* Number in parenthesis corresponds to run number of second statistical series

**Sample is round rod substrate (dimensions: 1 in. x 1/4 in., approximate surface area: 5.714 cm^2). Column headings denote time in hours.

APPENDIX XXII

OXIDATION TESTING: OXIDATION TEST RESULTS AT 2500°F OXIDATION TEMPERATURE FOR SAMPLES PREPARED IN DEPOSIT PHASE RUNS

OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*

RUN NUMBER	0.5	1.0	1.1	1.5	2.0	2.1	2.2	2.3	2.5	3.0	3.2	3.3	3.5	3.6	4.0	4.1	4.3	4.5	4.6	5.0	5.1	5.5	5.6	6.0	6.5	6.6	7.0	7.5	7.6
CLY-124-68	—	19.2	—	—	30.4	—	—	—	—	42.5	—	—	—	—	51.6	—	—	—	—	59.0	—	—	—	65.5	—	—	70.8	—	—
CLY-125-68	—	6.5	—	—	8.7	—	—	—	—	9.8	—	—	—	—	10.2	—	—	—	—	10.4	—	—	—	10.9	—	—	12.0	—	—
CLY-126-68	—	9.5	—	—	12.3	—	—	—	—	13.4	—	—	—	—	14.1	—	—	—	—	15.1	—	—	—	17.5	—	—	18.4	—	—
CLY-127-68	—	4.9	—	—	6.0	—	—	—	—	6.8	—	—	—	—	6.1	—	—	—	—	8.8	—	—	—	—	—	—	—	—	—
CLY-128-68	—	10.1	—	—	12.7	—	—	—	—	14.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-129-68	6.2	—	—	8.9	—	—	—	—	—	—	—	—	—	—	—	13.8	—	—	—	—	15.5	—	—	—	—	—	—	—	—
CLY-130-68	—	9.5	—	—	—	—	11.5	—	—	—	12.9	—	—	—	—	—	—	—	—	—	—	—	16.8	—	—	18.9	—	—	21.7
CLY-131-68	—	22.6	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-132-68	—	1.0	—	4.2	—	—	5.8	—	—	—	6.7	—	—	—	—	—	—	—	—	—	—	—	11.8	—	—	17.6	—	—	17.6
CLY-133-68	—	3.9	—	—	—	—	5.4	—	—	—	6.2	—	—	—	—	—	—	—	—	—	—	—	7.1	—	—	8.0	—	—	9.4
CLY-134^{N}-68	—	2.6	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-134^{U}-68	—	5.3	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-135-68	—	2.7	—	—	4.0	—	—	—	—	4.3	—	—	—	—	5.1	—	—	—	—	6.0	—	—	—	7.3	—	—	15.9	—	—
CLY-136^{1}-68	—	2.3	—	—	14.2	—	—	—	—	—	—	46.2	—	—	—	—	61.9	—	—	—	—	70.4	—	78.6	—	—	—	—	86.1
CLY-136^{3}-68	—	—	0.9	—	—	—	—	3.2	—	—	—	—	—	11.9	—	—	—	—	—	—	—	—	21.5	—	—	29.7	—	—	38.7
CLY-137^{1}-68	—	3.3	0.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-137^{2}-68	—	—	2.3	—	—	—	—	2.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10.8	—	—	15.2	—	—	19.1
CLY-138-68	—		—	—	—	—	—	2.9	—	—	—	—	5.4	—	—	—	—	6.2	—	—	—	9.3	—	—	11.4	—	—	18.5	—
CLY-139^{1}-68	—	4.2	1.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-139^{2}-68	—	—	—	—	—	—	—	2.4	—	—	—	—	13.2	—	—	—	—	21.7	—	—	—	30.4	—	—	36.4	—	—	41.4	—
CLY-140-68	—	1.7	—	—	—	3.9	—	—	—	—	7.2	—	—	—	—	—	—	9.7	—	—	—	18.7	—	—	31.5	—	—	40.1	—
CLY-141-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-143-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-144-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-145-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

RUN NUMBER	8.0	8.5	8.6	8.8	9.0	9.3	9.5	9.6	9.8	10.0	10.3	10.5	10.6	10.8	10.9	11.0	11.4	11.6	11.8	11.9	12.0	12.5	12.6	12.8	12.9	13.0	13.5	13.8
CLY-124-68	74.7	—	—	—	77.7	—	—	—	—	80.9	—	—	—	—	—	83.2	—	—	—	—	85.1	—	—	—	—	86.7	—	—
CLY-125-68	13.4	—	—	—	15.5	—	—	—	—	18.4	—	—	—	—	—	20.4	—	—	—	—	22.8	—	—	—	—	27.0	—	—
CLY-126-68	18.6	—	—	—	19.8	—	—	—	—	20.6	—	—	—	—	—	23.1	—	—	—	—	22.7	—	—	—	—	—	—	—
CLY-127-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	30.6	—
CLY-128-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	20.1	—	—	—	20.9	—	—
CLY-129-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-130-68	—	—	24.5	—	—	—	—	28.6	—	—	—	—	32.4	—	—	—	—	36.9	—	—	—	—	40.7	—	—	—	—	—
CLY-131-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-132-68	—	—	36.7	—	—	—	—	46.6	—	—	—	—	60.6	—	—	—	—	78.4	—	—	—	—	101.1	—	—	—	—	—
CLY-133-68	—	—	13.0	—	—	—	—	21.5	—	—	—	—	27.8	—	—	—	—	34.7	—	—	—	—	44.1	—	—	—	—	—
CLY-134^{N}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-134^{U}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-135-68	39.0	—	—	—	—	65.0	—	—	—	—	98.2	—	—	—	—	—	116.5	—	—	—	—	128.8	—	—	—	—	136.6	—
CLY-136^{1}-68	—	—	—	98.8	—	—	—	—	106.3	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-136^{3}-68	—	—	49.3	—	—	—	—	59.1	—	—	—	—	—	—	74.1	—	—	—	—	85.8	—	—	—	—	X	X	X	X
CLY-137^{1}-68	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-137^{2}-68	—	—	28.4	—	—	—	—	42.1	—	—	—	—	57.3	—	—	—	—	—	—	79.4	—	—	—	—	92.7	—	—	—
CLY-138-68	—	28.7	—	—	—	—	—	—	—	—	—	—	—	53.1	—	—	—	—	63.3	—	—	—	—	72.1	—	—	—	—
CLY-139^{1}-68	—	—	—	—	—	—	39.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CLY-139^{2}-68	—	46.9	—	—	—	—	54.2	—	—	—	—	—	—	69.3	—	—	—	—	X	X	X	X	X	X	X	X	X	X
CLY-140-68	—	49.4	—	—	—	—	58.5	—	—	—	—	69.7	—	—	—	—	—	87.9	—	—	—	—	—	99.2	—	—	—	110.1
CLY-141-68	—	—	—	—	—	—	—	—	—	—	—	64.6	—	—	—	—	—	71.5	—	—	—	78.3	—	—	—	—	—	—
CLY-143-68	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-144-68	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-145-68	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

RUN NUMBER	13.9	14.0	14.7	14.9	15.0	15.5	16.0	16.6	17.0	17.1	17.6	18.2	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.6	26.6	27.2	29.0	36.2
CLY-124-68	—	89.3	—	—	91.0	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-125-68	—	29.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	67.9	71.2	—	X	X	X	X	X
CLY-126-68	—	—	—	—	—	—	—	—	—	—	—	—	29.6	30.6	—	31.7	—	—	33.4	34.7	32.1	—	—	X
CLY-127-68	—	34.2	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-128-68	—	21.5	—	—	—	22.7	—	23.3	—	—	24.3	—	—	—	—	—	—	—	—	—	—	X	X	X
CLY-129-68	—	—	X	X	X	X	X	X	X	X-	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-130-68	45.8	—	—	50.6	—	—	52.9	—	—	59.6	—	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-131-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-132-68	131.2	—	—	155.5	—	—	176.4	—	—	195.3	—	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-133-68	62.0	—	—	79.9	—	—	99.0	—	—	124.2	—	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-134^{N}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-134^{U}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-135-68	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-136^{1}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-136^{3}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-137^{1}-68	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-137^{2}-68	101.1	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X
CLY-138-68	—	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X
CLY-139^{1}-68	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-139^{2}-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-140-68	—	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X
CLY-141-68	—	—	—	—	—	—	—	—	—	—	—	—	X	X	X	X	X	X	X	X	X	X	X	X
CLY-142-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-144-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
CLY-145-68	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

*Column headings denote time in hours.

OTHER RUN CONDITIONS

- Oxidation temperature: 2500°F
- Sample is threaded substrate (dimensions: 1 in. x 1/4-in. with 1/2 in. of 1/4-20 refractory threads one end)
- — denotes that weight gain of sample was not determined at that specific time.
- X denotes visible breakdown (i.e., visible oxidation of the substrate.)

APPENDIX XXIII

OXIDATION TESTING: 2200°F OXIDATION TEST RESULTS FOR SAMPLES PREPARED IN COATING OXIDATION SAMPLE RUNS

Run Number	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																			
	2	4	4.5	6	6.5	8	8.5	10	10.5	12.5	13	14.5	15	16.5	19.5	21.5	23.5	26.5	29.5	31.5	33.5
CLY-148-68	2.4	—	F(3.1)											7.8	8.4	9.2	F(9.5)				
CLY-149-68	3.6	—	4.7	—	5.3	—	6.1	—	6.6	7.2	—	7.7	—	8.6	9.4	10.1	F(10.4)				
CLY-149-68	3.5	4.2	—	5.3	—	5.5	—	5.8	—	—	6.3	—	F(6.9)	6.0	6.4	7.5	7.8	8.3	8.8	8.8	9.1
CLY-150-68	4.1	—	5.3	—	6.2	—	6.8	—	7.4	8.2	—	8.4	—	5.3	5.7	6.3	6.5	6.8	F(7.3)		
CLY-150-68	4.2	F(4.9)												4.2	4.8	F(5.7)					
CLY-151-68	2.2	—	3.4	—	3.4	—	4.0	—	4.5	5.2	—	5.6	—								
CLY-152-68	1.6	—	2.0	—	2.7	—	3.3	—	3.9	4.5	—	5.0	—								
CLY-153-68	0.7	—	1.0	—	1.7	—	2.2	—	2.6	3.1	—	3.7	—								
CLY-153-68	F(0.5)																				
CLY-154-68	F(1.9)																				
CLY-154-68	2.1	3.0	—	F(3.9)																	
CLY-155-68	4.5	—	F(4.8)																		

	2	4	7	10.5	13.5
CLY-156-68	F(.5)				
CLY-156-68	F(.8)				
CLY-157-68	F(-4.4)				
CLY-157-68	F(.8)				
CLY-158-68	F(1.0)				
CLY-158-68	F(-2.2)				
CLY-159-68	.2	.2	.5	1.0	1.3
CLY-159-68	F(.6)				

*Column headings denote time in hours

OTHER RUN CONDITIONS:

- Oxidation temperature: 2200°F
- Sample is coated threaded substrate (for threaded substrate prior to coating, dimensions: 1 in. x 1/4 in. with 1/2 in. of 1/4 - 20 refractory threads one end).
- — denotes that weight gain of sample was not determined at that specific time.
- F denotes visible breakdown, i.e., visible oxidation of substrate.
- Threaded substrate (dimensions: 1 in. x 1/4 in. dia. with 1/2 in. of 1/4 - 20 refractory threads one end, material: Cb 752 alloy)

Run Number	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																	
	36.5	38.5	40.5	42.5	44.5	47.5	50.5	52.5	55.5	58.5	60.5	74.5	77.5	79.5	95.5	98.5	101.5	103.5	117.5
CLY-149-68	9.6	9.9	10	10.3	10.5	10.9	11.5	11.9	12.2	13.2	13.6	15.6	16.4	16.8	19.0	19.6	20.7	21.6	F(26.7)

APPENDIX XXIV

OXIDATION TESTING: 2400°F OXIDATION TEST RESULTS FOR SAMPLES PREPARED IN COATING OXIDATION SAMPLE RUNS

	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																	
Run Number	2	5	7	9	11	13	16	19	21	24	27	29	32	34	37	40	42	56
CLY-148-68	F(3.3)																	
CLY-149 -68	4.8	F(6.2)																
CLY-149 -68	F(4.7)																	
CLY-150 -68	5.1	6.6	7.9	9.1	10.4	F(13.3)												
CLY-150 -68	F(6.7)																	
CLY-151-68	3.3	4.1	4.9	6.0	6.8	7.3	7.8	9.9	11.3	12.4	14.6	16.8	20.5	23.5	27.9	33.1	39.2	F
CLY-152-68	2.2	3.0	3.9	4.8	F(5.2)													
CLY-153 -68**	1.4	F(3.0)																
CLY-153 -68**	.9	F(2.6)																
CLY-154 -68	2.5	4.0	4.5	5.1	5.6	5.8	F(6.0)											
CLY-154 -68	2.8	4.1	4.7	4.2	5.6	5.6	6.1	6.6	7.4	8.1	9.4	10.9	14.1	16.5	18.8	21.2	24.6	F
CLY-155-68	6.6	7.8	8.8	9.3	10.6	11.3	11.8	12.3	12.9	13.5	14.1	14.9	15.9	16.8	F(17.5)			

