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TESTING OF HIGH-EMITTANCE COATINGS

by R. E. Cleary and C. Ammann

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UNITED AIRCRAFT CORPORATION
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NASA CR-1413

TESTING OF HIGH-EMITTANCE COATINGS

By R. E. Cleary and C. Ammann

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Prepared under Contract No. NAS 3-10609 by
PRATT & WHITNEY AIRCRAFT
East Hartford, Conn.

for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

Three coatings were applied to the platinum - 20 wt. % rhodium alloy substrate by plasma spraying at a temperature of $1000^{o} \pm 50^{o}$ F. These coatings were hafnium oxide, cerium oxide, and iron titanate. The hafnium oxide was also applied chemically by the vapor deposition process. Initially, emittance testing of the plasma-sprayed coatings for 200 hours at 2100^{o} F in a vacuum of 1×10^{7} torr or better disclosed these values for total hemispherical emittance: hafnium oxide, 0.51 to 0.64; cerium oxide, 0.87 to 0.91; iron titanate, 0.94. The emittance of the chemically vapor deposited hafnia was 0.63 to 0.71. The coatings were aged in air for 1500 hours at 1100^{o} F. They were subsequently tested in vacuum at temperatures of about 2100^{o} F. The emittance was cerium oxide, 0.86 to 0.91; iron titanate, 0.90; hafnium oxide, 0.74 to 0.75. The cerium oxide coating was also tested for 2000 hours at 2100^{o} F in a vacuum of 1×10^{-7} torr or better with an emittance of 0.85 to 0.93.

FOREWORD

This report describes the work carried out by Pratt & Whitney Aircraft, Division of United Aircraft Corporation, in fulfillment of Contract NAS 3-10609. The work was conducted under the direction of the Space Power Systems Division, NASA Lewis Research Center, with J. A. Milko as Project Manager.

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SUMMARY

A nineteen-month program was conducted to determine the emittance properties of selected coating materials applied to platinum-20 percent rhodium, to evaluate the effectiveness of a tungsten diffusion barrier coating between a columbium-1 percent zirconium substrate and an iron-titanate coating, and to compare two natural iron-titanate materials applied to AISI-310 stainless steel. The iron-titanate materials were FCT-11H obtained from the Continental Coatings Corporation and an iron-titanate powder obtained from duPont. Two of the coating materials for the platinum-20 percent rhodium program, iron titanate and hafnium oxide, were selected prior to initiation of the contract. A third material, cerium oxide, was selected on the basis of early work performed under the contract.

Initially, 200-hour emittance tests were performed in vacuum of 1×10^{-7} torr or better at temperatures between 2100°F and 2800°F to determine the emittance properties of each coating when applied to platinum-20 percent rhodium. Subsequently, untested specimens of each type were aged in air at 1100°F for 1597 hours, after which the vacuum emittance properties were determined. The specimen providing the best results was tested in vacuum at 2100°F for 2000 hours.

Initial vacuum emittance testing of the cerium-oxide-coated specimen resulted in an emittance of 0.82 at 2100°F. Heating the specimen to 2800°F increased the emittance to 0.93, and subsequent cooling to 2100°F resulted in an emittance of 0.88. Three specimens were aged in air for 1597 hours at 1100°F, and the emittance of these in a vacuum of about 1×10^{-7} torr at 2100°F after aging ranged between 0.86 and 0.93. Two attempts were made to increase the temperature of these specimens to 2800°F, and in both cases the specimen or the coatings failed at about 2400°F. Examination of the specimens tested during the program revealed several changes in color, which may be indicative of oxidation and reduction of the coating as a result of the various test conditions.

The iron titanate coating demonstrated good bond strengths and emittance values in the vicinity of 0.90 at 2100°F in a vacuum of about 1×10^{-7} torr. Aging in air at a temperature of 1100°F for 1597 hours did not appear to have a detrimental effect on either the emittance in vacuum at 2100°F or the bond strength.

The chemically vapor deposited hafnium oxide coating applied to platinum-20 percent rhodium proved unsatisfactory. The emittance values were low, and, because of the large difference in the thermal expansion coefficients of the hafnium oxide and the platinum-20 percent rhodium, all of the coatings spalled from their substrates after thermal cycling to 2100°F. An attempt was made to obtain better coatings by plasma spraying hafnia stabilized with 5 weight percent calcia or yttria. The resulting coatings were more adherent than the chemically vapor deposited coatings, but the emittance values were still below the level considered acceptable.

Two uncoated platinum-20 percent rhodium tubes were also vacuum emittance tested, one for 200 hours in the as-received condition between 2100°F and 2800°F, and the other for 2000 hours after being aged in air at 1100°F for 1597 hours. The emittance of the unaged specimen was 0.17, and the emittance of the aged specimen was 0.19.

In addition to the work performed with platinum-20 percent rhodium substrates, exploratory tests were performed with AISI-310 stainless steel and columbium-1 percent zirconium substrates. The coatings tested included FCT-11H iron titanate, duPont iron titanate, and a duplex tungsten and iron titanate coating.

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I. INTRODUCTION

A. SCOPE

The emittance properties of selected materials were determined during a nineteen-month program. The work was primarily directed toward evaluating high-emittance materials for use in space environments at an operating temperature of 2100°F with brief transients to 2800°F. Initially, the emittance properties of coated platinum-20 percent rhodium specimens were determined during 200-hour tests performed in vacuum at temperatures between 2100°F and 2800°F. Additional specimens were aged in air for more than 1500 hours at 1100°F and then subjected to four-hour emittance tests in vacuum to determine the effects of the aging process on the emittance properties. The cerium-oxide-coated specimens were shown to have the best combination of properties, and, therefore, two simlar specimens were tested for 2000 hours in vacuum at 2100°F.

In addition to the work performed with platinum-20 percent rhodium substrates, tests were performed with AISI-310 stainless steel and columbium-1 percent zirconium substrates. The coatings tested included FCT-11H iron titanate obtained from the Continental Coatings Corporation, duPont iron titanate, and a duplex plasma-sprayed tungsten and plasma-sprayed iron titanate coating.

B. EMITTANCE MEASUREMENT AND ERROR ANALYSIS

The specimens tested during the program were coated nine-inch long tubes one-quarter inch in diameter with a wall thickness of 0.010 inch. These specimens were electrically resistance heated, and temperatures were measured with thermocouples and with an optical pyrometer focused on one of two small black-body holes drilled into the specimen. With the specimen in a vacuum chamber supported in a manner that permits only negligible heat conduction from the specimen test section, all of the electrical energy supplied to the specimen test section is radiated. Since the chamber walls were blackened and cold and the specimen surface area was considerably smaller than the inside surface of the chamber, the net power radiated, as given by the Stefan-Boltzmann equation, could be equated to the electrical power supplied to the specimen. This equation was then solved for emittance:

$$\epsilon_{th} = \frac{IV}{\sigma A (T_s^4 - T_o^4)}$$

where:

ϵ_{th} = Total hemispherical emittance

I = Current through the test section

V = Voltage drop across the test section

σ = Stefan-Boltzmann constant

A = Surface area of the test section radiating power IV

T_S = Temperature of the test section

T_O = Temperature of the chamber wall

With the equipment used, the electrical currents and voltages could be measured to within 0.2 percent, the test section radiating area could be measured to within 0.25 percent, and temperatures could be measured to within 0.5 percent with thermoocuples or 0.4 percent with an optical pyrometer. Since errors from other sources were negligible, the maximum errors in the reported total hemispherical emittance values determined by this method are ±2.7 percent when temperatures were measured by thermocouples and ±2.3 percent when temperatures were measured by an optical pyrometer.

II. COATED PLATINUM-20 PERCENT RHODIUM SUBSTRATES

A. INTRODUCTION

Three materials were evaluated as coatings on platinum-20 percent rhodium. These were cerium oxide, iron titanate, and hafnium oxide. The cerium oxide and iron titanate coatings were applied by plasma spraying techniques at a substrate temperature within 50°F of 1000°F, and a higher temperature was used for applying chemically vapor deposited hafnium oxide. The high application temperatures were required to simulate the expected coating conditions for the intended application in the case of the plasma-sprayed coatings. A number of specimens were prepared with each type of coating material.

Two coated specimens of each type plus one uncoated specimen were subjected to 200-hour vacuum emittance testing at 2100°F. Subsequently, one specimen of each type was heated in 50°F increments to 2800°F with emittance readings being take at each point.

Three specimens of each type plus one uncoated specimen were aged in still air at atmospheric pressure at 1100°F for 1597 hours. The specimens were heated in an electric oven and were housed in a stainless-steel liner during aging. The air aging was intended to simulate the environment to which the assembly will be exposed after being coated. Following aging, two specimens of each type were tested in vacuum for four hours at 2100°F for emittance properties and a third specimen of each type was tested in vacuum for emittance between 2100°F and 2800°F in 25°F increments.

Based on the data obtained from these tests, the cerium-oxide coating was recommended to NASA for 2000 hours of endurance testing. With the approval of NASA, two specimens coated with cerium oxide and an uncoated specimen which had been aged in air at 1100°F for over 1500 hours were subjected to vacuum emittance testing for 2000 hours at 2100°F. One of these and the uncoated specimen were then heated to 2800°F in 25°F increments with emittance readings being taken at each point.

B. ANALYSIS OF PLATINUM-20 PERCENT RHODIUM

The platinum-20 percent rhodium was obtained from the J. Bishop and Company Platinum Works in the form of seamless tubes. Nominally, the tubes were nine inches in length with an outside diameter of 0.25 inch and a 0.010-inch wall thickness. The material was received in the cold-worked condition, as shown in Figure 1, and was subsequently annealed by Pratt & Whitney Aircraft for one-half hour at 2000°F in argon. The microstructure of the annealed material is shown in Figure 2. Annealing reduced the hardness from Rc 29 to Rb 60.

Emission spectrographic analysis of the material detected the presence of the following impurities: 200 ppm iron, 80 ppm nickel, 50 ppm chromium, and 60 ppm aluminum.



Mag: 500X

Figure 1 Photomicrograph of Platinum-20 Percent Rhodium Tube Showing Cold-Worked Condition M-52075



Mag: 500X

Figure 2 Photomicrograph of Platinum-20 Percent Rhodium Tube Showing Recrystallized Microstructure Produced by Annealing at 2000°F for One-Half Hour M-52074

C. COATING SELECTION AND SPECIMEN PREPARATION

Two of the coating materials, iron titanate and hafnium oxide, were selected prior to initiation of the contract. The iron titanate was to be applied by plasma spraying, and the hafnium oxide was to be applied by chemical vapor deposition. The third coating material was to be chosen on the basis of high temperature capabilities and short-term emittance testing.

The iron titanate was selected on the basis of the high emittance demonstrated by this material during long-term emittance tests reported in PWA-2206 and NASA CR-1278 (PWA-3278). The hafnium oxide was selected on the basis of chemical stability, high temperature capability, and reported acceptable emittance characteristics demonstrated during short-term emittance tests. Short-term emittance testing performed under this contract indicated that cerium oxide possessed the desired high temperature capabilities and an acceptable emittance level, and, therefore, this material was selected for testing on platinum-20 percent rhodium substrates.

Prior to plasma spraying, all platinum-20 percent rhodium tubes were degreased in a clean trichlorethylene vapor degreasing bath at 189°F and then grit blasted to enhance adherence of the coating. Number 60 alumina grit was used for grit blasting, and a snugly fitting rod was inserted in each tube during grit blasting to prevent deformation of the soft platinum-20 percent rhodium tube. The grit-blasting parameters are presented in the appendix. Following grit blasting, the roughness of the specimen surface was measured with a Hewlett-Packard Surfanalyzer 150 System using a stylus pressure of 50 milligrams. The surfaces were generally found to have a roughness height of about 120 microinches RMS. The accuracy of the results were verified by retracing several traverses. Identical results were obtained, indicating that the low stylus pressue used did not smooth the surface during measurement.

Because of the requirement for plasma spraying within 50°F of 1000°F, a special mandrel with a temperature monitoring system was designed and built. The mandrel, shown in Figure 3, houses six Chromel-Alumel thermocouples. The thermocouple wires are protected by 0.020-inch diameter stainless-steel sheaths which lie in axial grooves in the mandrel. Stainless-steel ribbons tack welded across the sheaths secure the sheaths in the grooves, as shown in Figure 4. The thermocouple junctions were located at intervals spaced one and one half to two inches apart.

The thermocouple leads were terminated in a slip ring assembly which was designed to minimize errors introduced by thermal gradients in the mandrel. Initially, the slip-ring area was plasma sprayed with a coating of aluminum oxide. Next, nine equally spaced strips of nickel were plasma sprayed over the alumina layer parallel to the mandrel axis. These were covered with a second layer of aluminum oxide. Circumferential masking was then applied in preparation for spraying seven circumferential nickel rings. Before the nickel was applied, however, a precision grit blaster was used to produce gaps in the aluminum-oxide layer to permit the circumferential rings to contact selected axial strips.

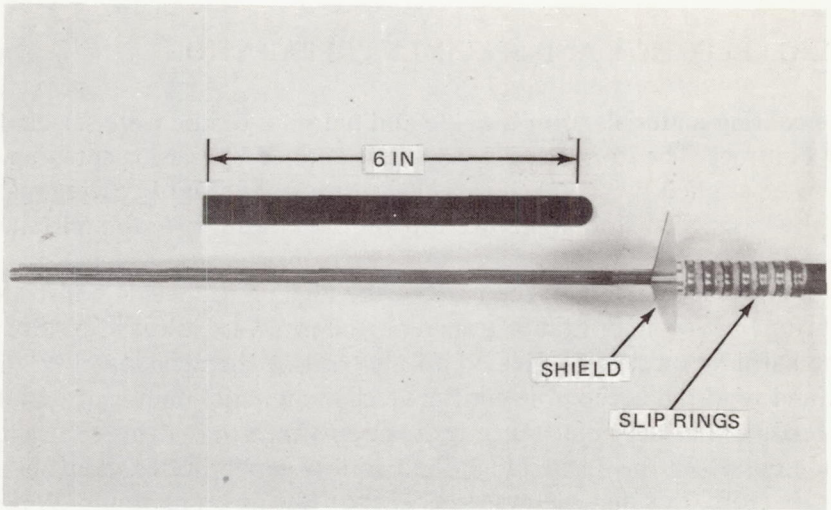


Figure 3 Mandrel Used for Plasma Spraying M-52057

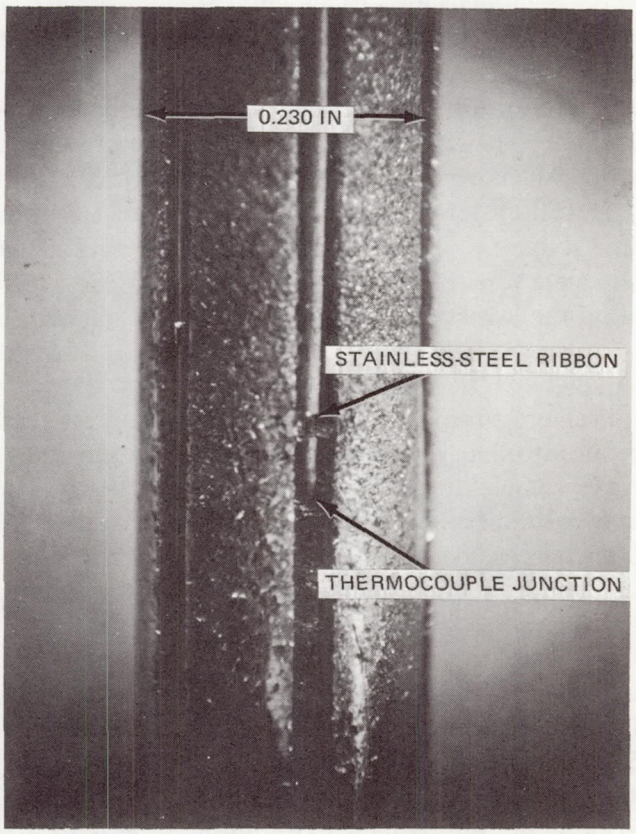
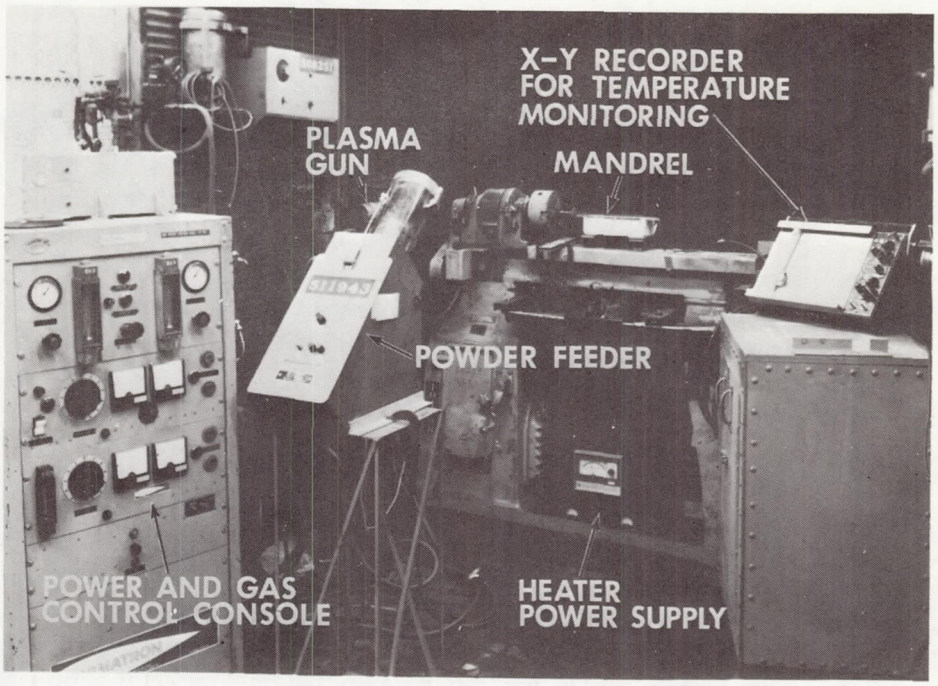


Figure 4 Closeup View of Thermocouple Junction on Mandrel Used for Plasma Spraying M-52056

The ring closest to the specimen support section of the mandrel was connected to every third axial strip, and each of the remaining rings was connected to one of the remaining axial strips. With this arrangement, one of the strips connected to the first, common ring was adjacent to each of the strips connected to the remaining six rings, which facilitated connection of the thermocouple wires. The brushes consisted of simple loops of Chromel or Alumel wire held against the rings by springs. Shallow grooves were machined in the rings to guide the brushes.

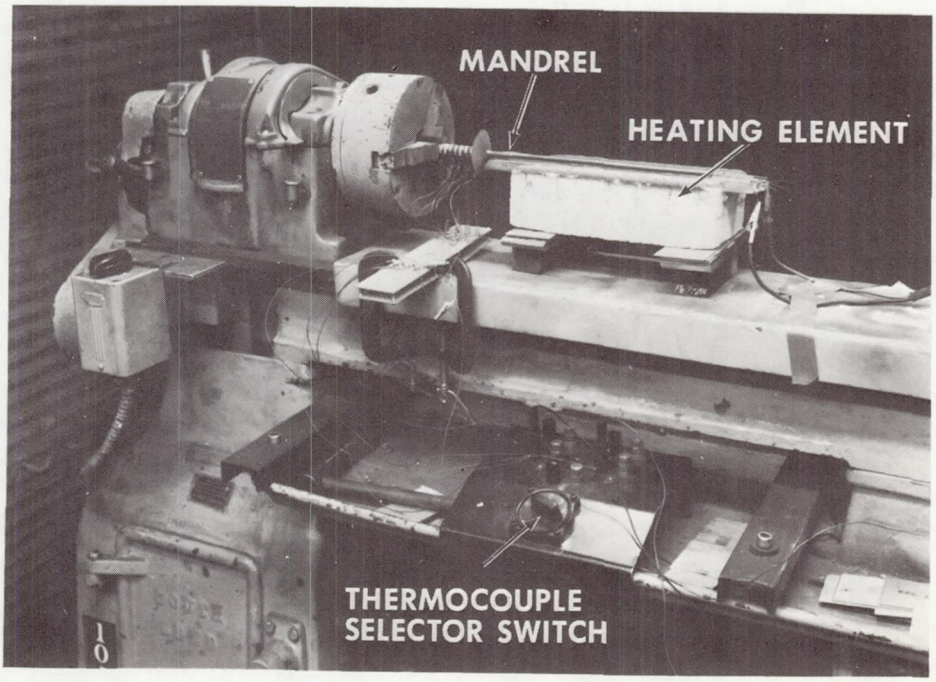
By connecting the Chromel leads from the thermocouples to the common ring and the Alumel leads to the remaining rings, the errors associated with the axial thermal gradient in the slip ring area were minimized. In the Chromel lead circuit, the slip ring circuit introduces one Chromel-nickel junction at the connection between the thermocouples and the slip ring assembly and one nickel-Chromel junction at the contact point between the slip rings and the brushes. Since the emf produced by these two junctions will be appreciable if the temperature difference is not small, connecting all of the Chromel leads to the first ring which is very close to the junctions of the thermocouples and the axial strip, results in a negligible temperature difference. The emf produced by Alumel-nickel junctions at different temperatures is extremely small. For the thermal gradient present in the slip-ring area of the mandrel, these junctions introduce negligible error.

During plasma spraying, the platinum-20 percent rhodium tube was slipped over the instrumented mandrel, and then the assembly was supported in the chuck of a lathe and rotated between 50 and 74 rpm. A heating element was used to bring the specimen up to 950°F, after which plasma spraying was initiated. The plasma spray parameters are tabulated in the appendix, and the spraying equipment is shown in Figures 5 and 6. The outputs of one thermocouple near the end of the specimen and one near the center of the specimen were monitored on an X-Y recorder during spraying. Typical temperature plots are shown in Figures 7 and 8. The temperature of the specimen increased during the application of both iron titanate and ceria. When iron titanate was being applied, several passes of the plasma gun could generally be completed before the specimen reached the upper temperature limit of 1050°F. When 1050°F was reached, it was necessary to interrupt the spraying while the specimen cooled to 950°F, after which the plasma spraying process was re-initiated. When ceria was being applied, however, only one pass could be completed before the upper temperature limit was reached. This may have been caused by reduction of the ceria in the plasma, which contained 10 percent hydrogen to raise the enthalpy of the flame, followed by reoxidation after the coating was applied. Alternatively, the short time required for the specimen to reach 1050°F could have been caused by the hotter flame produced with the hydrogen. Immediately after application, the coating was black. Within a few seconds, the color changed to a dark yellow, and after the specimen had cooled, the color was light cream. Color changes were also noted following emittance testing of cerium-oxide-coated specimens.