	2	4	7	10.5	13.5	16.5
CLY-156-69	3.3	4.8	F(7.3)			
CLY-156-69	F(3.6)					
CLY-157-69	3.3	4.6	7.6	13.3	27.9	F(40.1)
CLY-157-69	F(2.3)					
CLY-158-69	F(4.0)					
CLY-158-69	3.7	5.0	12.4	18.1	49.5	F(63.7)
CLY-159-69	F(3.4)					
CLY-159-69	F(3.2)					

* **Column headings denote time in hours**

** **Additional 2400°F oxidation results for 2 samples from CLY-153-68 are 1 hr. — 1.1 and 1.2 mg, 3 hrs. — 2.6 and 2.6 mg, 4 hrs. — F(5.3) and F(5.4) mg**

OTHER RUN CONDITIONS

- **Oxidation temperature: 2400°F**
- **Sample is coated threaded substrate (for threaded substrate prior to coating, dimensions: 1 in. x 1/4 in. with 1/2 in. of 1/4 - 20 refractory threads one end)**
- **— denotes that weight gain of sample was not determined at that specific time**
- **F denotes visible breakdown, i. e., visible oxidation of substrate**
- **Threaded substrate (dimention: 1 in. x 1/4 in. dia. with 1/2 in. of 1/4 - 20 refractory threads one end, material: Cb 752 alloy)**

APPENDIX XXV

OXIDATION TESTING: SUMMARY OXIDATION TEST RESULTS FOR 2200°F AND 2400°F TESTING FOR SAMPLES PREPARED IN COATING OXIDATION SAMPLE RUNS

Run Number	2200°F Test Results		2400°F Test Results	
	Relative Oxidation Resistance Ranking	Average Test Time in High Temp. Oxid. Env. Before Failure (hr.)	Relative Oxidation Resistance Ranking	Average Test Time in High Temp. Oxid. Env. Before Failure (hr.)
CLY-148-68(1)	3	2	1	below 2
CLY-149-68(3)	6	17.3	2	1
CLY-150-68(5)	5	11.8	4	6.5
CLY-151-68(7)	8	103.5	8	42
CLY-152-68(2)	7	26.5	5	9
CLY-153-68(4)	4	9.8	3	2
CLY-154-68(6)	1	2	6	27.5
CLY-155-68(8)	2	2	7	34.0
CLY-156-69	—	below 2	—	2
CLY-157-69	—	below 2	—	6.8
CLY-158-69	—	below 2	—	6.8
CLY-159-69	—	6.8	—	below 2

NOTE

- Average test time in high temperature oxidation environment before failure (detected by visible oxidation of substrate with large volumetric expansion) is based on test time and number of samples tested, i.e.,

$$\text{time, hr.} = \frac{(\text{test time, hr.})_1 + (\text{test time, hr.})_2 + \text{--------}}{1 + 2 + \text{----------}}$$

- Relative oxidation resistance ranking of coating is based on average test time before failure and a sample weight gain due to oxidation (weight gain used only if test time before failure is identical on samples). Higher numbers indicate better oxidation resistance (i.e., 8 = best ranking, 1 = poor ranking).
- Numbers in parenthesis reter to run number is statistical plan for initial coating oxidation sample runs.

APPENDIX XXVI

OXIDATION TESTING: ADDITIONAL 2400°F AND 2600°F TEST RESULTS FOR SAMPLES PREPARED IN COATING OXIDATION SAMPLE RUNS

Run Number	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																		Location of Failure
2400°F	0	1	3	5	7	9	11	13	14.5	16.5	18.5	20.5	22.5	24.5	26.5	28.5	30.5	32.5	34.5	
CLY-149-68	0	3.1	5.6	5.8	6.8	7.8	8.9	F(10.5)												Threads
CLY-149-68	0	2.9	5.6	6.2	6.9	7.6	F(8.5)													Threads
CLY-150-68	0	3.2	5.6	7.1	8.7	12.6	18.2	24	31	42.3	52.6	F(66.7)								Threads
CLY-150-68	0	3.8	F(6.2)																	Threads
CLY-154-68	0	1.9	3.5	3.9	4.3	4.9	5.0	5.7	6.0	6.4	7.7	9.0	14.9	21.2	36.1	45.1	51.1	56.8	F(64.3)	Threads
CLY-154-68	0	1.9	F(3.2)																	Threads
2600°F	0	10	20	30	40	50	60													
CLY-148-68	0	2.3	3.0	-	3.2	4.0	F													Threads
CLY-149-68	0	F(4.1)																		Threads
CLY-150-68	0	5.0	F(23.9)																	Threads
CLY-151-68	0	F(4.3)																		Threads
CLY-152-68	0	F(2.2)																		Threads
CLY-153-68	0	F(1.5)																		Threads
CLY-154-68	0	F(8.2)																		Threads
CLY-155-68	0	F(10.4)																		Threads
CLY-156-69	0	F(4.4)																		Threads
CLY-157-69	0	F(5.1)																		Threads
CLY-158-69	0	F(10.9)																		Threads
CLY-159-69	0	F(4.7)																		Threads

*Column headings denote time in hours and minutes for respective 2400°F and 2600°F oxidation testing.

OTHER RUN CONDITIONS

- Oxidation temperature: 2400°F and 2600°F
- Sample is coated threaded substrate (for threaded substrate prior to coating, dimensions: 1 in. x 1/4 in. with 1/2 in. of 1/4-20 refractory threads one end, material: Cb 752 alloy)
- — denotes that weight gain of sample was not determined at that specific time
- F denotes visible breakdown, i.e., visible oxidation of substrate

APPENDIX XXVII

METALLOGRAPHY: COATING THICKNESS OF SAMPLES PREPARED IN COATING OXIDATION SAMPLES

Run Number	Average Coating Deposit (mg)	Average Coating Thickness (mils)
CLY-147-68	128.5	1.7
CLY-148-68(1)	92.1	1.0
CLY-149-68(3)	165.5	2.3
CLY-150-68(5)	109.7	1.5
CLY-151-68(7)	111.1	1.3
CLY-152-68(2)	218.5	3.0
CLY-153-68(4)	82.0	1.4
CLY-154-68(6)	141.7	2.2
CLY-155-68(8)	209.8	3.0
CLY-156-69	134.9	2.0
CLY-157-69	106.9	1.5
CLY-158-69	94.3	1.3
CLY-159-69	139.4	2.0

Other Conditions:

- Average coating thickness determined from mounted cross section at high magnification
- Based on average thickness of coating at base of threaded substrate.
- Numbers in paranthesis refer to run number in statistical plan for initial coating oxidation sample runs.

APPENDIX XXVIII

METALLOGRAPHY: COATING THICKNESS OF SAMPLES PREPARED IN CYCLIC OXIDATION OPTIMIZATION RUNS

Run Number	Substrate Identification	Coating Deposit (mg)	Mean Coating Thickness (mils)
CLY-160-69	D	182.7	2.0
CLY-161-69	D	145.6	.8
CLY-162-69	D	297.0	2.1
CLY-163-69	D	296.7	2.3
CLY-164-69	D	—	—
CLY-165-69	D	331.6	—
CLY-166-69	D	193.1	1.5
CLY-167-69	A/B	218.5/120.1	2.3/2.3
CLY-168-69	A/B	264.1/111.7	2.8/1.5
CLY-169-69	A/B	276.5/118.9	3.0/1.5
CLY-170-69	A/B	166.1/ 67.1	1.3/ .8
CLY-171-69	A/B	208.5/ 94.4	2.0/1.5
CLY-172-69	A/B	351.7/102.3	4.9/1.7
CLY-173-69	A/B	160.0/133.1	1.8/1.9
CLY-174-69	A/B	154.9/178.0	1.5/1.3
CLY-175-69	D	702.5	5.4
CLY-176-69	A/B	346.8/104.0	3.3/ .9
CLY-177-69	D/C	538.8/141.9	4.4/1.4
CLY-178-69	D/C	221.0/ 50.8	2.0/ .75

Other Conditions:

- Average coating thickness determined from mounted cross section at high magnification
- Based on average thickness of coating at base of substrate.
- Substrate identification:

  A. 1 1/2-in. Round Rod
  B. Flat Panel (app. 1 in. x 1/2 in.)
  C. 1 in. Threaded Stud
  D. 1 1/2-in. Hex Head Bolt
  E. Hex Nut

APPENDIX XXIX

METALLOGRAPHY: ANALYSIS FOR COATING HARDNESS

Run Number	Hardness: Knoop Microhardness - 50 gram load	
	Substrate	Coating
CLY-148-68 (1)	237-237	1160-1260
CLY-149-68 (3)	223-223	1120-1195
CLY-150-68 (5)	221-226	1160-1288
CLY-151-68 (7)	221-221	1381-1220
CLY-152-68 (2)	227-207	1381-1215
CLY-153-68 (4)	223-235	1260-1160
CLY-154-68 (6)	226-226	1260-1120
CLY-155-68 (8)	213-213	1245-1245
As Rec'd	279-279	

Other Conditions:

- Hardness determined from mounted cross section of substrate base
- 1-in. Threaded stud substrate
- Numbers in paranthesis refer to run number in statistical plan for initial coating oxidation sample runs.

APPENDIX XXX

METALLOGRAPHY: ANALYSIS FOR COATING THICKNESS

Run Number	Substrate Identification	Coating Deposit (mg)	Mean Coating Thickness
CLY-177-69	D	538.8	4.8
CLY-178-69	D/C	221.0/50.8	2.0/.75
CLY-179-69	A	171.5	1.4
CLY-180-69	A	310.6	2.8
CLY-181-69	A	270.7	2.5
CLY-182-69	D	202.1	1.6
CLY-183-69	D/C	458.3/151.2	4.1/2.2
CLY-184-69	D/C	323.3/107.2	2.6/1.5
CLY-185-69	D	307.8	2.6

Other Conditions:

- Average coating thickness determined from mounted cross section at high magnification
- Based on average thickness of coating at base of substrate.
- Substrate identification:

  A. 1 1/2-in. Round Rod
  B. Flat Panel (app. 1 in. x 1/2 in.)
  C. 1-in. Threaded Stud
  D. 1 1/2-in. Hex Head Bolt
  E. Hex Nut

APPENDIX XXXI

METALLOGRAPHY: ANALYSIS FOR COATING THICKNESS

Run Number	Substrate Identification	Deposit (mg)	Mean Coating Thickness (mils)
CLY-186-69	D	492.4	4.9
CLY-187-69	D	307.9	3.05
CLY-188-69	D	157.9	1.8
CLY-189-69	D	268.8	2.5
CLY-194-69	D	481.5	4.85
CLY-195-69	D	502.2	5.15
CLY-196-69	D	305.2	2.75
CLY-197-69	D	259.8	1.6
CLY-202-69	D	463.16	4.0 (3.75)
CLY-203-69	E	84.0	2.1
CLY-205-69	D	358.0	2.65 (2.9)
CLY-206-69	D	299.5	2.2 (2.45)
CLY-210-69	D	376.9	3.1 (3.05)
CLY-211-69	D	493.1	4.2 (4.0)

Other Conditions:

- Average coating thickness determined from mounted cross section at high magnification
- Based on average thickness of coating at base of substrate.
- Substrate identification:

  A. 1 1/2-in. Round Rod
  B. Flat Panel (app. 1 in. x 1/2 in.)
  C. 1-in. Threaded Stud
  D. 1 1/2-in. Hex Head Bolt
  E. Hex Nut

APPENDIX XXXII

ELECTRON MICROPROBE: COATING COMPOSITION OF SAMPLES PREPARED IN SECOND STATISTICAL SERIES

Run Number	Coating Composition: Average Component Concentration (wt %)		
	Cr	Ti	Si
CLY-107-68	—	—	—
CLY-108-68	24.8	47.7	27.5
CLY-109-68	22.6	47.0	30.4
CLY-110-68	6.7	61.8	31.5
CLY-111-68	2.6	66.6	30.8
CLY-112-68	—	—	—
CLY-113-68(5)	26.7	47.2	26.1
CLY-114-68	25.2	45.0	29.8
CLY-115-68(4)	8.8	63.5	27.7
CLY-116-68(8)	7.8	65.0	27.2
CLY-117-68(1)	8.3	64.6	27.1
CLY-118-68(6)	20.6	55.2	24.2
CLY-119-68	19.8	52.5	27.7
CLY-120-68(2)	19.7	55.0	25.3
CLY-121-68(3)	18.4	50.9	30.7
CLY-122-68 (7)	31.4	48.5	20.1
CLY-123-68	17.2	60.5	22.3

Other Conditions:

- Coating composition in component concentration is based on average coating composition calculated from electron microprobe analysis for each component in coating on round-rod substrate.
- Electron microprobe analysis calculations involve three operations of straight calculation on reference value, correction for component concentration level and normalization.
- Numbers in parenthesis refer to run number in second statistical series.

APPENDIX XXXIII

ELECTRON MICROPROBE: COATING COMPOSITION OF SAMPLES FROM COATING OXIDATION SAMPLE RUNS

Run Number	Coating Composition: Average Component Concentration (wt %)		
	Cr	Ti	Si
CLY-148-68(1)	8.7	61.0	30.3
CLY-149-68(3)	8.7	61.3	30.0
CLY-150-68(5)	19.3	52.5	28.2
CLY-151-68(7)	14.5	55.2	30.3
CLY-152-68(2)	11.5	53.7	34.8
CLY-153-68(4)	11.9	55.6	32.5
CLY-154-68(6)	17.5	54.3	28.2
CLY-155-68(8)	18.4	51.0	30.6
CLY-156-69	12.2	55.7	32.1
CLY-157-69	14.8	51.0	34.2
CLY-158-69	11.7	54.2	34.1
CLY-159-69	13.6	58.0	28.4

Other Conditions:

- Coating composition in component concentration is based on average coating composition calculated from electron microprobe analysis for each component in coating at base of threaded substrate.
- Electron microprobe analysis calculations involve three operations of straight calculation on reference value, correction for component concentration level and normalization.
- Numbers in parenthesis refer to run number in statistical plan for initial coating oxidation sample runs.

APPENDIX XXXIV

STRAINED EFFECT TEST: 2200°F AND 2400°F CYCLIC OXIDATION TESTS RESULTS FOR SAMPLES AT TWO STRAIN LEVELS

Run Number	Strain Level	Oxidation Test Results: Weight Gain of Sample (mg)*							Location of Failure	
2200°F		0	.33	.67	1	2	3	4	Section	Strain Section
CLY-161-69	Low	0	.8	1.5	2.7	5.5	8.6	F(12.5)	Threads	Some failure on compressive side, no failure on tension side
CLY-162-69	Low	0	1.3	2.1	3.0	4.0	4.4	F(4.4)	Threads	Some failure on compressive side, no failure on tension side
CLY-165-69	Low	0	1.1	2.0	F(3.2)				Threads	Some failure on compressive side, no failure on tension side
2400°F		0	.33	.67	1	2	3	4		
CLY-161-69	Low	0	6.3	8.3	10.8	17.1	27.0	F(40.2)	Threads, some failure on hex head	Some failure on compressive side, no failure on tension side
CLY-162-69	Low	0	3.5	4.7	6.5	10.3	12.2	F(19.4)	Threads, some failure on hex head	Some failure on compressive side, no failure on tension side
CLY-165-69	Low	0	2.9	3.9	5.3	6.2	9.1	F(13.8)	Threads, some failure on hex head	Some failure on compressive side, no failure on tension side
2400°F		0	.5	1	1.5	2	2.5	3		
CLY-161-69	High	0	4.6	6.6	F(7.4)				Threads	Some failure on compressive side, no failure on tension side
CLY-162-69	High	0	3.3	6.0	8.0	9.6	11.8	F(15.5)	Threads	Some failure on compressive side, no failure on tension side
CLY-163-69	High	0	3.6	5.7	F(7.4)				Threads	Some failure on compressive side, no failure on tension side
CLY-165-69	High	0	4.0	6.5	8.4	10.8	11.6	F(16.6)	Threads, some failure on hex head	Some failure on compressive side, no failure on tension side

*Column heading denote time in hours

OTHER RUN CONDITIONS

- Oxidation temperature: 2200°F and 2400°F
- Strain Level: low-about 5 mils deflection, high-about 10 mils deflection
- Sample is coated 1-1/2-in. hex head bolt prior to coating, dimensions: 1-1/2 in. length x 1/4 in. diameter, 1/2 in. of 1/4 - 20 refractory threads one end, hex head other end, material: Cb 752 alloy)
- — denotes that weight gain of sample was not determined at that specific time
- F denotes visible breakdown, i.e., visible oxidation of substrate

APPENDIX XXXV

CYCLIC OXIDATION AND STRAIN EFFECT TEST: 2200°F, 2400°F AND 2600°F
CYCLIC OXIDATION TEST RESULTS FOR SAMPLES PREPARED IN DUPLICATE BEST COATING RUNS

Run Number	Oxidation Test Results: Weight Gain of Sample (mg)																Location of Failures	Remarks
2200°F*	0	1	1.5	2	4	6												
CLY-160-69	0	—	—	1.5	4.5	F(7.1)											Threads	
CLY-161-69	0	F(2.4)															Threads	
CLY-162-69	0	.6	F(1.7)														Threads	
CLY-163-69	0	.9	F(2.0)														Threads	
CLY-164-69	0	F(.5)															Threads	
CLY-165-69	0	F(1.5)															Threads	
2400°F*	0	.33	.67	1	1.5	2	3	6		8		10						
CLY-160-69	0	—	—	—	—	F(15.1)											Threads	
CLY-160-69	0	3.7	5.3	6.5	7.6	F(8.8)											Threads	
CLY-161-69	0	—	—	—	—	F(21.3)											Threads	
CLY-161-69	0	4.0	F(6.2)														Threads	
CLY-162-69	0	—	—	3.8	—	—	5.1	F(9.1)									Threads	
CLY-162-69	0	1.9	3.7	F(4.7)													Threads	
CLY-163-69	0	—	—	4.2	—	—	5.1	9.0		10.2		F(12.7)					Threads	
CLY-163-69	0	3.5	4.2	F(5.2)													Threads	
CLY-164-69	0	—	—	F(5.1)													Threads	
CLY-164-69	0	3.1	F(5.8)														Threads	
CLY-165-69	0	—	—	2.1	—	—	F(4.6)										Threads	
CLY-165-69	0	3.1	4.0	4.9	F(5.7)												Threads	
2600°F**	5	10	15	20	25	30	35	40	45	50	55	60	65	70	80	90		
CLY-160-69	4.9	5.6	7.9	8.3	9.1	10.3	F(11.9)										Threads	
CLY-161-69	5.7	F(7.1)															Threads	
CLY-162-69	3.1	4.1	4.9	—	5.9	—	6.9	—	7.9	—	8.7	—	F(10)				Threads	
CLY-163-69	3.2	4.4	—	5.9	—	6.7	—	7.8	—	8.5	—	8.3	—	10.5	10.7	F(12)	Threads	
CLY-164-69	3.7	8.0	—	F(13.9)													Threads	
CLY-165-69																	Threads	
2400°F* Strained Samples	0	.5	1	1.5	2	2.5	3.0											
CLY-161-69	0	4.6	6.6	F(7.4)													Threads	Some oxidation at point
CLY-162-69	0	3.3	6.0	8.0	9.6	11.8	F(15.5)										Threads	where load for applying
CLY-163-69	0	3.6	5.7	F(7.4)													Threads	strain plunger contacted
CLY-165-69	0	4.0	6.5	8.4	10.8	11.6	F(16.6)										Threads	sample

*Column headings denote time in hours (for 2200°F and 2400°F test results)

**Column headings denote time in minutes (for 2600°F test results)

OTHER RUN CONDITIONS:

- Oxidation temperature: 2200°F, 2400°F and 2600°F
- Sample is coated hex head threaded substrate (for hex head bolt prior to coating, dimensions: 1 1/2 in. x 1/4 in.with 1/2 in. of 1/4-20 refractory threads one end material: Cb 752 alloy)
- — denotes that weight gain of sample was not determined at that specific time.
- F denotes visible breakdown, i.e., visible oxidation of substrate.
- For strained samples, each sample subjected to several hundred pounds load pressure to bend sample. Approximate deflection of 10 mil from vertical obtained on each sample.
- Further for strained samples, substrate oxidation on backside of bend (i.e. side opposite point of load plunger contact for applying strain) was not detected for above samples.

APPENDIX XXXVI

CYCLIC OXIDATION: 2400°F CYCLIC OXIDATION TEST RESULTS FOR COATED FLAT PANELS, 1 1/2-IN. ROUND RODS AND 1 1/2-IN. HEX HEAD BOLT SUBSTRATES

RUN NUMBER	SUBSTRATE IDENTIFICATION	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*								
		.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0
CLY-166-69	Flat Panel (1/2 in. x 1 in.)	3.9	F(5.2)							
CLY-166-69	Flat Panel (1/2 in. x 1 in.)	4.2	5.0	6.3	7.0	F(8.0)				
CLY-166-69	Flat Panel (1/2 in. x 1 in.)	3.5	5.1	5.6	F(6.4)					
CLY-166-69	Flat Panel (1/2 in. x 1 in.)	F(4.6)								
CLY-166-69	1-in. Threaded Stud (1/4 in. dia.)	3.1	3.9	4.1	4.6	5.2	—	F(6.4)		
CLY-166-69	1-in. Threaded Stud (1/4 in. dia.)	3.1	3.8	4.2	4.9	F(5.4)				
CLY-166-69	1-in. Threaded Stud (1/4 in. dia.)	2.9	3.9	4.1	4.4	—	—	F(4.9)		
CLY-166-69	1-in. Threaded Stud (1/4 in. dia.)	3.2	F(4.1)							
CLY-166-69	1 1/2-in. Round Rod (1/4 in. dia.)	1.9	3.4	3.7	5.4	6.8	—	F(8.6)		
CLY-166-69	1 1/2-in. Round Rod (1/4 in. dia.)	2.8	3.9	4.3	5.0	5.4	—	F(6.2)		
CLY-166-69	1 1/2-in. Round Rod (1/4 in. dia.)	1.4	2.6	F(3.2)						
CLY-166-69	1 1/2-in. Round Rod (1/4 in. dia.)	1.8	F(3.2)							
CLY-166-69	1 1/2-in. Hex Head Bolt (1/4 in. dia.)	6.4	F(7.5)							
CLY-166-69	1 1/2-in. Hex Head Bolt (1/4 in. dia.)	6.6	7.6	9.0	9.8	10.3	—	F(11.4)		
CLY-166-69	1 1/2-in. Hex Head Bolt (1/4 in. dia.)	6.6	7.5	7.5	8.1	—	—	F(8.6)		
CLY-166-69	1 1/2-in. Hex Head Bolt (1/4 in. dia.)	7.5	8.3	F(8.6)						

* Column heading denotes time in hours.

APPENDIX XXXVII

CYCLIC OXIDATION: 2400°F CYCLIC OXIDATION TEST RESULTS FOR COATED FLAT PANEL SUBSTRATES

RUN NUMBER	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																														
	.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0	14.0	16.0	18.0	20.0	22.0	24.0	26.0	28.0	30.0	32.0	35.0				
CLY-166-69	3.9	F(5.2)																													
CLY-166-69	4.2	5.0	6.3	7.0	F(8.0)																										
CLY-166-69	3.5	5.1	5.6	F(6.4)																											
CLY-166-69	F(4.6)																														
CLY-167-69	1.7	2.5	—	3.3	—	4.1	—	4.7	4.9	5.5	6.0	6.8	7.1	7.5	8.6	10.0	—	—	—	—	—	—	—	33.2	37.3	F(55.5)					
CLY-167-69	1.7	2.4	—	3.1	—	3.8	—	4.4	4.7	5.2	5.7	6.1	6.4	6.9	7.7	8.7	10.5	73.5	85.7	F											
CLY-167-69	—	2.6	—	3.5	—	—	—	4.2	—	5.2	—	6.0	—	7.0	—	8.1	8.8	—	10.3	—	11.4	—	13.0	—	14.6	—	F(18.3)				
CLY-167-69	—	3.0	—	3.9	—	—	—	4.9	—	5.9	—	6.9	—	7.9	—	9.2	10.0	—	12.1	—	F(14.4)										
	.33	.67	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	19	20	21	—	24	25	—	28	30	32	34	36
CLY-168-69	F(1.4)																														
CLY-168-69	.8	1.9	2.2	—	4.1	—	4.7	—	6.6	—	36.8	—	50.1	—	53.7	—	58.0	F(62.3)													
CLY-168-69	1.0	1.3	1.8	2.3	—	3.3		4.3	—	5.3	—	6.1	—	F(7.3)																	
CLY-168-69	1.4	1.7	2.0	2.7	—	3.7		4.8	—	5.9	—	6.9	—	F(8.3)																	
CLY-169-69	—	—	—	3.6	—	—		16.0	—	—	—	27.2	—	—	—	F(32.9)															
CLY-169-69	—	—	—	F(3.0)																											
CLY-169-69	—	—	F(2.0)																												
CLY-169-69	—	—	2.0	2.7	3.0	—	4.1	—	—	—	3.5	—	—	—	8.2	—	11.0	—	—	33.9	—	39.7	—	—	F(69.4)						
CLY-170-69	—	—	—	3.3	—	—	—	8.5	—	—	—	F(14.7)																			
CLY-170-69	—	—	—	3.2	—	—	—	9.0	—	—	—	F(15.2)																			
CLY-170-69	—	—	4.2	5.1	5.8	—	8.2	—	—	—	F(12.0)																				
CLY-170-69	—	—	F(15.2)																												
CLY-171-69	—	—	—	F(4.4)																											
CLY-171-69	—	—	—	3.9	—	—	—	7.8	—	—	—	66.3	—	—	—	F															
CLY-171-69	—	—	F(2.3)																												
CLY-171-69	—	—	2.1	3.3	F(5.1)																										
CLY-172-69	—	—	F(2.9)																												
CLY-172-69	—	—	2.9	4.2	—	F(40.0)																									
CLY-173-69	—	—	2.8	3.5	—	3.8	—	—	—	4.9	—	5.9	—	—	—	7.1	—	8.4	—	—	10.4	—	—	12.3	—	—	14.0	15.6	16.7	17.8	(19.9)
CLY-173-69	—	—	3.1	4.0	—	4.6	—	—	—	6.4	—	7.4	—	—	—	10.1	—	11.6	—	—	15.8	—	—	18.3	—	—	19.8	F(20.8)			
CLY-174-69	—	—	8.6	—	—	—	F(14.4)																								
CLY-174-69	—	—	9.7	—	—	—	F(17.1)																								

*Column heading denotes time in hours.