Mag: Approx. 0.05X

Figure 5 Equipment Used for Plasma Spraying at Controlled Temperature M-52132



Mag: Approx. 0.12X

Figure 6 Plasma Spray Mandrel Installed in Lathe and Ready for Spraying M-52131

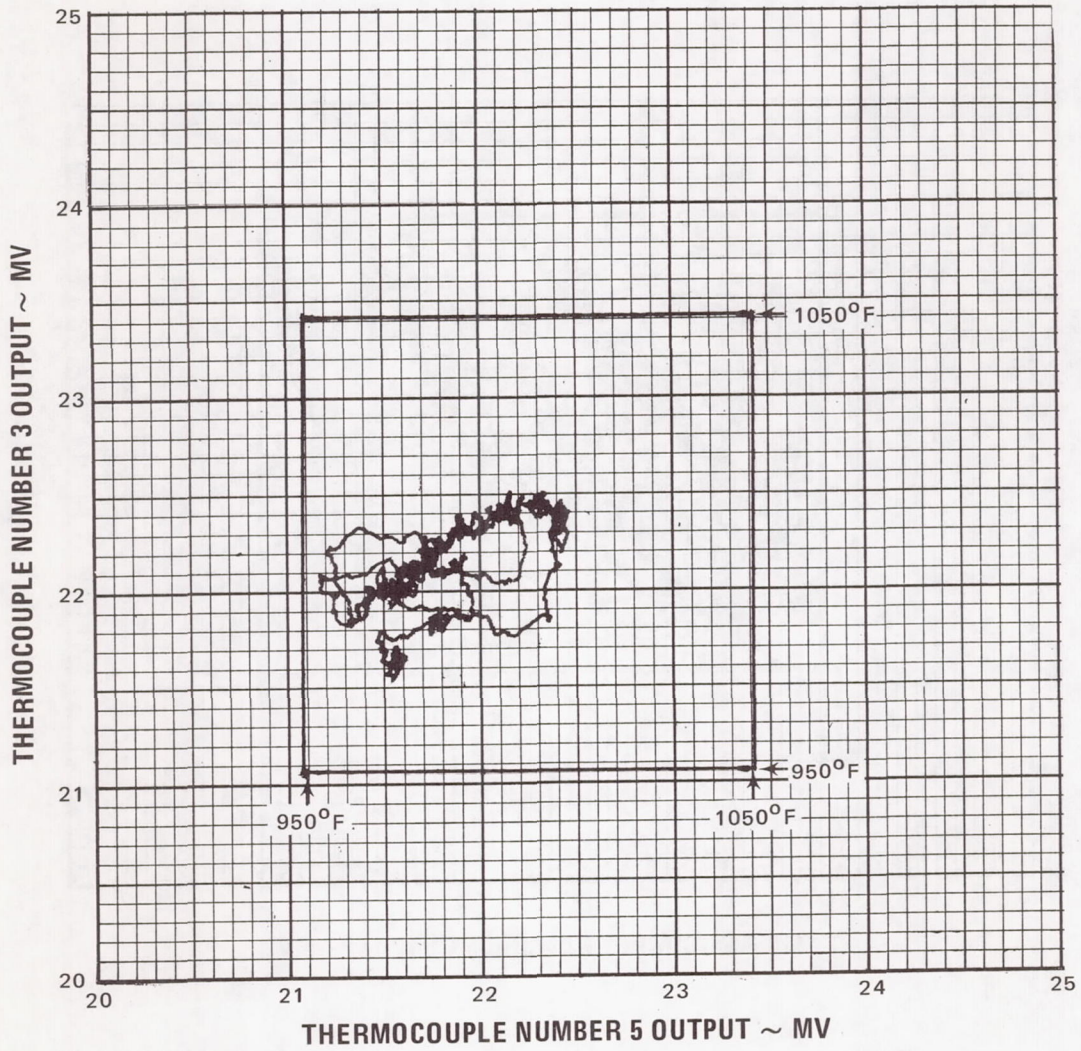


Figure 7 Typical Temperature Excursions of Platinum-20 Percent Rhodium Tube During Plasma Spraying With Iron Titanate at 1000°F

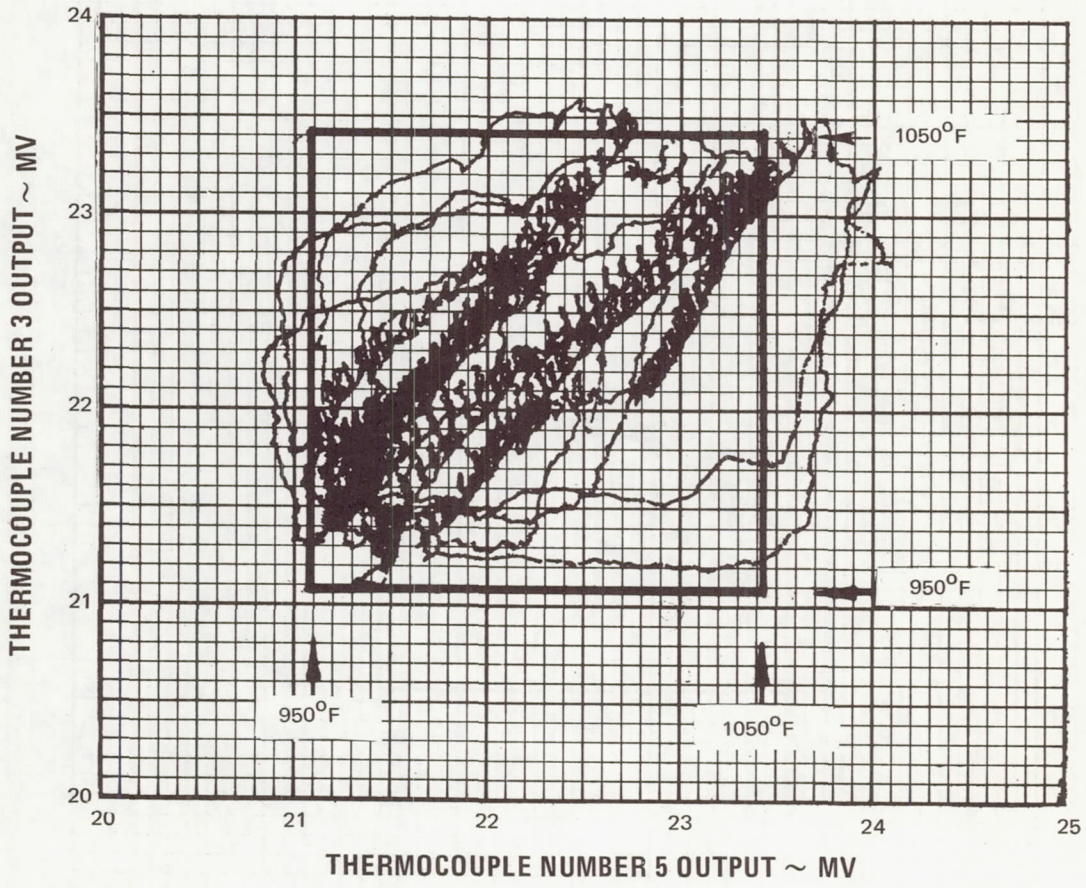


Figure 8 Typical Temperature Excursions of Platinum-20 Percent Rhodium Tube During Plasma Spraying With Ceria at 1000°F M-52087

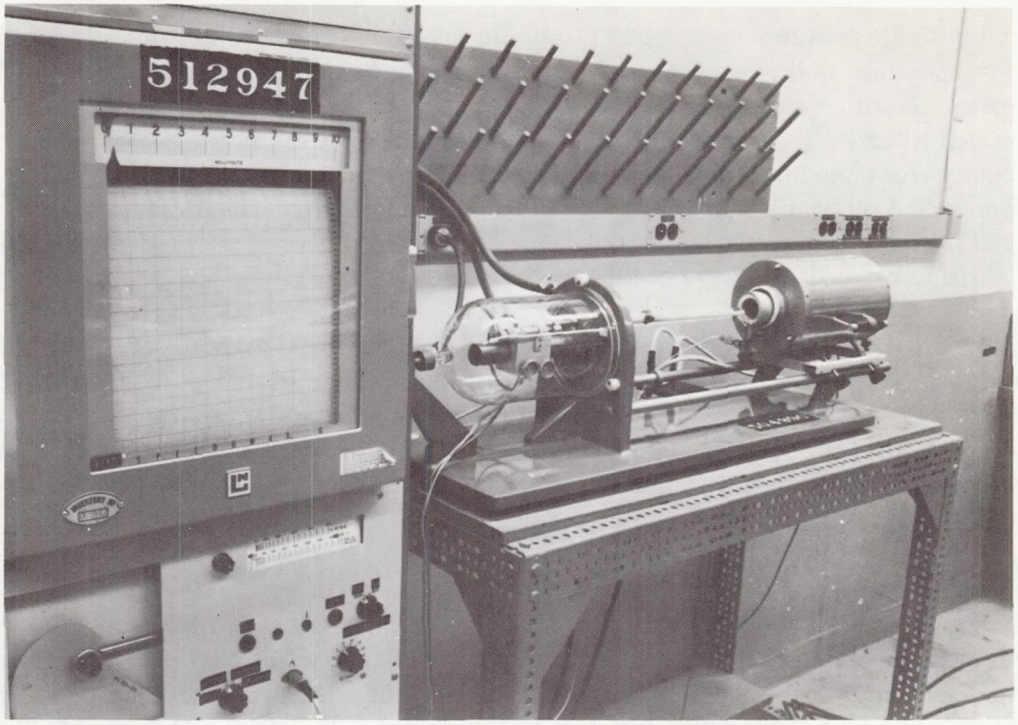
Hafnium-oxide coatings were applied to platinum-20 percent rhodium tubes by chemical vapor deposition at the San Fernando Laboratories[1]. As reported by San Fernando Laboratories, the tubes were initially cleaned in acetone. They were then heated in argon and hydrogen to 1850°F and coated for a one-hour-and-forty-five-minute period. Three of the specimens contained unbonded material after plating which required stripping. This was accomplished by heating the specimens in air at 1112°F, after which the specimens were dipped in sodium carbonate. The parts were then replated, using the original procedure, and satisfactory coatings were obtained.

In addition to the chemically vapor deposited hafnia coatings, two other types of hafnia coatings were tested on platinum-20 percent rhodium substrates. One of these was hafnia stabilized with 5 weight percent calcia, and the other was hafnia stabilized with 5 weight percent yttria. Both of these coatings were applied by the plasma spray process at ambient temperature. No attempt was made to plasma spray this material within 50°F of 1000°F. The plasma spraying parameters used are listed in the appendix.

As a part of the program to evaluate the quality of the coatings, the thermal expansion properties of each coating material were determined. Specimens of each of the coating materials were prepared by plasma spraying thick self-supporting coatings of each material over a short length of AISI-310 stainless steel strip. The lengths ranged from one-half to one and one-half inches. The metal strip was degreased but only lightly grit blasted before the coating was applied so that the coating could be removed easily in a single piece after spraying. The specimens were then installed in a Linseis dilatometer, and the linear thermal expansion was measured over a range of temperatures. A sample of platinum-20 percent rhodium was used as a standard. The equipment used is shown in Figure 9. The results of these measurements are shown in Figure 10 together with published values for some additional materials.

Generally, ceramic coatings applied to metal substrates are selected such that the coatings are in slight compression at the temperatures at which they are used. This practice may not provide the best results for high-emittance coatings, however, since failure of the coating under compression results in separation of the coating and possibly spalling from the substrate, which causes a drop in the power radiated from the specimen. If the coating were in slight tension, however, mechanical failure would result in crazing with no separation between the coating and the substrate, resulting in a small if not negligible effect on the emittance.

[1]San Fernando Laboratories, 10258 Norris Street, Pacoima, California 91331



Mag: Approx 0.15X

Figure 9 Dilatometer With Recorder and Controller Used to Measure Thermal Expansion Characteristics of Coating and Substrate Materials M-52129

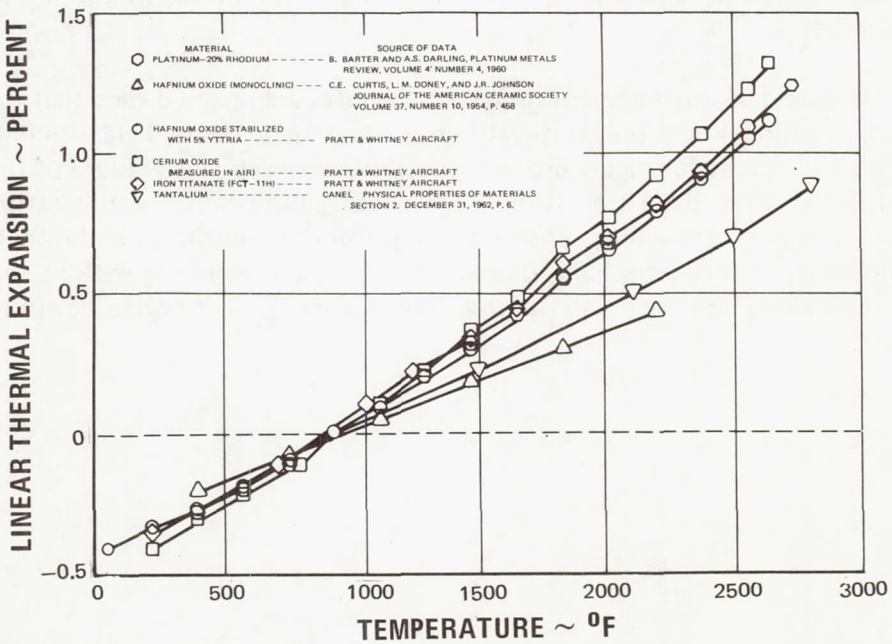


Figure 10 Relative Linear Thermal Expansion of Selected Coating and Substrate Materials M-52086

D. TEST APPARATUS AND PROCEDURES

1. Short-Term Endurance Emittance Test Chamber

The four-hour emittance tests conducted to provide a basis for selecting the coating material to be tested for 2000 hours at 2100°F were performed in the equipment shown in Figures 11 and 12. As shown, the test chamber consisted of a vacuum chamber with support structures for the specimen and instrumentation, an evacuation system, a specimen heating power supply, and temperature measurement instrumentation.