APPENDIX XXXVIII

CYCLIC OXIDATION: 2400°F CYCLIC OXIDATION TEST RESULTS FOR COATED 1 1/2-IN. ROUND ROD SUBSTRATES

RUN NUMBER	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																				
	.5	1	1.5	2	2.5	3	3.5	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24
CLY-166-69	3.2	F(4.1)																				
CLY-166-69	1.9	3.4	3.7	5.4	6.8	–	F(8.6)															
CLY-166-69	2.8	3.9	4.3	5.0	5.4	–	F(6.2)															
CLY-166-69	1.4	2.6	F(3.2)																			
CLY-167-69	1.0	1.4	–	1.8	–	2.6	–	3.2	3.7	4.3	4.8	5.4	5.9	5.4	7.7	9.1	12.5	109.6	122.8	136.1	144.6	157.5
CLY-167-69	1.1	1.6	–	2.2	–	3.0	–	3.8	4.0	4.9	5.4	6.0	6.7	7.4	8.4	10.3	–	–	–	–	–	–
CLY-167-69	–	1.9	–	2.4	–	–	–	3.0	–	4.0	–	5.2	–	6.0	–	7.3	8.5	–	10.5	–	12.0	–
CLY-167-69	–	1.9	–	2.3	–	–	–	3.0	–	4.1	–	6.1	–	6.0	–	7.2	8.3	–	10.4	–	12.0	–
	.33	.67	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	20	22	24
CLY-168-69	1.3	2.0	2.9	–	4.2	–	5.3	–	6.8	–	24.6	–	59.6	–	61.9	–	62.7	62.3	–	64.1	64.5	64.9
CLY-168-69	1.3	2.1	2.5	–	3.7	–	5.1	–	6.5	–	7.8	–	59.4	–	66.0	–	66.7	67.4	–	68.2	68.8	69.9
CLY-168-69	1.6	2.2	2.2	3.0	–	3.8	–	4.7	–	6.0	–	7.1	–	8.7	–	10.0	–	–	12.5	–	14.3	–
CLY-168-69	1.2	1.9	2.0	2.9	–	3.6	–	4.8	–	6.2	–	7.4	–	9.0	–	10.4	–	–	13.0	–	14.7	–
CLY-168-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	F(3.6)					
CLY-169-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.7	3.1	–	–	101.0	–
CLY-169-69	–	–	–	0	–	–	–	.1	–	–	–	1.6	–	–	2.5	–	–	F(4.6)				
CLY-169-69	–	–	–	0	–	–	–	-.4	–	–	–	.9	–	–	1.3	–	–	2.4	–	5.1	–	34.6
CLY-169-69	–	–	–	1.2	–	–	–	14.0	–	–	–	30.6	–	–	–	33.1	–	34.9	–	–	–	47.1
CLY-169-69	–	–	–	1.3	–	–	–	7.5	–	–	–	26.5	–	–	–	29.8	–	32.1	–	–	–	45.5
CLY-170-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	7.6	12.0	–	–	F(41.0)	
CLY-170-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	F(12.3)					
CLY-170-69	–	–	–	1.2	–	–	–	2.2	–	–	–	4.1	–	–	5.9	–	–	9.9	–	14.9	–	30.0
CLY-170-69	–	–	–	1.0	–	–	–	1.9	–	–	–	3.8	–	–	5.5	–	–	9.7	–	14.4	–	27.0
CLY-170-69	–	–	–	3.3	–	–	–	7.7	–	–	–	–	–	14.9	–	–	17.0	–	20.3	–	–	32.1
CLY-170-69	–	–	–	3.2	–	–	–	7.9	–	–	–	–	–	15.2	–	–	17.9	–	22.0	–	–	37.8
CLY-171-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	F(12.3)					
CLY-171-69	–	–	–	1.8	–	–	–	5.3	–	–	–	8.5	–	–	11.0	–	–	12.8	–	15.1	–	119.8
CLY-171-69	–	–	–	F(2.1)																		
CLY-171-69	–	–	–	3.0	–	–	–	42.1	–	–	–	90.4	–	–	–	108.4	–	F				
CLY-171-69	–	–	–	2.4	–	–	–	6.3	–	–	–	52.0	–	–	–	56.8	–	59.0	–	–	–	F
CLY-172-69	–	–	1.2	2.0	4.5	–	–	–	–	24.1	–	40.9	–	–	–	127.8	–	162.4	–	211.0	–	F
CLY-172-69	–	–	1.4	2.5	4.2	–	–	–	–	44.5	–	71.6	–	–	–	155.4	–	179.5	–	217.8	–	F
CLY-173-69	–	–	6.0	6.5	7.1	–	–	–	–	7.9	–	8.9	–	–	–	10.5	–	11.3	–	13.0	–	14.5
CLY-173-69	–	–	5.8	6.4	7.4	–	–	–	–	8.3	–	9.0	–	–	–	10.0	–	10.9	–	13.0	–	15.2
CLY-173-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	13.0	–	17.4	19.1	–	20.3
CLY-173-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10.0	–	16.0	17.3	–	19.8
CLY-174-69	–	–	9.8	–	–	–	13.2	–	14.8	–	–	–	16.4	–	–	–	17.7	–	18.3	19.3	F(20.0)	
CLY-174-69	–	–	10.7	–	–	–	16.1	–	17.6	–	–	–	19.1	–	–	–	F(20.5)					

*Column headings denote time in hours.

APPENDIX XXXVIII (CONTD)

RUN NUMBER	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLE (mg)*																										
	26	28	30	32	35	39	42																				
CLY-167-69	F																										
CLY-167-69	–	56.9	63.5	F(83.9)																							
CLY-167-69	14.1	–	15.9	–	19.1	112.8	F																				
CLY-167-69	13.9	–	16.0	–	18.7	112.9	F																				
	26	28	30	32	34	35	36	39	40	42	44	46	49	51	53	55	56	59	60	63	64	68	72	75	82	88	94
CLY-168-69	65.3	65.8	–	67.0	–	–	66.9	–	68.1	–	68.4	–	69.4	–	70.4	–	71.7	–	73.8	–	75.4	76.9	78.4	79.6	85.8	104.0	F
CLY-168-69	69.9	70.5	–	71.5	–	–	71.4	–	72.5	–	72.7	–	73.4	–	73.5	–	74.7	–	74.8	–	78.0	79.9	81.7	83.2	96.4	252.3	F
CLY-168-69	17.5	–	20.2	–	–	23.1	–	26.6	–	30.4	–	57.9	–	F(68.1)													
CLY-168-69	17.5	–	20.3	–	–	24.5	–	29.7	–	38.2	–	38.5	–	46.1	–	97.3	–	113.9	–	F(164.2)							
CLY-168-69																											
CLY-169-69	133.6	151.00	–	F(796.7)																							
CLY-169-69																											
CLY-169-69	–	40.8	–	45.1	–	–	–	53.9	–	–	F																
CLY-169-69'	–	–	–	109.1	–	–	F																				
CLY-169-69	–	–	–	F(51.7)																							
CLY-170-69	–	35.4	–	36.5	–	–	–	F(39.0)																			
CLY-170-69	–	34.2	–	F(36.8)																							
CLY-170-69	–	–	F(45.9)																								
CLY-170-69	–	–	F(89.1)																								
CLY-171-69																											
CLY-171-69	–	F																									
CLY-171-69																											
CLY-171-69																											
CLY-171-69																											
CLY-172-69																											
CLY-172-69																											
CLY-173-69	–	15.8	17.3	18.3	19.8	–	21.5	23.2	25.5	–	F(28.5)																
CLY-173-69	–	15.3	17.5	18.9	20.4	–	22.1	23.6	25.1	–	F(27.0)																
CLY-173-69	22.0	–	22.9	furnace control failed overnight, overheat burned up furnace temperature heating elements																							
CLY-173-69	21.9	–	24.2	furnace control failed overnight, overheat burned up furnace temperature heating elements																							

*Column headings denote time in hours.

APPENDIX XXXIX

CYCLIC OXIDATION: 2400°F CYCLIC OXIDATION TEST RESULTS FOR COATED 1 1/2-IN. ROUND ROD SUBSTRATES

Run Number	Oxidation Test Results: Weight Gain of Samples (mg)*																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	17.3	–	–
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	14.5	–	–
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	12.7
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10.1
CLY-180-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	12.3
CLY-180-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	13.1
CLY-180-69	–	–	–	8.1	–	9.2	–	–	–	–	–	11.5	–	–	–	–	–
CLY-180-69	–	–	–	8.7	–	9.9	–	–	–	–	–	12.6	–	–	–	–	–
CLY-181-69	–	–	–	–	–	4.6	–	5.8	–	–	–	–	–	15.6	–	–	–
CLY-181-69	–	–	–	–	–	5.5	–	6.9	–	–	–	–	–	10.7	–	–	–
CLY-181-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	26.0	–	–
CLY-181-69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10.9	–	–

	18	19	20	21	22	23	24	25	26	29	30	31	33	34	35	36
CLY-176-69	–	21.4	–	–	–	–	–	27.2		30.3	–	31.4	31.1	–	35.3	–
CLY-176-69	–	17.0	–	–	–	–	–	24.0		26.0	–	28.3	29.8	–	31.8	–
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	18.9	–	–	–	–
CLY-176-69	–	–	–	–	–	–	–	–	–	–	–	18.9	–	–	–	–
CLY-180-69	–	–	–	–	–	–	–	–	–	–	–	22.7	–	–	–	–
CLY-180-69	–	–	–	–	–	–	–	–	–	–	–	21.2	–	–	–	–
CLY-180-69	15.8	–	18.1	–	–	–	–	–	–	–	–	–	–	35.0	–	–
CLY-180-69	17.2	–	19.6	–	–	–	–	–	–	–	–	–	–	30.4	–	–
CLY-181-69	–	–	24.5	–	–	–	–	–	69.8	–	–	82.9	–	–	–	–
CLY-181-69	–	–	16.6	–	–	–	–	–	71.6	–	–	84.5	–	–	–	–
CLY-181-69	–	–	–	–	–	–	–	–	–	–	67.7	–	–	–	–	–
CLY-181-69	–	–	–	–	–	–	–	–	–	–	8.7	–	–	–	–	–

APPENDIX XXXIX (CONTD)

Run Number	Oxidation Test Results: Weight Gained Samples (mg)*																
	38	39	40	42	44	45	46	48	50	51	52	54	56	58	60	62	
CLY-176-69	–	38.7	–	–	–	42.0	–	–	–	46.4	47.6	–	–	63.6	–	–	
CLY-176-69	–	46.0	–	–	–	49.4	–	–	–	–	59.6	–	–	66.7	–	–	
CLY-176-69	–	–	–	–	–	–	–	27.4	–	–	–	–	–	–	–	126.1	
CLY-176-69	–	–	–	–	–	–	–	52.0	–	–	–	–	–	–	–	72.4	
CLY-180-69	–	–	–	–	–	–	–	63.7	–	–	–	82.3	–	–	–	–	
CLY-180-69	–	–	–	–	–	–	–	42.0	–	–	–	54.7	–	–	–	–	
CLY-180-69	–	–	–	–	–	–	–	–	44.4	–	–	–	47.9	–	–	50.4	
CLY-180-69	–	–	–	–	–	–	–	–	63.5	–	–	–	73.7	–	–	81.1	
CLY-181-69	F(106.5)																
CLY-181-69	93.7	–	–	–	103.4	–	–	–	F(532.7)								
CLY-181-69	–	–	–	–	–	–	F(283.4)										
CLY-181-69	–	–	–	–	–	–	F(283.0)										

	64	66	68	70	71	74	76	77	78	79	80	82	83	84		86	88
CLY-176-69	69.6	–	–	–	78.1	–	–	85.8	–	–	–	–	F(118.2)				
CLY-176-69	70.4	–	–	–	F(98.9)												
CLY-176-69	–	–	–	–	–	–	–	–	–	F(213.0)							
CLY-176-69	–	–	–	–	–	–	–	–	–	F(93.7)							
CLY-180-69	–	–	107.3	–	–	–	–	–	–	–	–	–	–	F(624.4)			
CLY-180-69	–	–	74.6	–	–	–	–	–	–	–	–	–	–	F(1200.3)			
CLY-180-69	–	–	51.9	–	–	55.0	–	–	–	–	55.6	–	–	–		59.3	–
CLY-180-69	–	–	86.6	–	–	92.0	–	–	–	–	96.3	–	–	–		F(107.2)	
CLY-181-69																	
CLY-181-69																	
CLY-181-69																	
CLY-181-69																	

*Column heading denotes time in hours.