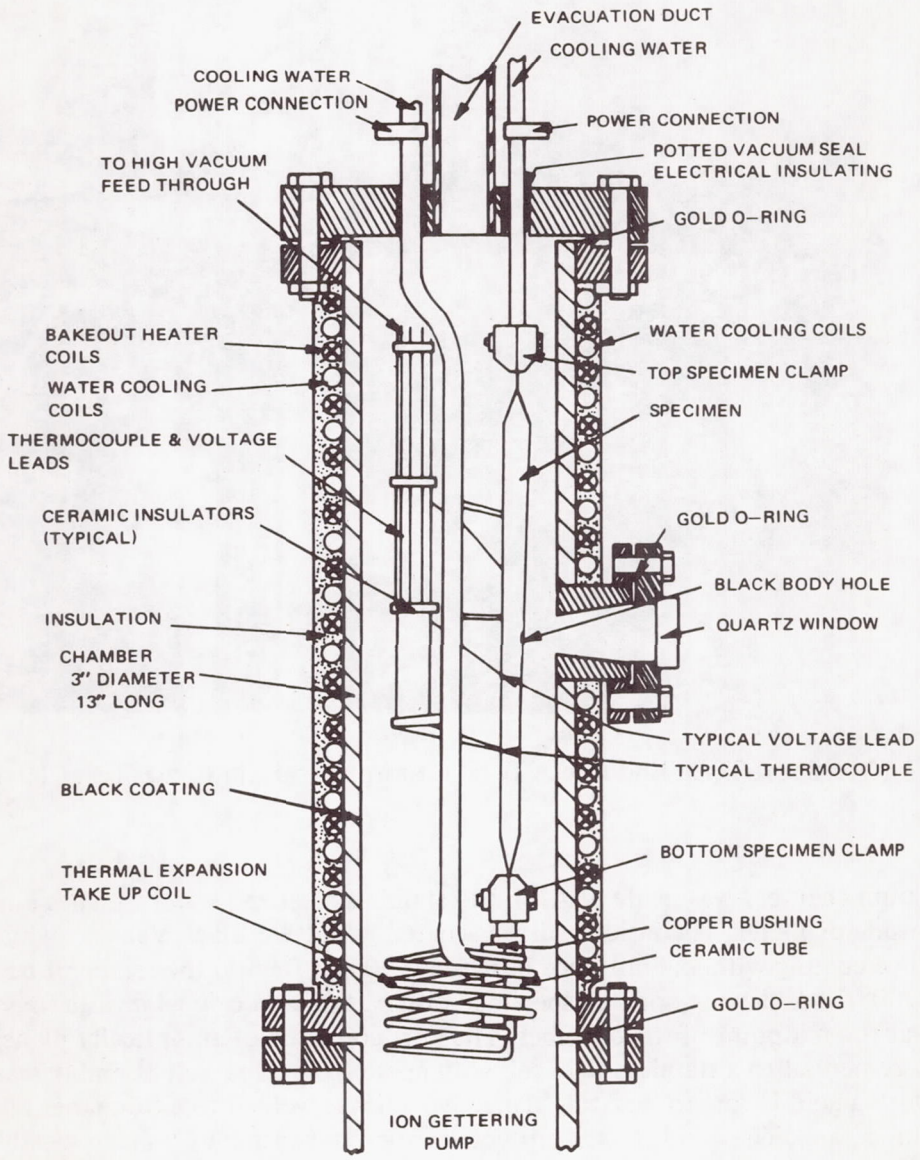


Figure 11 Sketch of Short-Term Endurance Emittance Test Chamber Showing the Relative Location of Specimen and Various Components

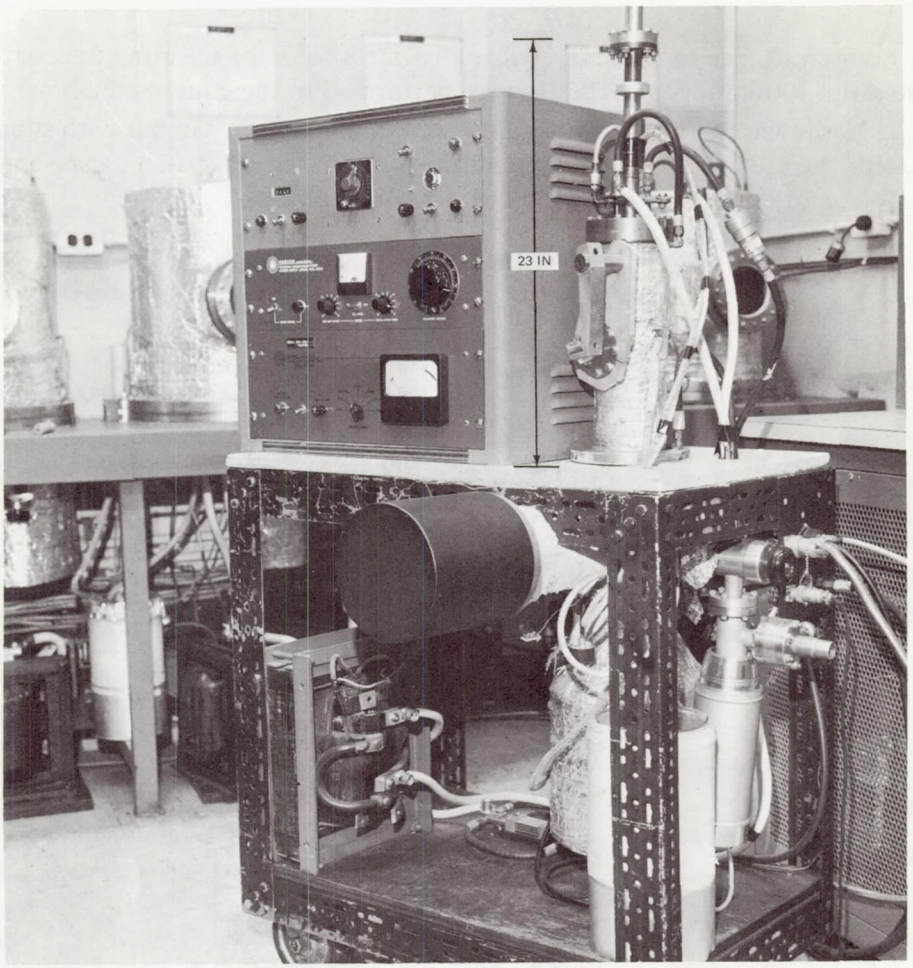


Figure 12 Short-Term Endurance Total Hemispherical Emittance Test Chamber
X-18512

The vacuum chamber was made of AISI-304 stainless steel and was 12 inches long with a 3-inch inside diameter. The inside wall was coated with "3M Black Velvet," which is a low reflectance coating with an emittance between 0.90 and 0.95 in the temperature range from 200 to 700°F. A viewing port for specimen observation and optical measurements was located at the midpoint of the chamber. The port consisted of an optically plane quartz window cemented to a stainless-steel cell with epoxy resin. The cell assembly was bolted and sealed with a gold O-ring to a mating flange, which was welded to a tubular extension from the chamber wall. The window was protected from condensate by a magnetically controlled rolling-disk shutter installed in a slot between the cell and the flange. The chamber was wrapped with 3/16-inch diameter copper tubing for water cooling the walls, and a heating element was wound over the cooling coil to bake out the chamber during initial evacuation.

The evacuation system consisted of a 40-liter-per-second ion-gettering pump and a titanium sublimation pump backed by a mechanical roughing pump and a liquid-nitrogen cold trap. The chamber pressure was measured by a Bayard-Albert type ionization gage and by measuring the ion-gettering pump current and determining the pressure from calibration curves.

The power supply for heating the specimens consisted of a multitap step-down power transformer, the primary of which was controlled by a variable autotransformer. Power measurements were made by measruing the voltage drop across the specimen test section and across a current shunt by means of an AC-DC differential voltmeter. Thermocouple outputs for temperature measurement were measured with a slide-wire millivolt potentiometer used in conjunction with an ice-bath reference junction.

2. Air-Aging Equipment

The specimens were aged in air in the general-prupose, box-type bench furnaces shown in Figure 13. During aging, the specimens were supported in the stainless-steel specimen holder shown in Figure 14.

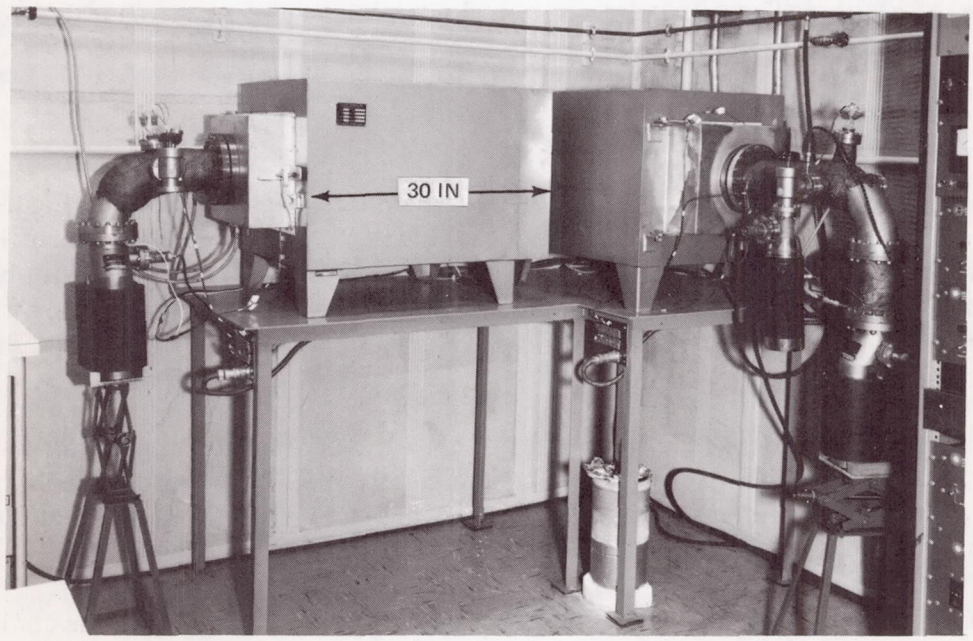


Figure 13 Furnaces Used for Aging Specimens in Air

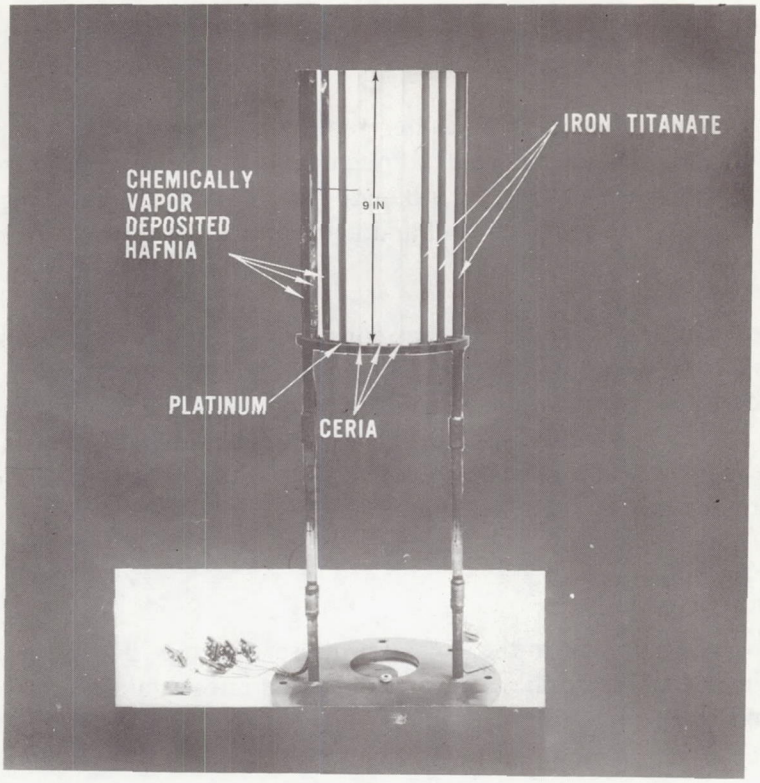


Figure 14 Specimens Supported in Specimen Holder After Being Aged at 1100°F for 1597 Hours M-52066

3. Long-Term Emittance Test Apparatus

The test equipment used for the 200- and 2000-hour emittance tests is shown in Figure 15. The vacuum chambers for these units are 20 inches high and have inside diameters of 15 1/2 inches. These chambers are fabricated from AISI-304 stainless steel and coated with black paint. Each chamber has a 5.4-inch diameter window for observation of the specimen and for radiation measurements. The windows are protected by magnetically controlled shutters when not in use.