APPENDIX XXXIX (CONTD)

Run Number	Oxidation Test Results: Weight Gained Samples (mg)*							
	90	92	94	96	98	100	102	104
CLY-176-69								
CLY-176-69								
CLY-176-69								
CLY-176-69								
CLY-180-69								
CLY-180-69								
CLY-180-69	—	60.2	—	—	62.5	—	—	67.0
CLY-180-69								
CLY-181-69								
CLY-181-69								
CLY-181-69								
CLY-181-69								

*Column heading denotes time in hours.

APPENDIX XL

CYCLIC OXIDATION: 2400°F CYCLIC OXIDATION TEST RESULTS FOR COATED 1 1/2-IN. HEX HEAD BOLT SUBSTRATES

Run Number	Oxidation Test Results: Weight Gain of Samples (mg)*																									
	1	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	44	45	50	54	56	58
CLY-175-69	4.7	6.0	7.0	–	7.7	10.3	11.8	13.0	15.0	16.6	18.9	–	20.4	–	30.6	33.5	–	35.2	–	–	57.9	–	66.8	75.9	–	F(119.8)	
CLY-175-69	5.1	6.1	7.4	–	8.1	9.6	10.9	12.9	17.4	19.8	F(25.6)																
CLY-175-69	–	–	–	–	–	–	–	14.0	16.7	–	F(22.8)																
CLY-175-69	–	–	–	–	–	–	–	15.4	19.4	–	21.7	25.6	–	29.7		–	F(33.9)										
CLY-177-69	–	–	–	–	–	–	–	32.3	37.5	–	–	51.0	–	–	F(69.0)												
CLY-177-69	–	–	10.2	12.5	–	14.0	–	–	16.5	–	20.1	–	–	28.5	–	–	36.2	–	–	F(47.5)							
CLY-177-69	–	–	9.2	11.1	–	12.6	–	–	17.1	–	22.3	–	–	37.9	–	–	47.6	–	22.3	–	30.5	38.1	43.3	–	61.2	–	F(84.4)
CLY-177-69	–	–	–	–	–	–	–	20.7	–	–	52.3	–	–	60.4	–	–	–	F(69.9)									
CLY-178-69	–	–	–	21.6	–	–	F(59.2)																				
CLY-178-69	–	–	–	23.5	–	–	31.8	–	36.3	–	F(52.8)																
CLY-178-69	–	–	–	5.7	–	–	F(31.1)																				
CLY-178-69	–	–	–	36.3	–	–	26.8	–	–	40.9	46.2	–	–	F(72.1)													
CLY-182-69	–	–	–	–	–	–	–	–	F(146.5)																		
CLY-182-69	–	–	–	–	–	–	–	–	F (62.3)																		
CLY-182-69	–	–	–	–	–	–	–	–	F(146.5)																		
CLY-182-69	–	–	–	–	–	–	–	–	F (62.3)																		
CLY-183-69	–	–	–	–	–	–	–	–	29.4	–	–	–	–	–	–	–	50.3	–	65.1	–	–	F(75.2)					
CLY-183-69	–	–	–	–	–	–	–	–	29.3	–	–	–	–	–	–	–	78.0	–	63.0	–	–	F(75.1)					
CLY-183-69	–	11.0	–	–	–	–	–	–	F (31.0)																		
CLY-183-69	–	12.3	–	–	–	–	–	–	28.2	–	–	–	–	–	–	–	–	F(52.0)									
CLY-184-69	–	–	–	–	–	–	–	–																			
CLY-184-69	–	–	–	–	–	–	–	–																			
CLY-184-69	–	–	–	F(29.8)																							
CLY-184-69	–	–	–	F(18.2)																							
CLY-185-69	–	–	–	–	–	–	–	–	30.7	–	–	F(61.9)															
CLY-185-69	–	–	–	–	–	–	–	–	34.6	–	–	F(57.1)															
CLY-185-69	–	8.2	–	–	–	–	–	–	–	–	(F)																
CLY-185-69	–	8.7	–	–	–	–	–	–	–	–	(F)																

*Column heading denotes time in hours.

APPENDIX XLI

CYCLIC OXIDATION: 2600°F CYCLIC OXIDATION TEST RESULTS FOR COATED 1 1/2-IN. ROUND ROD SUBSTRATES

Run Number	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLES (mg)*																				
	.25	.5	.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0	4.25	4.5	4.75	5.25	5.5
CLY-167-69	2.4	2.6	–	3.0	–	–	–	5.0	–	–	–	86.9	–	–	–	115.4	–	–	–	134.1	–
CLY-167-69	2.4	3.0	–	3.0	–	–	–	9.3	–	–	–	76.9	–	–	–	100.4	–	–	–	123.1	–
CLY-167-69	–	2.0	–	–	–	3.5	–	–	–	42.4	–	–	–	81.4	–	–	–	105.8	–	–	122.7
CLY-167-69	–	2.4	–	–	–	3.7	–	–	–	53.8	–	–	–	74.7	–	–	–	94.5	–	–	108.2
CLY-168-69	9.3	13.9	16.8	17.3	18.0	19.7	20.7	22.7	25.1	F(33.3)											
CLY-168-69	9.3	13.9	16.8	17.3	18.0	19.7	20.7	22.7	25.1	25.6	32.7	37.9	43.2	48.7	59.7	66.4	72.1	77.9	88.8	–	–
CLY-168-69	2.7	6.3	5.8	7.0	9.0	10.6	13.7	22.8	34.5	43.3	40.5	49.4	55.2	62.7	–	–	–	76.0	–	96.8	–
CLY-168-69	2.4	4.4	4.1	5.6	7.0	8.1	12.4	28.4	37.5	42.3	44.2	48.9	56.6	63.9	–	–	–	74.2	–	107.2	–
CLY-169-69	1.2	1.1	–	1.4	–	–	–	4.0	–	–	–	72.9	–	–	–	102.8	–	–	–	144.0	
CLY-169-69	1.1	1.2	–	1.5	–	–	–	4.3	–	–	–	65.9	–	–	–	90.9	–	–	–	131.6	
CLY-169-69	–	0.4	–	1.7	–	1.9	–	–	–	5.7	–	9.9	–	–	–	64.6	–	–	–	90.5	
CLY-169-69	–	0.5	–	1.6	–	2.0	–	–	–	4.9	–	12.3	–	–	–	57.4	–	–	–	85.6	
CLY-171-69	2.1	F(3.1)																			
CLY-171-69	1.9	F(2.8)																			
CLY-171-69	–	2.0	–	9.9	–	58.0	–	–	–	89.3	–	108.8	–	–	–	126.9	–	–	135.5	–	–
CLY-171-69	–	1.5	–	3.5	–	49.7	–	–	–	70.3	–	84.3	–	–	–	(F)					
CLY-173-69	7.7	8.6	9.3	9.5	10.4	11.4	12.6	13.9	14.5	16.1	–	17.1	–	–	19.6	–	–	24.3	–	27.9	–
CLY-173-69	6.6	7.7	14.3	13.6	14.5	15.2	15.6	17.1	17.5	19.2	–	19.9	–	–	21.7	–	–	24.4	–	31.5	–
CLY-173-69	5.1	7.8	7.5	8.4	10.5	11.3	12.1	12.4	13.0	13.6	14.8	15.5	15.4	16.7	–	17.5	–	–	20.9	–	25.8
CLY-173-69	5.0	7.8	7.9	9.1	11.5	12.6	13.7	14.8	16.0	17.3	19.0	19.6	19.8	21.1	–	22.0	–	–	26.0	–	31.2
CLY-180-69	–	8.4	–	9.4	–	9.7	–	–	–	10.3	–	10.3	–	–	–	11.1	–	–	11.3	–	–
CLY-180-69	–	7.6	–	8.7	–	8.9	–	–	–	10.7	–	9.7	–	–	–	10.6	–	–	10.7	–	–
CLY-181-69	–	–	–	–	–	–	–	3.5	–	–	–	–	–	–	–	18.6	–	–	–	–	–
CLY-181-69	–	–	–	–	–	–	–	3.3	–	–	–	–	–	–	–	18.9	–	–	–	–	–

*Column heading denotes time in hours

APPENDIX XLI (CONTD)

	OXIDATION TEST RESULTS: WEIGHT GAIN OF SAMPLES (mg)*																	
Run Number	5.75	6.0	6.25	6.5	6.75	7.0	7.5	7.75	8.5	9.25	9.5	10.0	10.5	11.0	11.5	12.0	13.0	14	15
CLY-167-69	–	134.6	–	–	–	148.7	–	–	152.6	166.6	–	160.7	–	F(209.6)					
CLY-167-69	–	135.1	–	–	–	144.8	–	–	152.3	156.6	–	160.5	–	F(305.0)					
CLY-167-69	–	–	–	137.1	–	–	142.0	–	146.1	–	151.6	–	155.3	–	F(205.4)				
CLY-167-69	–	–	–	132.7	–	–	143.4	–	F(163.2)										
CLY-168-69	F(111.0)																		
CLY-168-69	–	124.4	–	–	F(164.3)														
CLY-168-69	–	120.7	–	–	141.9	–	F(198.1)												
CLY-169-69	–	157.4	–	–	–	165.8	–	171.0	–	175.0	–	179.0	–	182.0	–	F(140.4)			
CLY-169-69	–	151.0	–	–	–	164.1	–	170.9	–	174.4	–	178.3	–	182.0	–	F(170.2)			
CLY-169-69	–	129.7	–	–	–	150.4	–	–	–	F(169.7)									
CLY-169-69	–	123.4	–	–	–	146.9	–	–	–	175.9	–	–	–	182.5	–	–	188.9	–	F(283.9)
CLY-171-69	–	(F)																	
CLY-173-69	–	35.3	–	–	F(41.6)														
CLY-173-69	–	42.2	–	–	F(53.2)														
CLY-173-69	–	–	32.5	–	–	41.8	–	42.7	68.5	F(86.6)									
CLY-173-69	–	–	37.2	–	–	F(52.2)	–												
CLY-180-69	–	14.2	–	–	–	17.0	–	–	–	33.4	–	–	–	59.4	–	–	72.0	–	78.0
CLY-180-69	–	15.3	–	–	–	21.2	–	–	–	47.4	–	–	–	61.5	–	–	69.8	–	71.1
CLY-181-69	–	59.0	–	–	–	–	–	80.6	–	–	–	98.8	–	–	–	111.5	–	121.2	–
CLY-181-69	–	54.0	–	–	–	–	–	75.6	–	–	–	92.1	–	–	–	103.6	–	112.7	–

Run Number	16	17	18	19	21	23	25	27	29	31	33	35	37	39	41	43
CLY-180-69	–	82.4	–	94.7	86.1	91.0	92.4	95.8	98.9	102.4	108.7	116.4	120.7	122.9	127.4	F(-)
CLY-180-69	–	77.4	–	79.3	80.7	84.0	84.6	86.8	88.7	91.2	95.6	99.2	103.0	106.8	110.2	F(-)
CLY-181-69	125.4	–	F(132.4)													
CLY-181-69	119.0	–	F(184.8)													

*Column heading denotes time in hours

APPENDIX XLII

CYCLIC OXIDATION: 1800°F, 2200°F AND 2600°F TEST RESULTS

Oxidation Test Results: Weight Gain of Samples (mg)*

Run Number	Substrate Identification	2	4	6	8	10	12	16	20	24	28	32	36	40	44	48	52	56	60	64	68	72	76	80	84	88	92	96	100	Source of Failure
	1800°F																													
CLY-200-69	D, E	–	–	–	F(63.8)																									Nut
CLY-201-69	D, E	–	–	–	F(183.3)																									Nut
CLY-202-69	D, E	42.2	67.5	–	F(170.5)																									Nut
CLY-205-69	D, E	44.2	F(79.3)																											Nut, Threads
CLY-206-69	D, E	67.2	F(150.5)																											Nut
CLY-210-69	D, E	48.1	64.1	F(79.8)																										Nut
CLY-211-69	D, E	13.2	37.7	F(55.7)																										Nut
	2200°F																													
CLY-200-69	D, E		18.8	–	F(68.3)																									Threads
CLY-201-69	D, E	–	11.0	–	14.1	–	17.0	19.5	22.0	24.7	27.6	32.0	40.5	50.7	64.2	78.3	91.8	103.8	F(148.3)											Nut
CLY-202-69	D, E	–	15.1	–	23.4	–	34.1	42.6	F(54.7)	F(61.5)																				Nut
CLY-205-69	D, E	–	9.7	–	14.1	–	18.1	20.3	21.9	23.2	25.0	26.5	28.4	30.0	31.5	32.9	34.9	36.0	38.0	38.4	38.7	45.7	46.8	5.02	63.9	56.3	70.2	74.2	79.4	
CLY-206-69	D, E	–	8.0	–	13.6	–	22.8	39.3	59.0	79.4	F(96.6)																			Nut
CLY-210-69	D, E	–	8.7	–	19.9	F(67.0)																								Nut, Threads
CLY-211-69	D, E	–	9.5	–	13.6	–	19.1	22.7	26.7	36.9	39.6	42.8	44.9	47.1	47.2	51.1	51.6													
		0.25	0.50		0.75	1.0																								
	2600°F																													
CLY-197-69	D	F																												Head, Shank, Threads
CLY-198-69	D	F																												Head, Shank, Threads
CLY-199-69	D	F																												Head, Shank, Threads
CLY-196-69	D	4.9	F(6.4)																											Threads
CLY-196-69	D	F(11.6)																												Threads
CLY-202-69	D, E	6.5	F(122.5)																											Slight-Threads
CLY-205-69	D, E	21.4	F(42.7)																											Nut, Threads
CLY-206-69	D, E	F(40.5)																												Slight-Threads
CLY-210-69	D, E	10.9	F(18.5)																											Slight-Threads
CLY-211-69	D, E	15.3	F(33.5)																											Slight-Threads

*Column heading denotes time in hours.