The evacuation system for each unit consisted of a 40-liter-per-second ion gettering pump operated in conjunction with a mechanical vacuum pump with a liquid-nitrogen cold trap. As for the short-term units, chamber pressures were measured with a Bayard-Alpert type ionization gage and by measuring the ion-gettering pump current.

All instrumentation readout equipment and chamber controls were located in the control console shown in Figure 16. A manually operated slide-wire potentiometer was used to provide highly accurate temperature data for emittance calculation. Voltage and current measurements were made with a precision AC differential voltmeter.

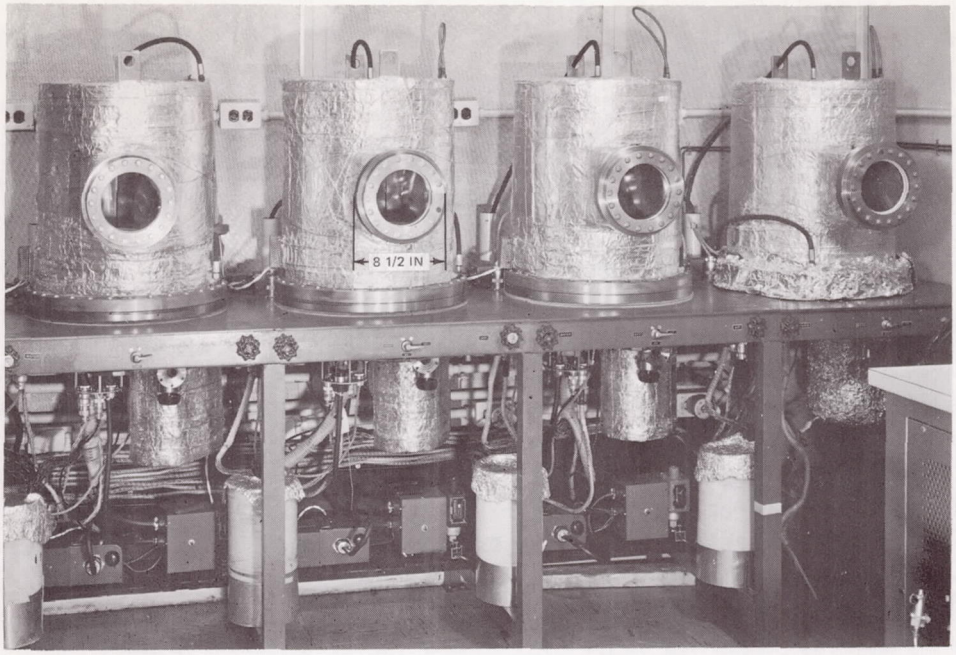


Figure 15 Long-Term Endurance Total Hemispherical Emittance Test Chambers
XP-23123

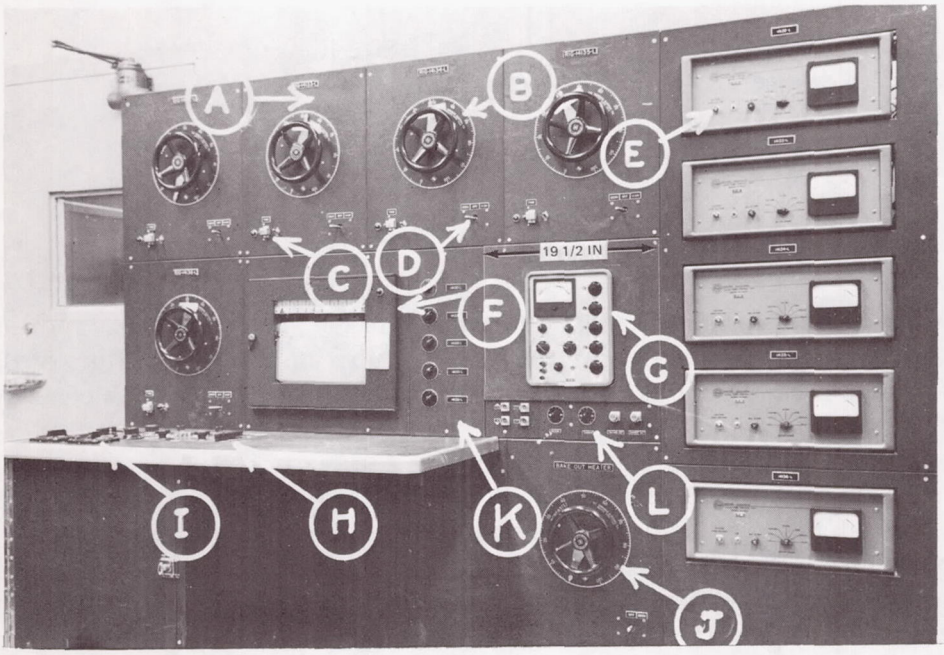


Figure 16 Control and Instrumentation Console for Endurance Test Chambers

A. Test Chamber Control Panel
B. Test Chamber Voltage Control
C. Cycle Timer
D. Voltage Switch
E. Vacuum Pump Power Supply
F. Multipoint Recorder
G. AC-DC Differential Voltmeter
H. Potentiometer
I. Thermocouple Selector Switch
J. Bake-Out Heater Control
K. Thermocouple Mode Switch Panel
L. Specimen I and V Selection Panel

X-14520

E. TEST RESULTS

1. Cerium Oxide Coating on Platinum-20 Percent Rhodium

a. Material Description

The ceria used for this program was obtained from the Lindsay Rare Earth Division of the American Potash and Chemical Corporation. The material was designated Code 217 ceria, and it was air classified by TRW, Incorporated, to provide a particle size distribution suitable for plasma arc spraying.

X-ray diffraction analysis performed on the as-received material and on the material after plasma spraying indicated that CeO_2 was the only phase present. Emission spectrographic analyses were performed, and the impurities detected are listed in the appendix. The particle size distribution as determined by screen analysis of the as-received material is shown in Table 1.

TABLE 1

PARTICLE SIZE DISTRIBUTION OF CERIA AS RECEIVED

Weight Percent	Size Range (Microns)	(Mesh Size)
2.5	greater than 74	+200
57.8	74 to 44	-200 to +325
39.7	less than 44	-325

The particles possessed an angular form, as shown in Figure 17. The material was applied by plasma arc spraying to the platinum-20 percent rhodium tube, and the temperature of the substrate was maintained to within 80°F of 1000°F. The plasma spraying parameters are listed in the appendix.

Although thermal expansion data were obtained for ceria (CeO_2), there is considerable evidence that the material loses oxygen at high temperatures in vacuum.[1] The loss of oxygen may be expected to affect the thermal expansion characteristics, and, since the measurements were made in air with constantly shifting cerium-oxygen equilibrium conditions, the thermal expansion values shown in Figure 10 may not be representative of the material at equilibrium in vacuum.

[1] P. Kofstad and A.A. Hed, "Defect Structure Model for Nonstoichiometric CeO_2," Journal of the American Ceramic Society, December 1967, pp. 681 - 682.

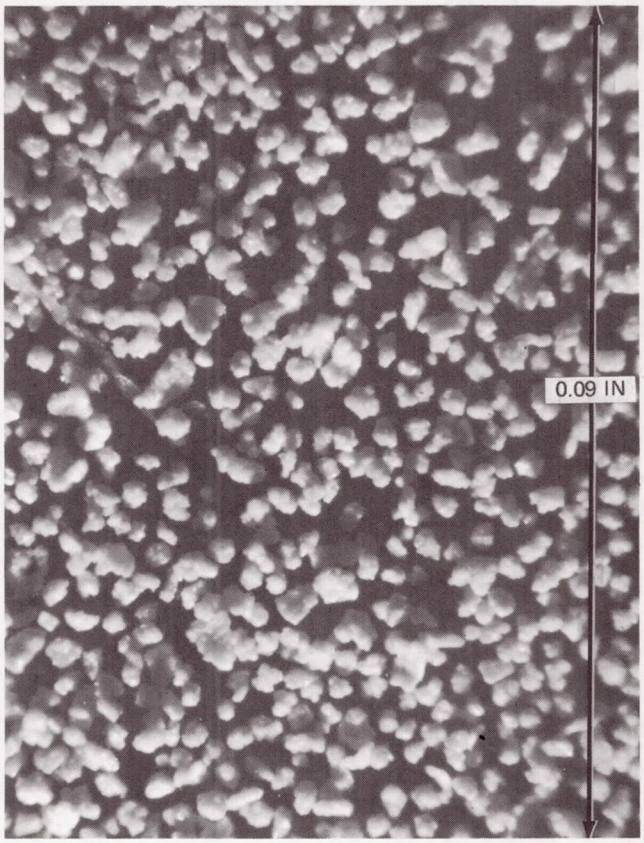


Figure 17 Ceria in As-Received Condition

b. Two-Hundred-Hour Screening Tests

Two platinum-20 percent rhodium specimens coated with ceria were vacuum emittance tested at 2100°F for 200 hours. The test results of the first specimen are shown in Figure 18. The emittance remained nearly constant at 0.82 throughout the test. After 200 hours of testing, the specimen was heated to 2800°F in 50°F increments. During this portion of the test, the emittance ranged from 0.86 to 0.93. When the specimen was subsequently cooled to 2100°F, the emittance was 0.88. After testing, the coating was discontinuous with sections where the substrate was exposed (see Figure 19). The specimen had been a light cream color before being tested, but was black at the completion of the test.