OTHER RUN CONDITIONS

- Substrate Identification
  - A. 1 1/2-in. Round Rod
  - B. Flat Panel (app. 1 in. x 1/2 in.)
  - C. 1-in. Threaded Stud
  - D. 1 1/2-in. Hex Head Bolt
  - E. Hex Nut
- In CLY-205-69, hex nut is from CLY-203-69

APPENDIX XLIII

CYCLIC OXIDATION: 2400°F TEST RESULTS

Oxidation Test Results: Weight Gain of Samples (mg)*

Run Number	Substrate Identification	4	8	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	56	Source of Failure
CLY-186-69	D	–	–	–	11.6	–	–	17.6	–	–	25.2	–	–	F(31.8)												–
CLY-186-69	D	–	–	–	13.2	–	–	21.4	–	–	38.0	–	–	F(65.1)												–
CLY-186-69	D	–	–	–	–	20.1	–	–	–	–	–	–	–	F(32.8)												–
CLY-187-69	D	–	–	–	–	27.8	–	–	F(53.7)																	–
CLY-187-69	D	–	–	–	–	27.9	–	–	F(50.4)																	–
CLY-188-69	D	–	–	–	F(49.9)																					Threads
CLY-188-69	D	–	–	–	F(92.7)																					Threads
CLY-189-69	D	–	–	–	F(30.1)																					–
CLY-189-69	D	–	–	–	F(23.1)																					–
CLY-190-69	D	–	–	F(109.1)																						–
CLY-190-69	D	–	–	F(171.0)																						–
CLY-191-69	D	–	–	–	21.6	–	–	–	F(47.8)																	Threads
CLY-191-69	D	–	–	–	22.7	–	–	–	F(36.9)																	Threads
CLY-192-69	D	–	–	F(64.3)																						
CLY-193-69	D	–	F(30.4)																							Threads
CLY-194-69	D	–	–	–	F(29.1)																					Thread & Head
CLY-194-69	D	9.3	F(16.0)																							Threads, Head
CLY-194-69	D	–	–	20.0	–	F(37.9)																				Threads, Head
CLY-195-69	D	–	30.1	–	F(52.9)																					Threads, Head
CLY-196-69	D	–	–	–	30.5	–	93.3	–	117.2	–	134.2	–	151.0	–	F(172.0)											Threads, Head
CLY-196-69	D	9.7	13.3	18.3	–	23.3	–	36.0	–	43.7	–	49.0	–	55.7	–	F(55.4)										Threads, Heads
CLY-197-69	D	–	–	–	24.2	–	36.9	–	47.2	–	50.3	–	75.7	–	F(95.0)											Threads
CLY-197-69	D	9.7	11.7	14.1	–	19.0	–	24.4	–	30.2	–	40.3	–	46.7												Threads
CLY-199-69	D	–	–	–	–	13.4	–	24.2	–	19.5	–	152.8	–	F(178.9)												Threads, Head
CLY-199-69	D	12.4	26.2	21.2	–	30.0	–	162.2	–	–	203.5	–	F(227.7)													Threads, Head
CLY-200-69	D, E	–	41.6	–	88.9	–	–	F(136.7)																		Threads, Head
CLY-200-69	D, E	–	F(41.4)																							Threads, Head
CLY-201-69	D, E	–	31.0	53.9	–	81.7	–	103.2	–	124.4	–	142.6	–	163.9	–	209.2	–	226.9		250.3		F(305.6)				Nut
CLY-201-69	D, E	23.5	39.5	61.9	–	90.4	–	105.8	–	123.6	–	162.1	–	174.9	–	192.5	–	212.6		221.7		F(245.2)				Nut
CLY-202-69	D, E	–	70.4	96.2	–	117.5	–	119.5	–	–	–	–	F													Threads, Nut
CLY-202-69	D, E	–	60.4	83.7	–	95.8	–	98.7	–	–	–	–	F													Threads, Nut
CLY-203-69	E	2.3	3.0	4.0	–	5.1	–	6.8	–	7.9	–	8.5	–	9.6	–	13.2	–	15.4		19.3		25.9		35.8	F(58.6)	Threads
CLY-204-69	D, E	–	20.6	25.8	–	42.6	–	56.6	–	76.1	–	101.5	–	F(141.5)												Threads
CLY-204-69	D	–	14.4	17.0	–	18.8	–	22.0	–	27.2	–	35.3	–	53.0	–	58.8	–	F(70.0)								Threads
CLY-205-69	D, E	32.7	36.8	47.2	–	57.6	–	62.7	–	89.7	–	105.8	–	–	120.8	140.9	–	151.7		F(188.3)						Threads
CLY-205-69	D	22.1	28.0	35.5	–	39.8	–	43.8	–	46.1	–	49.4	–	–	52.9	58.8	F(70.0)									Threads
CLY-206-69	D, E	–	–	–	92.8	–	112.3	–	122.0	–	137.2	–	152.8	–	166.4	–	178.8		191.8		203.9		F(263.5)			Threads
CLY-209-69	D, E	–	92.5	124.8	–	137.9	–	169.5	–	F(189.4)																Nut
CLY-210-69	D, E	–	25.5	40.7	–	F(126.6)																				Nut
CLY-210-69	D, E	–	–	–	–	108.3	–	F(168.1)																		Nut
CLY-211-69	D, E	–	–	–	39.1	45.6	53.2	–	–	61.4		F(70.0)														Threads
CLY-211-69	D, E	–	–	–	–	43.1	–	60.4	–	66.7	–	74.1	–	85.4	–	96.4	–	109.9								Threads

OTHER RUN CONDITIONS

- Substrate Identification
  - A. 1 1/2-in. Round Rod
  - B. Flat Panel (Approximately 1 in. x 1/2 in.)
  - C. 1-in. Threaded Stud
  - D. 1 1/2-in. Hex Head Bolt
  - E. Hex Nut
- In CLY-204-69 and CLY-205-69, hex nut is from CLY-203-69

*Column heading denotes time in hours

APPENDIX XLIV

CYCLIC OXIDATION: ADDITIONAL 2400°F TEST RESULTS

Run Number	Substrate Identification	Oxidation Test Results: Weight Gain of Samples (mg)*															
		2	4	6	8	10	12	16	20	24	28	32	36	40	44	48	52
CLY-202-69	D, E	–	15.3	–	–	–	70.5	–	125.2	–	F(153.7)						
CLY-202-69	D, E	–	12.5	–	–	–	48.2	–	81.0	–	F(126.2)						
CLY-205-69	D	–	–	–	–	–	–	39.3	–	–	–	45.9	–	51.1	–	59.7	F(73.6)
CLY-205-69	D	–	–	–	–	–	–	40.0	–	–	–	F(57.3)					
CLY-205-69	D	–	–	–	–	–	–	11.9	–	–	–	48.1	–	54.7	–	66.8	F(86.6)
CLY-205-69																	
CLY-206-69	E	–	8.5	–	–	–	33.4	–	78.0								
CLY-206-69	E	–	8.7	–	–	–	28.1	–	69.3								
CLY-206-69	E	–	9.5	–	–	–	35.8	–	85.5								
CLY-206-69	E	–	10.2	–	–	–	27.6	–	F(30.6)								
CLY-210-69	E	–	–	–	–	–	–	10.7									
CLY-210-69	E	–	–	–	–	–	–	F(10.2)									
CLY-210-69	E	–	–	–	–	–	–	F(10.1)									
CLY-210-69	E	–	–	–	–	–	–	F(51.2)									
CLY-211-69	D, E	–	25.1	–	–	–	28.8	–	30.8	–	63.6	–	82.9	–	F(106.6)		
CLY-211-69	D, E	–	24.6	–	–	–	37.2	–	37.2	–	58.4	–	99.7	–	F(146.4)		

OTHER RUN CONDITIONS

- Substrate Identification

  A. 1 1/2-in. Round Rod
  B. Flat Panel (Approximately 1 in. x 1/2 in.)
  C. 1-in. Threaded Stud
  D. 1 1/2-in. Hex Head Bolt
  E. Hex Head

- In CLY-204-69 and CLY-205-69, hex nut is from CLY-203-69

*Column heading denotes time in hours

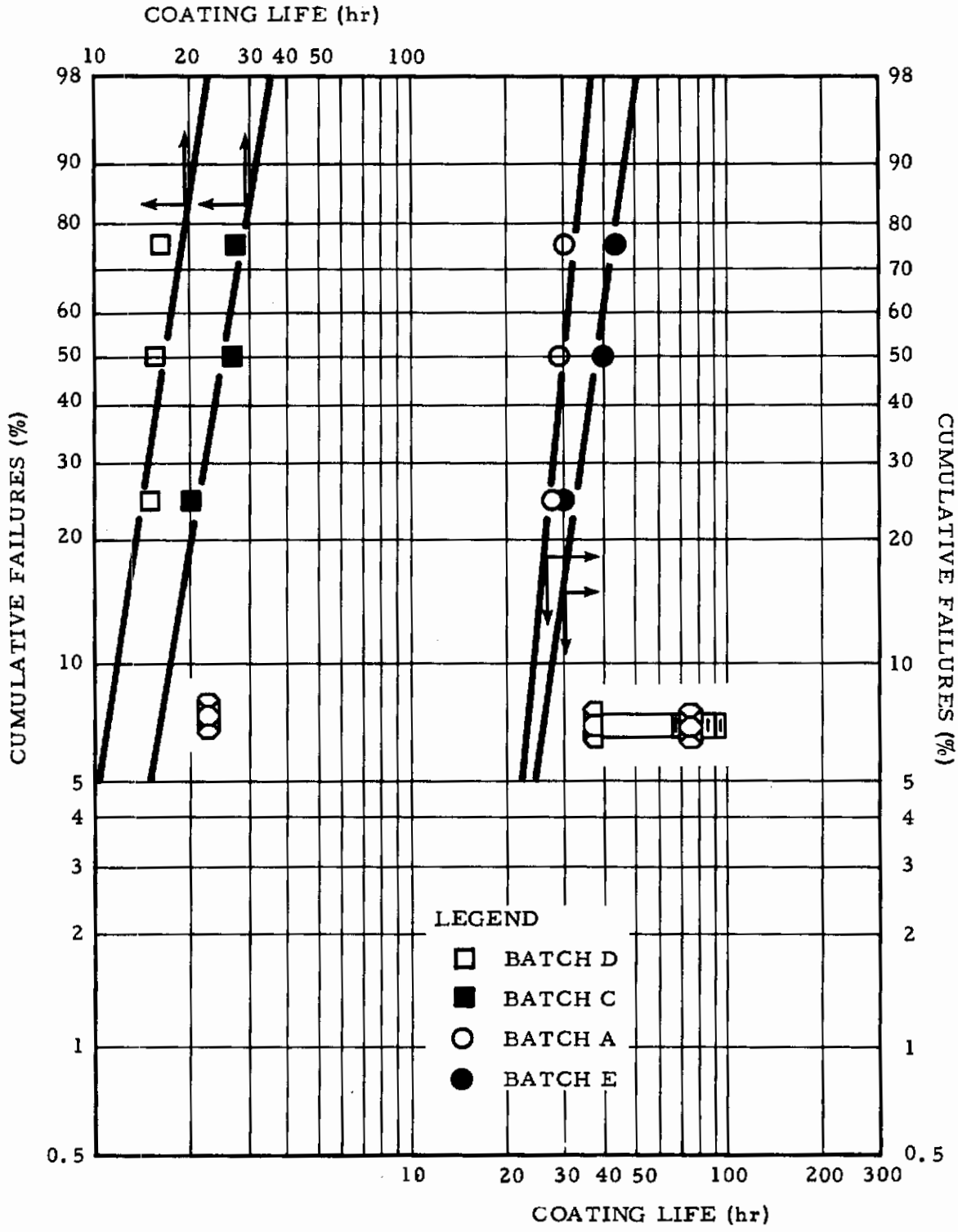
APPENDIX XLV

CYCLIC OXIDATION: 2400°F OXIDATION TEST RESULTS FOR WEIBULL PLOT

Identification	Source of Failure	Cumulative Failure (%)	Test Time To Failure (hr)
Batch A	Threads	25	28
D, E-Hex Head	Threads	50	28
Bolt and Nut	Threads, Nut	75	30
	Threads, Nut	100	30
Batch E	Threads	25	28
D, E-Hex Head	Threads	50	40
Bolt and Nut	Threads	75	44
	Threads	100	44
Batch B	Threads	25	32
D-Hex Head Bolt	Threads	50	38
	Threads	75	52
	Threads	100	52
Batch C	Nut	25	20
E-Hex Nut	Nut	50	28
	Nut	75	28
	Nut	100	28
Batch D	Nut	25	16
E-Hex Nut	Nut	50	16
	Nut	75	16
	Nut	100	32