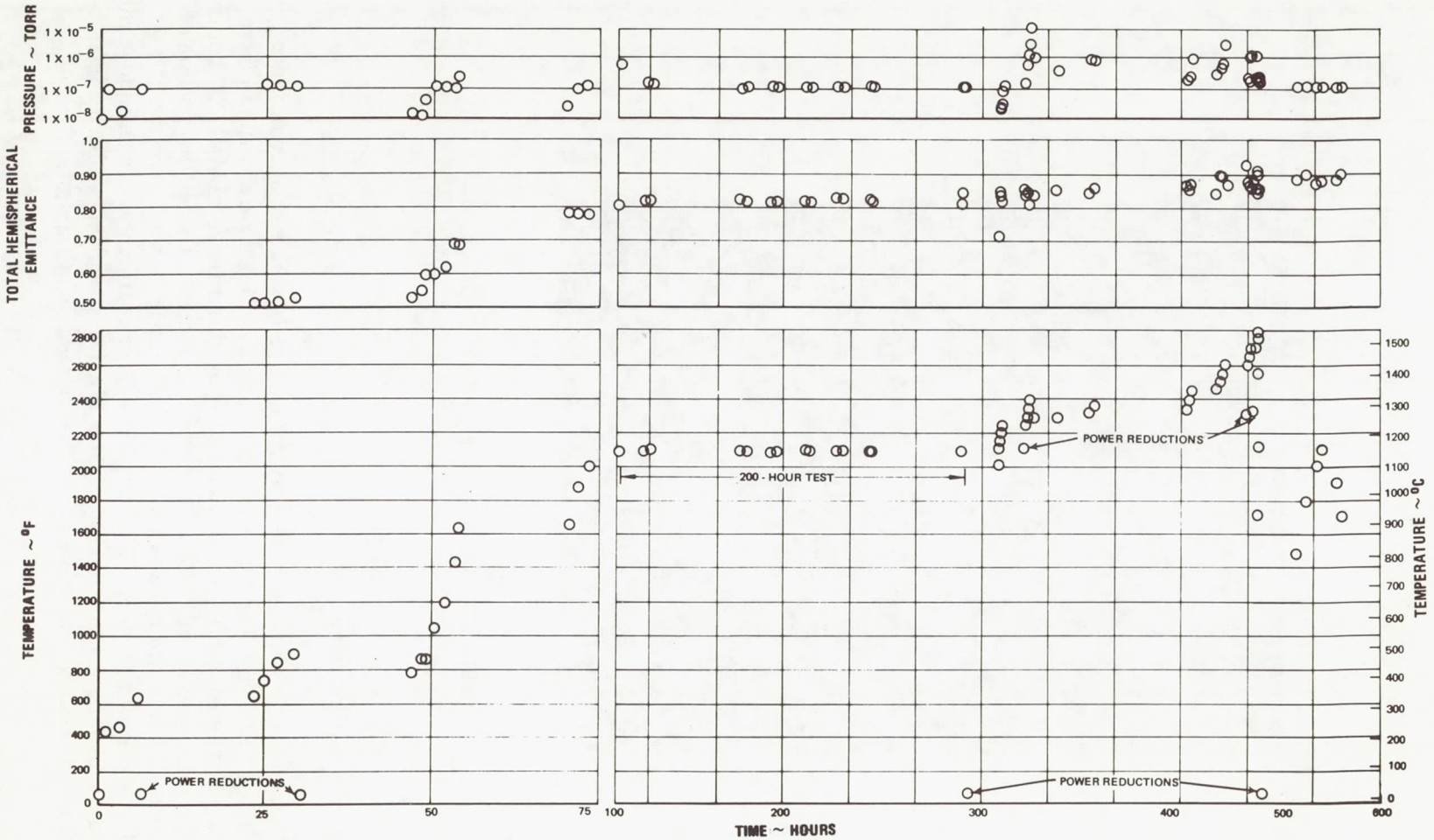


Figure 18 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria

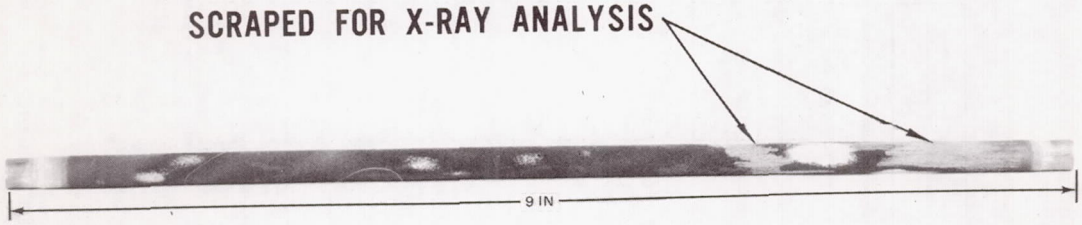


Figure 19 Condition of Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria and Vacuum Emittance Tested at 2100°F and 2800°F M-52072

Two interesting phenomena occurred after the test was completed. After the specimen had cooled, air was admitted to the test chamber, and the temperature of the specimen increased from 54°F to 75°F, after which it cooled to the ambient temperature. As noted above, the specimen was black immediately after testing, and no change in color occurred at this time, but when the specimen was re-examined later, the color of the specimen was lighter with some white spots.

The second 200-hour test resulted in slightly higher emittance values, as shown in Figure 20. Initially, the emittance was 0.87, and the emittance level increased during the test, ultimately reaching a value of 0.91. The increase may have resulted from a gradual loss of oxygen from the coating or from an increase in the density of the coating during the test. Inspection of the coating before and after testing indicated that some changes did occur. Before testing, the coating was a light cream color, was relatively hard, and had an acceptable bond to the substrate. After testing, the coating was black, harder than before testing, and was more strongly bonded to the substrate.

The behavior of this specimen when air was admitted to the test chamber was similar to that for the first specimen. The specimen temperature increased from 64°F to 81°F, after which it returned to the ambient temprature. No change in color occurred at this time, but when the specimen was inspected eight days later, it was found to have a lighter color.

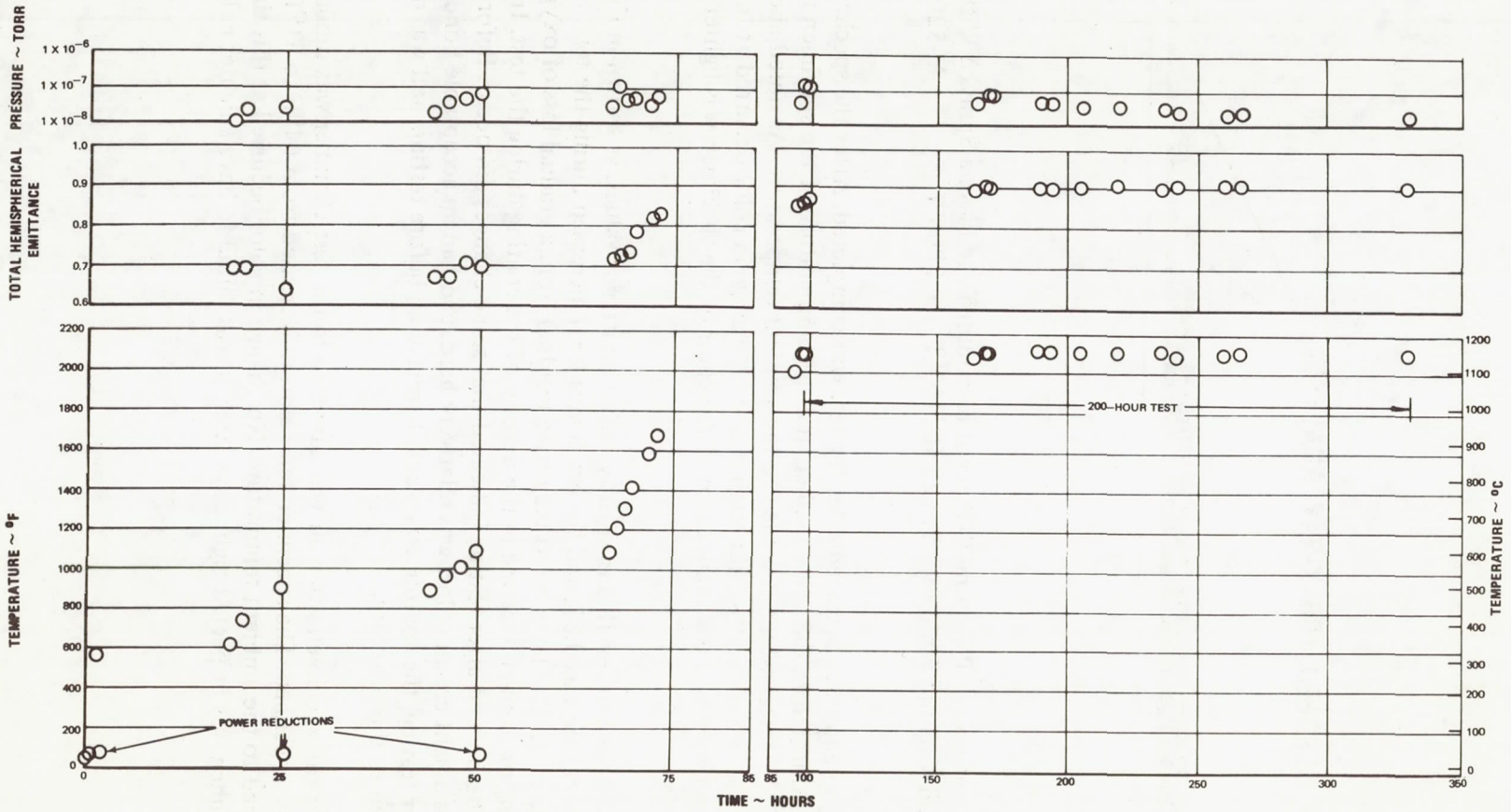


Figure 20 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria

c. Air-Aged Specimens

Three ceria-coated platinum-20 percent rhodium specimens were aged in air at 1100°F for 1597 hours. Vacuum emittance testing of the first of these for four hours resulted in an emittance of 0.90 at 2100°F, as shown in Figure 21. An attempt was then made to heat the specimen to 2800°F in 25°F increments. During initial heating, the emittance increased to 0.91 at a temperature of 2450°F. At this point, however, the substrate failed, apparently as a result of localized overheating in an area where the coating had been lost. The condition of the specimen at the end of the test is shown in Figure 22. Spectrographic analysis showed no cerium in the substrate in the vicinity of the melted area. In addition, the thickness of the coating decreased smoothly from the unaffected area to the melted area, indicating that spalling probably had not occurred.

The second ceria-coated specimen which had been aged similarly to the first was subjected to a four-hour vacuum emittance test at 2100°F. During this period, the emittance was 0.86.

d. Two-Thousand-Hour Emittance Tests

In view of the test results obtained up to this point with the cerium oxide coated specimens, which included results from the 200-hour vacuum emittance tests, four-hour vacuum emittance tests following aging in air at 1100°F for 1597 hours, and attempts to heat the specimens in vacuum to 2800°F, it was decided to recommend to NASA that cerium-oxide coated platinum-20 percent rhodium specimens be tested in vacuum for 2000 hours between 2100°F and 2800°F. With approval of NASA, the second specimen which had been aged in air and subjected to vacuum emittance testing for four hours was endurance tested in vacuum for 2000 hours at 2100°F, and the results are shown in Figure 23. The emittance increased steadily during the 2000-hour period, with an emittance of 0.91 being reached by the end of the test.

The third ceria-coated specimen aged in air was subjected to similar vacuum emittance testing. The emittance of this specimen remained constant at about 0.93 throughout the 2000-hour test at 2100°F, as shown in Figure 24. Subsequently, an attempt was made to increase the temperature to 2800°F in 25°F increments. However, when the temperature reached 2450°F, the emittance dropped to 0.85, and dark areas appeared on the surface of the specimen. The test was terminated, and a portion of the coating from an area which appeared dark during testing was examined. The coating separated from the substrate, leaving no residue, indicating that the bond had failed. The thickness of the chip was found to be 0.003 inch, whereas the original coating had been 0.005 inch thick, indicating that either considerable sintering or loss of the coating material had occurred.

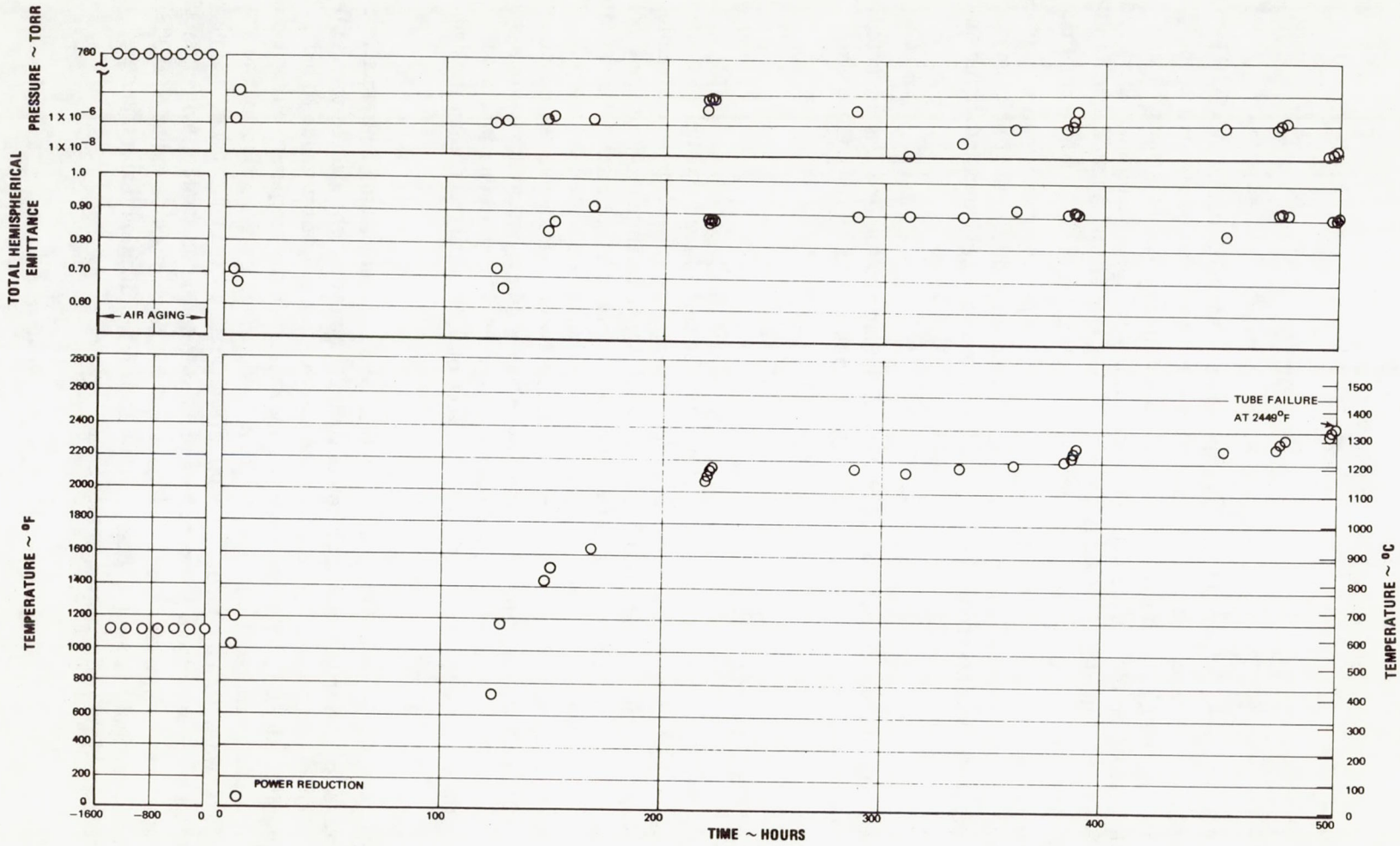


Figure 21 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria and Aged in Air at 1100°F for 1597 Hours

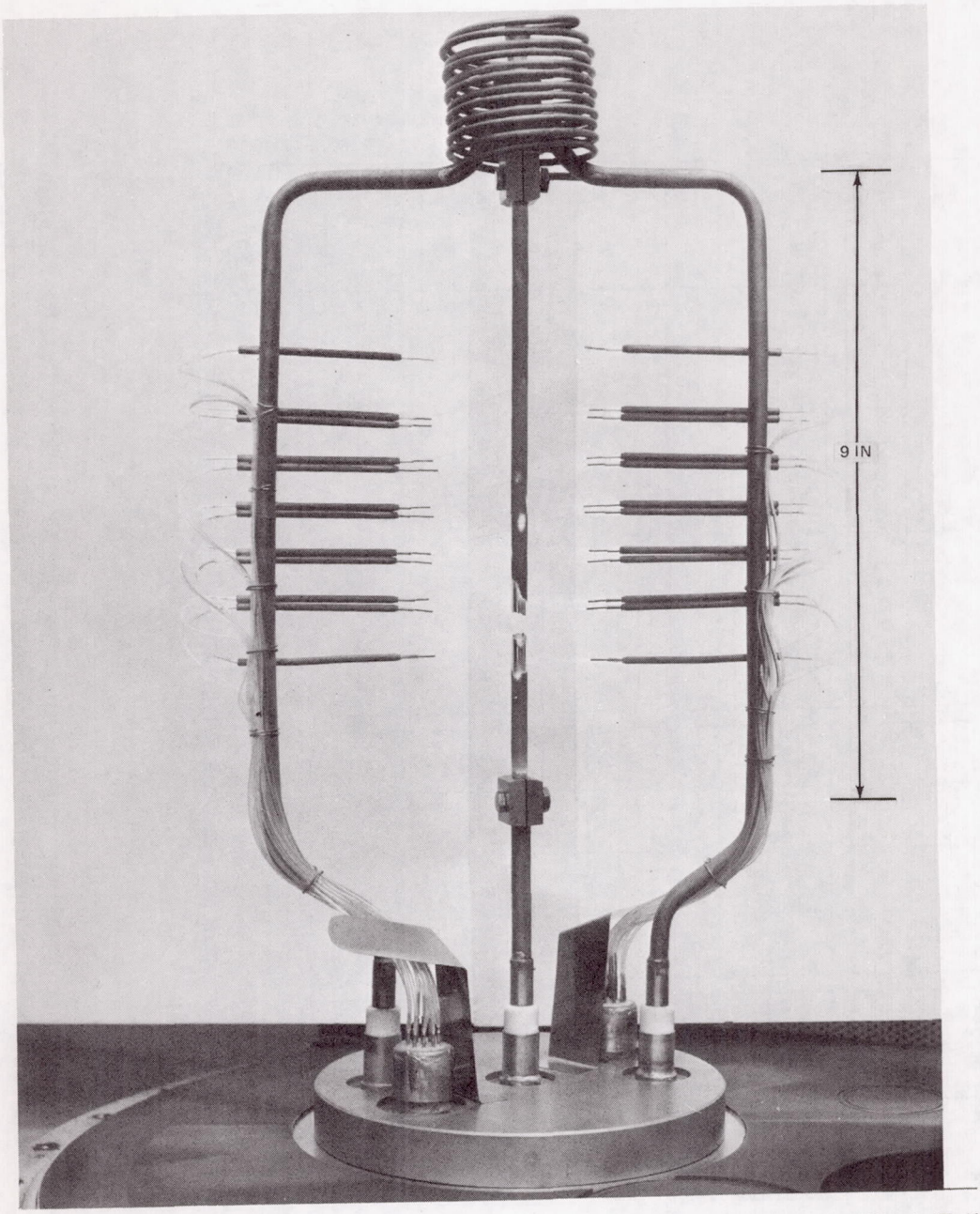


Figure 22 Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria Which Failed During Heating at 2450°F Following Aging in Air at 1100°F for 1597 Hours and Vacuum Emittance Testing for 200 Hours at 2100°F X-29271

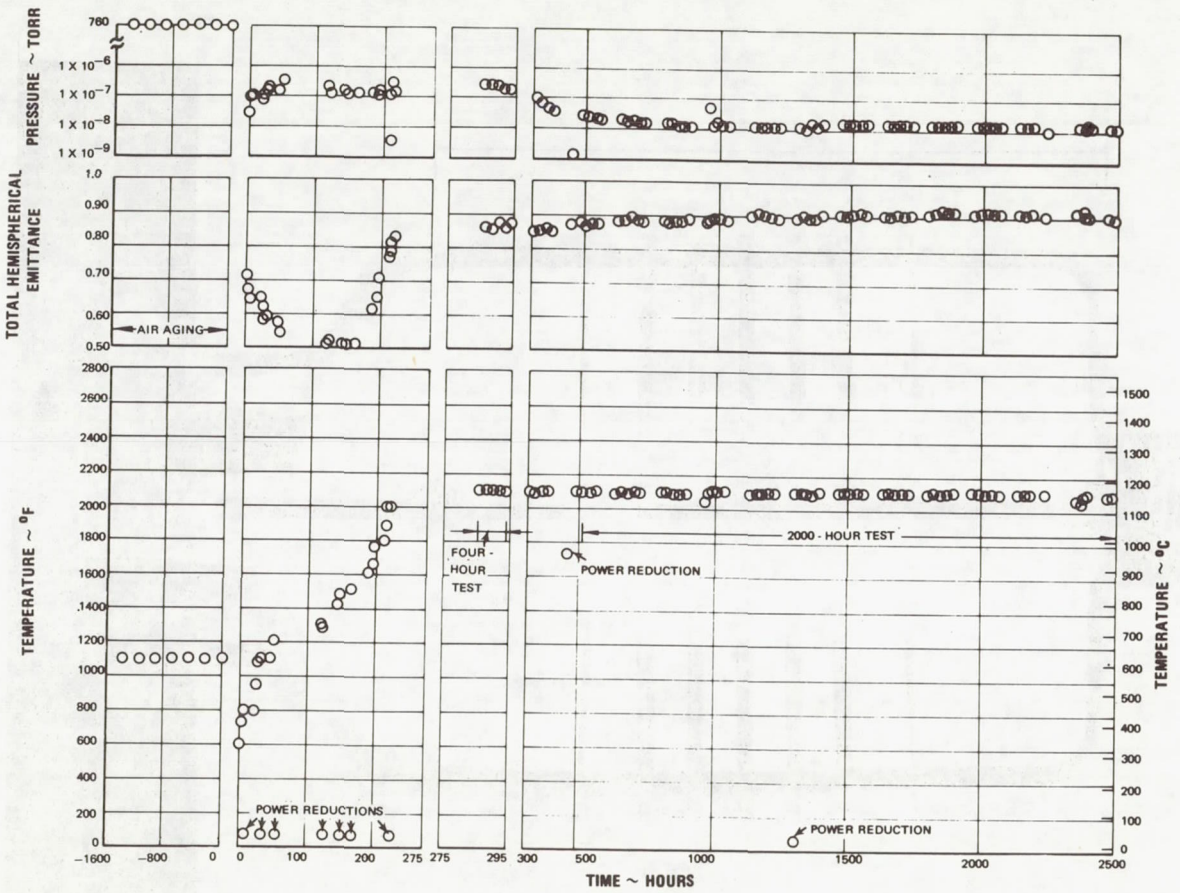


Figure 23 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria and Aged in Air at 1100°F for 1597 Hours

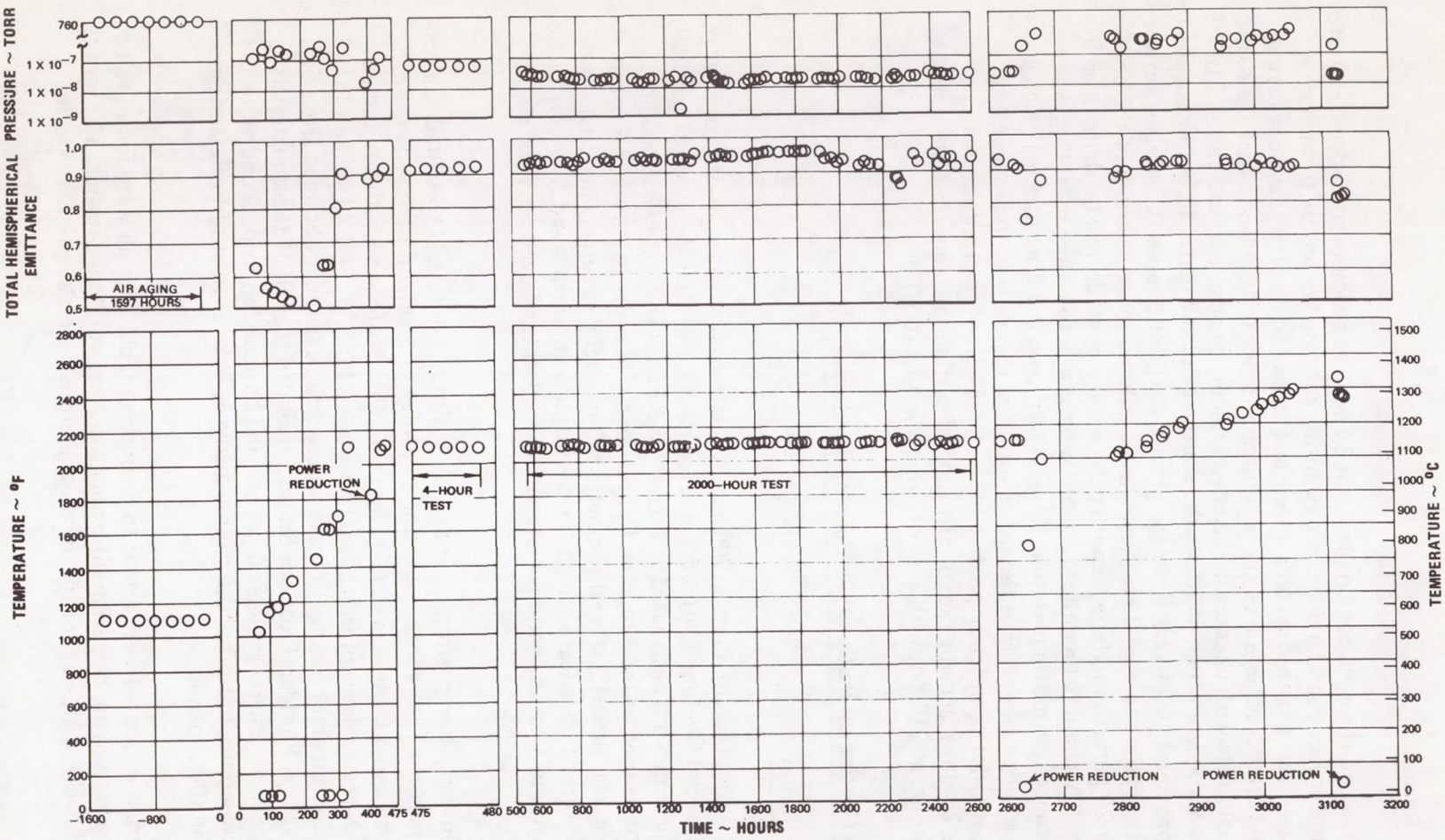


Figure 24 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Ceria and Aged in Air at 1100°F for 1597 Hours