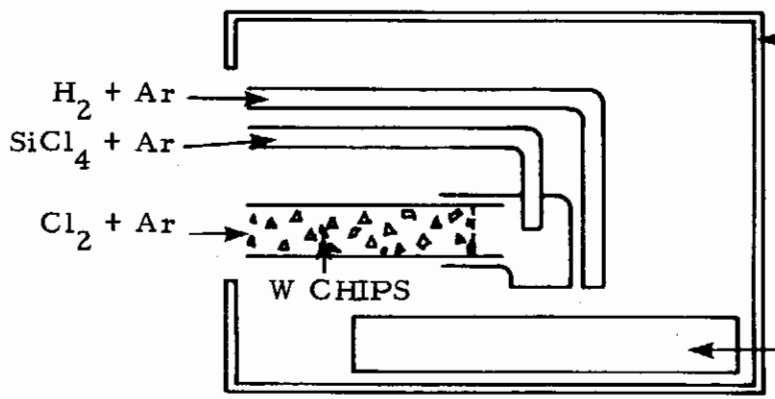
APPENDIX XLVI

CYCLIC OXIDATION: WEIBULL PLOT OF CUMULATIVE FAILURES VERSUS 2400°F COATING LIFE

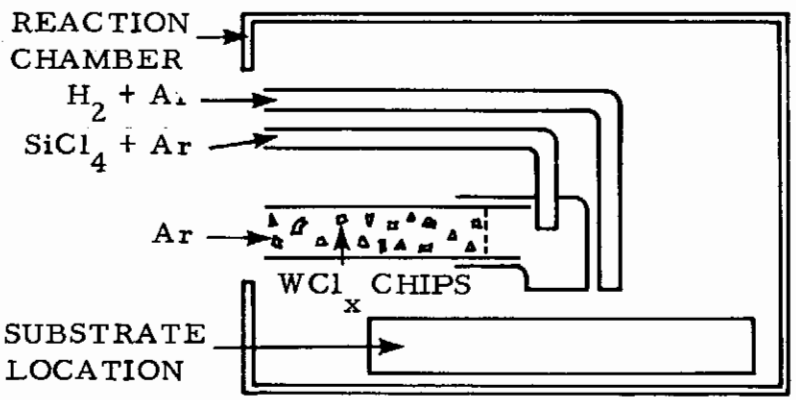


APPENDIX XLVII

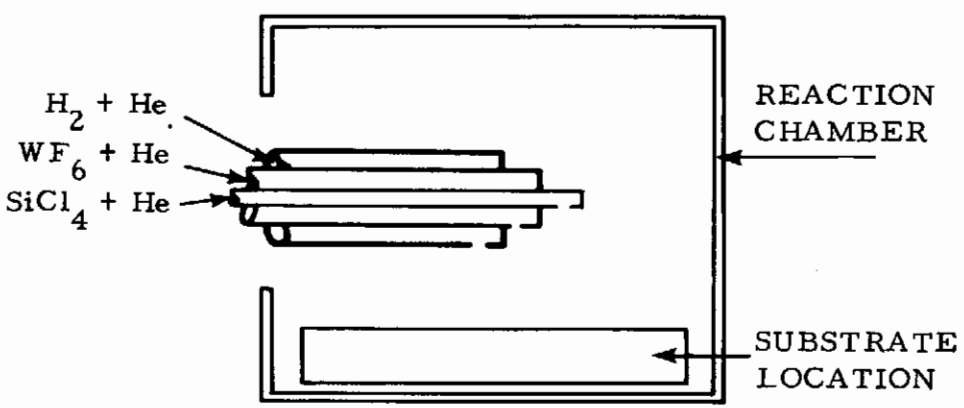
COATING PREPARATION STUDIES: GAS FEED GEOMETRIES (i.e., FEED NOZZLES) FOR CHLORIDE AND FLUORIDE ROUTES



(a) GAS FEED GEOMETRY E



(b) GAS FEED GEOMETRY F



(c) GAS FEED GEOMETRY G

APPENDIX XLVIII

COATING PREPARATION STUDIES: ADDITIONAL PROCESS CONDITIONS AND RESULTS FOR FLUORIDE ROUTE

Run Number	WF_6 Flow (ℓ/min)	H_2 Flow (ℓ/min)	Inert Gas Dilution of H_2 (He, ℓ/min)	Inert Gas Flow (He, ℓ/min)		Total Flow Measured (ℓ/min)	Reaction Temp. (°C)	Deposition Time (min)	Rotation Speed (rpm)	Reactor Loading via Quantity of Substrates
				$SiCl_4$ Bubbler	Dilution					
CLY3-24-69	.180	.077	.872	—	.100	1.229	650	180	12	1
CLY3-25-69	.180	.077	.872	—	—	1.129	650	75	12	2
CLY3-26-69	.180	.077	.872	—	—	1.129	650	180	12	2
CLY3-27-69	.180	.077	.872	—	—	1.129	650	180	12	2
CLY3-28-69	.180	.077	.872	—	—	1.129	650	240	12	2
CLY3-29-69	.180	.077	.872	—	—	1.129	650	240	12	2
CLY3-30-69	.180	.150	.830	.100	.900	2.160	650	180	12	2
CLY3-31-69	.180	.150	.830	.100	.900	2.160	650	240	12	2
CLY3-32-69	.180	.150	.830	.100	.900	2.160	650	240	12	2
CLY3-33-69	.180	.150	.830	.100	.900	2.160	650	240	12	2
CLY3-34-69	.180	.150	.830	.100	.900	2.160	650	240	12	2
CLY3-35-69	.180	.150	.830	—	.900	2.060	650	120	2	2
CLY3-36-69	.180	.150	.830	—	.010	1.161	650	120	1	3
CLY3-37-69	.180	.150	.830	—	.010	1.161	650	240	1	3
CLY3-38-69	.180	.150	.830	—	.010	1.161	650	180	1	2

OTHER RUN CONDITIONS

- Equipment utilized as shown in Figure 52

APPENDIX XLIX

COATING PREPARATION STUDIES: ADDITIONAL OBSERVATIONS FOR FLUORIDE ROUTE

Run Number	Observations
CLY3-25-69	• Deposition run conducted for one plus hour with stabilizing supports • Rotation speed maintained constants during run
CLY3-26-69	• Conducted deposition run for three hours with stabilizing supports • Constant rotation speed again maintained during run • Silver gray coating obtained on T222 substrates • Some etching (chipping) substrate edges
CLY3-27-69	• Some gray coating deposit obtained on T222 substrates • Some etching (chipping) on substrate edges
CLY3-28-69	• Conducted four hour run with graphite reactor • Substrates (T222) experienced weight gain (432.1, 431.8 mg) • Above result suggests that metal cage reactor rotation was causing substrate chipping
CLY3-30-69	• Conducted tungsten-tungsten silicide deposition run • No pluggage even with $SiCl_4$ flow for two hours
CLY3-31-69	• Conducted tungsten-tungsten silicide deposition run with two hour run time for each deposition • Silver gray coating obtained on substrates • Bonding appears to be problem on basis of flake off upon sawing for mounting

APPENDIX XLIX (CONTD)

Run Number	Observations
CLY3-32-69	• Conducted tungsten silicide deposition run with four hour run time • Bonding problem still exists – evidenced by flake off of coating upon cutting for mounting
CLY3-33-69	• Conducted tungsten-tungsten silicide deposition run with degreased substrates (degreased immediately before run with MEK and acetane) • MEK sample experienced 956.4 mg weight gain • Acetane sample experienced 385.8 mg weight gain
CLY3-34-69	• Conducted tungsten-tungsten silicide deposition run with three substrates • Substrates experienced some coating deposit
CLY3-35-69	• Conducted tungsten deposition run • Substrates experienced some coating deposit and some etching
CLY-36-69	• Conducted tungsten deposition for two hour run • Silver grey coating obtained on T222 substrates • Partial bonding problem evidenced by partial flake off upon sawing for mounting
CLY3-37-69	• Conducted deposition run for four hour deposition • Silver gray coating deposit obtained on three substrates • Reactor broke while unloading system at end of run

APPENDIX XLIX (CONTD)

Run Number	Observations
CLY3-38-69	• Conducted deposition run with special metal attachment on graphite reactor • Several rotation stops during run • Quartz substrate completely etched (i. e., disappeared) at end of run • Reactor rotation attachment broken at end of run

APPENDIX L

COATING PREPARATION STUDIES: ADDITIONAL INITIAL PROCESS CONDITIONS AND RESULTS FOR CHLORIDE ROUTE

Run Number	WCl_x Feed			H_2 Feed		Inert Gas Flows Ar, (ℓ/min)		Total Flow Measured (ℓ/min)	Reaction Temp. (°C)	Deposition Time (min)	Rotation Speed (rpm)	Reactor Loading via Quantity of Substrates	Reaction Chamber	Gas Feed Geometry
	Approx. Cl_2 Flow (ℓ/min)	W Chips Wt. Loss (gm)	Inert Gas Dilution (Ar, ℓ/min)	H_2 Feed (ℓ/min)	Inert Gas Dilution (Ar, ℓ/min)	$SiCl_4$ Bubbler	Dilution							
CLY3.1-20-69	.080	4.1614	4.5	0.2	4.8	–	0.5	10.080	1000	45	.5	2	A	E
CLY3.1-21-69	.020	2.9687	–	4.0	7.0	–	5.0	16.020	800	90	.5	2	A	E
CLY3.1-22-69	0.5	3.9708	5.0	4.0	7.0	–	5.0	21.5	800	90	.5	2	A	E
CLY3.1-23-69	1.5	5.3974	–	4.0	7.0	–	5.0	22.5	1005	120	.5	2	A	E
CLY3.1-24-69	1.5	Yes	–	–	7.0	–	5.0	13.5	1005	120	.5	2	A	E
CLY3.1-25-69	1.5	Yes	–	1.0	7.0	–	5.0	9.5	1005	60	.5	2	A	E
CLY3.1-26-69	1.5	Yes	–	0.5	7.0	–	7.0	16.0	1005	60	.5	2	A	E

APPENDIX LI

COATING PREPARATION STUDIES: INITIAL OBSERVATIONS FOR CHLORIDE ROUTE

Run Number	Observations
CLY3.1-20-69	• Conducted deposition run with lower hydrogen concentration • Substrates experienced weight loss
CLY3.1-21-69	• Conducted deposition run with longer W chip holder for longer reaction time to generate tungsten chloride • Breakage of chip holder and other feed nozzles was not experienced • Measured temperature profile (for every 3 inches: 800, 760, 515, 175, and 80°C)
CLY3.1-22-69	• Conducted deposition run with higher Cl_2 flow over W chips to increase tungsten chloride concentration • Substrates experienced very slight weight gain
CLY3.1-23-69	• Conducted run at higher reaction temperature • Substrates lost weight possibly due to chloride etching • Silver gray coating deposit obtained at end of chip holder nozzle
CLY3.1-24-69	• Conducted deposition run without any hydrogen • Silver gray coating not obtained at end of chip holder nozzle • Substrates did not experience any weight change (possibly weight loss but too small for accuracy at .0008 and .0004 mg) • Suggested hydrogen back up into nozzle

APPENDIX LI (CONTD)

Run Number	Observations
CLY3.1-25-69	• Conducted deposition run with modified gas feed geometry shown • Did not obtain any coating deposit
CLY3.1-26-69	• Conducted deposition run with intermediate H_2 concentration • Did not get any silver gray deposit on substrates • Switched work effort to work on deposition via chloride route with tungsten hexachloride feed

APPENDIX LII

COATING PREPARATION STUDIES: INITIAL PROCESS CONDITIONS AND RESULTS FOR CHLORIDE WITH TUNGSTEN HEXACHLORIDE FEED

Run Number	WCl_x Feed		H_2 Feed		Inert Gas Flows Ar, (ℓ/min)		Total Flow Measured (ℓ/min)	Reaction Temp. (°C)	Deposition Time (min)	Rotation Speed (rpm)	Reactor Loading via Quantity of Substrates	Reaction Chamber	Gas Feed Geometry
	Chips Wt. Loss	Inert Gas (Ar, ℓ/min)	H_2 Feed (ℓ/min)	Inert Gas Dilution (Ar, ℓ/min)	$SiCl_4$ Bubbler	Dilution							
CLY3.1-27-69	Yes	6.0	2.0	7.0	–	–	15.0	800	120	0.5	2	A	F
CLY3.1-28-69	Yes	6.0	2.0	7.0	–	–	15.0	1000	120	0.5	2	A	F
CLY3.1-29-69	Yes	6.0	0.5	7.0	–	6.0	19.5	800	120	0.5	2	D	F
CLY3.1-30-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	120	0.5	2	D	F
CLY3.1-31-69	Yes	2.0	2.0	7.0	–	6.0	17.0	1000	120	0.5	2	A	F
CLY3.1-32-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	180	0.5	2	A	F
CLY3.1-33-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	600	0.5	2	A	F
CLY3.1-34-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	480	0.5	2	A	F
CLY3.1-35-69	Yes	2.0	2.0	7.0	–	6.0	17.0	1000	300	0.5	2	A	F
CLY3.1-36-69	Yes	.036	1.0	1.0	0.2	1.8	4.036	1000	120	0.5	3	E	F
CLY3.1-37-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	180	0.5	3	D	F
CLY3.1-38-69	Yes	2.0	2.0	7.0	–	6.0	17.0	800	240	0.5	4	D	F
CLY3.1-39-69	Yes	4.5	2.0	7.0	–	6.0	19.5	800	180	0.5	4	D	F
CLY3.1-40-69	Yes	4.5	2.0	7.0	–	6.0	19.5	1000	180	0.5	4	D	F
CLY3.1-41-69	Yes	2.0	2.0	7.0	–	6.0	17.0	500	240	0.5	4	D	F

APPENDIX LIII

COATING PREPARATION STUDIES: INITIAL PROCESS CONDITIONS AND RESULTS FOR CHLORIDE WITH TUNGSTEN HEXACHLORIDE FEED

Run Number	Observations
CLY3.1-27-69	• Conducted deposition run at 800°C with WCl_6 powder • Coating deposit obtained on nozzle
CLY3.1-28-69	• Conducted coating run at 1000°C with WCl_6 powder • Coating deposit obtained on nozzle
CLY3.1-29-69	• Conducted deposition run with increased WCl_6 dilution, lower H_2 concentration and small reaction chamber • Coating deposit was not achieved on substrate
CLY3.1-30-69	• Conducted deposition run with increased hydrogen • Silver gray coating obtained on small ractor (walls and end) • This is first time that coating has been obtained from chloride feed
CLY3.1-32-69	• Conducted deposition run for three hours with large reaction chamber • Substrates experienced small weight gain (3.1 and 2.5 mg)
CLY3.1-33-69	• Partially completed four hour deposition run • Substrates chipping on edges
CLY3.1-34-69	• Conducted deposition run with shorter feed nozzle extension • Substrates experienced weight gain (12.8 and 11.7 mg). Some substrate chipping on edge on third substrate • Approximately one-half of chips remained from run

Run Number	Observations
CLY3.1-35-69	• Conducted deposition run with shorter nozzle extension and higher reaction temperature • Substrates experienced weight gain (11-13 mg) • No edge etching of substrate
CLY3.1-36-69	• Conducted WSi_x deposition run at 1000°C • Substrates – tungsten rod pieces – experienced weight gain. Coating dark in color.
CLY3.1-37-69	• Conducted deposition run with small reactor • Substrates did not coat much • Reactor walls coated with silver coating
CLY3.1-38-69	• Conducted deposition run with shorter feed nozzle • Reactor walls and end coated with silver deposit • Dark deposit obtained on substrates
CLY3.1-39-69	• Conducted deposition run with increased gas flow over chips • Coating obtained on reactor walls and substrates on outside, coating dark grey color. On inside, coating silver grey color.
CLY3.1-40-69	• Conducted deposition run at increased reaction temperature • Some etching of substrate edges in part of reactor loading other experienced weight gain (19.4 mg) higher than previous run.

APPENDIX LIV

MECHANICAL TESTS — EXTERNAL TEST: MECHANICAL PROPERTY EVALUATION BY STANDARD PRESSED STEEL CO. OF COATED REFRACTORY FASTENERS FROM PRODUCTION DEMONSTRATION BATCHES

APPENDIX LV

MECHANICAL TESTS – EXTERNAL TEST: MECHANICAL PROPERTY EVALUATION BY STANDARD PRESSED STEEL CO. OF COATED REFRACTORY FASTENERS WITH POST-HEAT TREATMENT FROM PRODUCTION DEMONSTRATION BATCHES

PURPOSE:

To evaluate the mechanical properties of Texas Instruments Cr-Ti-Si coated Cb 752 hexagon head bolts at various temperatures from room to 2600°F.

BACKGROUND:

Texas Instruments Incorporated is currently conducting a program for the Air Force Manufacturing Technology Group on the chemical vapor deposition of protective coatings on refractory alloy fasteners. A portion of this program involved the deposition of a Cr-Ti-Si coating on Cb 752 hex head bolts and nuts purchased from Standard Pressed Steel Co.

The basis for evaluation of mechanical properties was to be a comparison with the results obtained under the SPS Air Force Program "Structural Fasteners For Extreme Elevated Temperatures" on Vitro Cr-Ti-Si coated Cb 752 fasteners.

Purchase order H-03810-4X was issued by Texas Instruments Incorporated to cover the cost of this testing.

PROCEDURE:

Test procedures and fixtures were exactly the same as those utilized under Air Force contract AF33(657)-11684. These are described in the final report of that contract, AFFDL-TR-66-107.

Test Program:

The mechanical tests on Cb 752 columbium alloy, Cr-Ti-Si coated fasteners consisted of the following:

1. Ultimate tensile strength at room temperature, 600°F, 2000°F, 2400°F, and 2600°F. Eight tests were made at each temperature, two pieces per lot, for a total of 40 tests.

2. Shear strength at room temperature, 600°F, 2000°F, and 2400°F. Eight tests each were performed at the room temperature and 600°F temperature levels. For the 2000°F and 2400°F temperatures, four tests were performed at each of these levels.

PROCEDURE:

Test Program: (continued)

3. Relaxation at 2000°F and 2400°F. Three pieces were tested at each temperature.

4. Reusability - Evaluation of nut removal of parts tensile tested at 2000°F and 2400°F.

RESULTS:

Tables of results for test run are:

TABLE I - Ultimate Tensile Strength
" II - Shear Strength
" III - Relaxation
" IV - Reusability

TABLE I
ULTIMATE TENSILE STRENGTH OF TEXAS INSTRUMENTS
Cr-Ti-Si COATED 1/4-20 COLUMBIUM (Cb 752) HEX HEAD BOLTS

Test Temp. °F	Batch B		Batch E		Batch A		Batch D	
	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)
80	1800 1350	49,500	1670 1430	48,700	1050 1000	32,200	1640 1420	48,100
600	2015 2080	64,300	1960 2110	63,900	2065 2090	65,300	1855 1955	59,800
2000	1390 1320	42,500	1430 1410	44,600	1390 1500	45,400	1200 1150	36,900
2400	835 860	26,600	760 746	23,600	760 826	24,800	763 680	22,700
2600	635 638	20,000	635 640	20,000	670 690	21,400	595 637	19,400

(All tensile stresses based on Tensile Stress Area of 0.03182 square inches)

TABLE II
DOUBLE SHEAR STRENGTH OF TEXAS INSTRUMENTS
Cr-Ti-Si COATED 1/4-20 COLUMBIUM (Cb 752) HEX HEAD BOLTS

Room Temp. °F	Batch B		Batch E		Batch A		Batch D	
	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)	Pounds	psi (Av.)
80	3250 5450	41,900	3400 2600	28,900	2540 2310	23,400	5320 5300	51,100
600	4275 4275	41,200	4320 4240	41,300	4375 4375	41,800	4275 4180	40,800
2000	3335	32,100	3125	30,100	3065	29,500	3080	29,700
2400	2125	20,500	2205	21,300	2220	21,400	2050	19,800

TABLE III

RELAXATION TEST DATA ON TEXAS INSTRUMENT Cr-Ti-Si COATED 1/4-20 COLUMBIUM (Cb752) HEX HEAD BOLTS PRELOADED TO 15,000 psi AND EXPOSED TO ELEVATED TEMPERATURES AS SHOWN FOR TWO HOURS.

Batch Type	Temperature °F	Length After Soak (Seated)	Length After Soak (Unseated)	Change In Length	Residual Load, psi
A	2000	1.6755	1.6752	0.0003	3750
B	2000	Broke	Loading		
D	2000	1.6650	1.6648	0.0002	2500
E	2000	1.6764	1.6761	0.0003	3750
A	2400	Broke	Loading		
B	2400	1.6855	1.6854	0.0001	1250
D	2400	1.6638	1.6637	0.0001	1250
E	2400	1.6809	1.6808	0.0001	1250

TABLE IV

TEXAS INSTRUMENT Cr-Ti-Si COATED 1/4-20 COLUMBIUM (Cb 752) BOLTS
NUT REMOVAL OF PARTS TENSILE TESTED
AT 2000°F AND 2400°F

Batch Type	Difficulty of Nut Removal		Coating Damage
	Starting	Turning	
	Test Temperature - 2000°F		
A	Very high breakaway	hard (wrench required)	slight
A	high breakaway	easy (finger loose)	Nil
B	high breakaway	easy (finger loose)	Nil
B	Very high breakaway	easy (finger loose)	Severe
D	high breakaway	easy (finger loose)	slight
D	Very high breakaway	hard (wrench required)	slight
E	high breakaway	easy (finger loose)	Nil
E	finger loose	easy (finger loose)	Nil
	Test Temperature - 2400°F		
A	no movement		
A	no movement		
B	Very high breakaway	hard (wrench required)	severe
B	no movement		
D	no movement		
D	no movement		
E	no movement		
E	no movement		

Table I

ROOM TEMPERATURE ULTIMATE TENSILE STRENGTH OF 1/4-20 COLUMBIUM (Cb 752) HEX HEAD BOLTS (RANDOM PRODUCTION DEMONSTRATION BATCHES WITH POST-HEAT TREATMENT)

Spec. No.	Pounds	psi	Type of Failure
Uncoated Bolt			
1	3380	106,200	Threads
Cr-Ti-Si Coated Bolts			
2	2400	75,400	Head
3	2800	88,000	Threads
4	2900	91,000	Threads
Avg.	2700	84,800	

Table II

ROOM TEMPERATURE SHEAR STRENGTH OF 1/4-20 COLUMBIUM (Cb 752) HEX HEAD BOLTS (RANDOM PRODUCTION DEMONSTRATION BATCHES WITH POST-HEAT TREATMENT)

Spec. No.	Pounds	psi
Cr-Ti-Si Coated Bolts		
5	6400	65,300
6	6450	65,800
7	6460	65,900
Avg.	6437	65,700

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11. SUPPLEMENTARY NOTES

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13. ABSTRACT

Potential manufacturing-production equipment was developed via CVD-barrel coating technology in this program for applying CVD coatings to large quantities of small parts (i.e., refractory fasteners for aerospace structures). In Phase I, the practical equipment was designed, constructed, installed and tested in start-up. In these initial runs, trideposition reaction of hydrogen reduction of gas phase silicon, titanium and chromium chlorides was demonstrated as a CVD chemistry base for depositing chromium-titanium-silicon (Cr-Ti-Si) coating on small parts. In Phase II, optimization, production and evaluation studies were conducted with the designed equipment. Coatings improvements including apparent optimum region and key process parameter effects were achieved with statistical runs and analyses (i.e., T- and F-tests at 95% confidence level). Process development was scaled-up to large quantities by uniform coating many small parts: (a) 1/4-in. dia. round rods, 3 per run; (b) 1-in. threaded studs, 6-10 per run; (c) 1 1/2-in. hex head bolts, 10 per run; (d) mixed shapes-bolts, studs, rods and flat panels, 20 per run; (e) refractory fasteners-bolts studs and nuts, 30 per run; and (f) production demonstration-refractory fastener bolts and nuts, 30-50 per run. More than twenty demonstration runs at the increased capability (i.e., coating 30-50 substrates per run) were conducted with reproducibility to illustrate that the CVD-barrel coating technology is within potential manufacturing production scope. Important coating properties (i.e., oxidation resistance for substrate protection, Cr-Ti-Si concentrations, mechanical strengths, etc.) were evaluated. For 2400°F oxidation environment, more than eighty and twenty hours of protection was achieved for round rod and refractory fastener small parts from production demonstration batches. Uncoated parts experienced severe failure in less than one-half hour. Cursory literature screening revealed favorable state-of-art comparison based on this program and two independent literature sources. In Phase III, fluoride and chloride route were investigated for tungsten-tungsten silicide (W-WSi_2) coating of tantalum. For the fluoride route, tungsten coating of tantalum T222 was demonstrated with uniform coverage of round rod small parts.

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