e. Discussion of Results

The testing performed on the ceria-coated platinum-20 percent rhodium specimens indicates that this material undergoes considerable changes during extended exposure to vacuum at elevated temperatures. The changes in color during and immediately after plasma spraying as well as during and after completion of the vacuum emittance tests indicate that the oxide form of this material shifts with changes in the environment. Exposure to vacuum at 2100°F may result in a loss of oxygen which increases the emittance of the material, but increasing the temperature to approximately 2400°F after the previous exposure raises the stresses between the coating and the substrate to a level greater than the adhesive bond strength of the coating to the platinum-20 percent rhodium, resulting in coating separation and a sharp drop in the radiated power. This material requires further investigation to ensure reliability when used as a high-emittance coating on platinum-20 percent rhodium during thermal cycling above 2100°F. In addition, the shift in the oxide equilibrium results in thermal performance which is presently not completely predictable. The results of microprobe analyses presented in Figure 25 show that the rate of diffusion of cerium into the substrate is not detectable after 200 hours at 2100°F with a short excursion to 2400°F.

2. Iron Titanate Coating on Platinum-20 Percent Rhodium

a. Material Description

At the initiation of this program, Pratt & Whitney Aircraft was informed by the supplier of iron titanate, Continental Coatings Corporation, Cleveland, Ohio, that the stock of naturally occurring iron titanate mineral designated as FCT-11 and FCT-11SP was exhausted and, therefore, could not be used in this program. Consequently, in order to establish a continuing source of acceptable iron titanate, several synthetic and naturally occurring materials were investigated. The results of chemical analysis for the major components and X-ray diffraction data obtained before and after the various materials were plasma sprayed are presented in the appendix.

In addition to the investigation performed at Pratt & Whitney Aircraft, NASA funded a concurrent evaluation performed under the direction of Professor Sigmund L. Smith at the University of Arizona under Contracts C26615 and C32376. Professor Smith conducted spectrographic and X-ray analyses of iron titanate materials FCT-11, FCT-11SP, and FCT-11H obtained from the Continental Coatings Corporation as well as samples obtained from E. I. duPont mined at Lawtey, Florida. Professor Smith concluded that all of these materials "originated from the same general geological deposit and have under proper conditions the same chemical, microscopic, and X-ray diffraction analysis." An extract of Professor Smith's report is presented in the appendix.

The synthetic materials evaluated were found to be unacceptable since all were found to be unstable during plasma spraying or during subsequent vacuum emittance testing. The results of the chemical and X-ray analyses for some of these materials are also presented in the appendix.

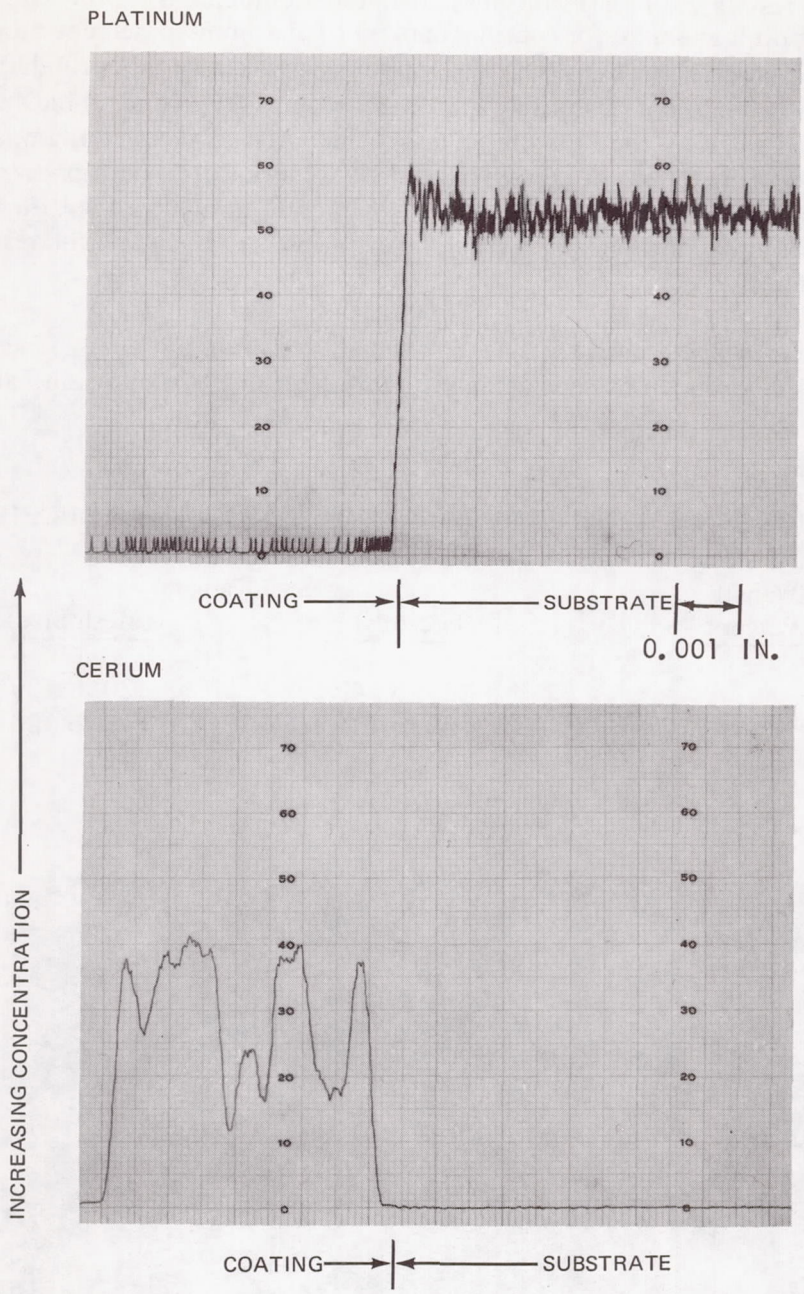


Figure 25 X-Ray Line Scan Intensities for Platinum and Cerium Across Ceria-Coated Platinum-20 Percent Rhodium Tube Aged in Air at 1100°F for 1597 Hours and Vacuum Emittance Tested for 250 Hours at 2100°F

In view of these results, FCT-11H iron titanate material obtained from the Continental Coatings Corporation was used for coatings applied to platinum-20 percent rhodium. The X-ray diffraction analysis for the as-received material showed a very poorly defined diffraction pattern which could not be entirely identified. Rutile (TiO_2) and an indication of psuedobrookite (Fe_2TiO_5) were the only phases evident. After the material was plasma sprayed, however, a clear pattern was obtained, indicating that the major phase present was pseudobrookite (Fe_2TiO_5) and that rutile was also present in smaller quantities. Wet chemical analyses and emission spectrography were also performed, and the results are presented in the appendix.

As received, the iron-titanate particles were rounded, as shown in Figure 26. The particle size distribution was determined by screen analysis, and the results are shown in Table 2.

TABLE 2

PARTICLE SIZE DISTRIBUTION OF IRON TITANATE AS RECEIVED

Weight Percent	Size Range (Microns)	(Mesh Size)
63	125 to 149	120 to 100
37	88 to 125	170 to 120

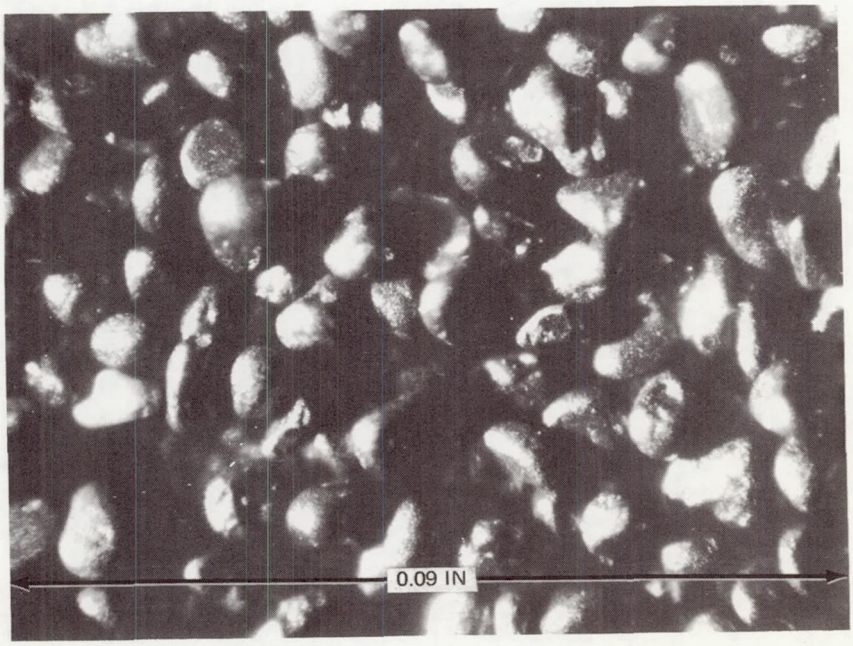


Figure 26 FCT-11H Iron Titanate in As-Received Condition M-52059

Plasma spraying was performed at a temperature within 50°F of 1000°F, and very well bonded coatings were obtained. One reason for the high quality of the coatings is that the coefficient of thermal expansion for iron titanate is very close to that for the platinum-20 percent rhodium. No spalling or separation of the iron titanate from the substrate occurred on any of the specimens. The plasma spray parameters are listed in the appendix.

b. Two-Hundred-Hour Screening Tests

Three platinum-20 percent rhodium tubes coated with iron titanate were tested in vacuum for 200 hours at 2100°F, with the temperature of one of these being increased to 2800°F in 50°F increments. The third specimen was required because of the failure of the substrate of the second specimen.

The emittance test results of the first specimen are shown in Figure 27. The emittance at the beginning of the test was 0.92, and it gradually increased to 0.95 during the 200-hour test period.

The second specimen was tested for 200 hours, but the emittance data appeared to be unreliable, apparently because of a faulty voltage lead. The difficulty was corrected, and a second 200-hour test was run. The results are shown in Figure 28. The emittance was 0.94 throughout the 200-hour test. Following this test, an attempt was made to increase the specimen temperature to 2800°F in 50°F increments. The emittance during initial heating ranged between 0.91 and 0.94, but when a temperature of 2300°F was reached, the uncoated substrate near the upper electrode failed, terminating the test prematurely. The appearance of the specimen at the end of the test is shown in Figure 29.

Because of the failure of the second specimen, a third specimen was prepared and tested. As shown in Figure 30, the emittance of this specimen was about 0.90 for 200 hours at 2100°F. Heating the specimen to 2800°F in 50°F increments increased the emittance to 0.96. The specimen was then cooled to room temperature and reheated to 2100°F. The emittance at 2100°F was still found to be 0.96. After testing, the coating was still very adherent, although visual examination revealed that the specimen had a higher luster than before testing, indicating that incipient melting had occurred. The appearance of the specimen at the end of the test is shown in Figures 31 and 32 This coating was not selected for 2000-hour vacuum endurance testing because of the possibility that this material is nearly molten at the upper temperatures. Analysis of this specimen by microprobe techniques indicated that considerable diffusion of iron into the platinum-20 percent rhodium occurred, as shown in Figures 33 and 34. Very little if any titanium diffused into the substrate.

In view of the overall results of this program and the poor performance of the other candidate materials, it may be necessary to operate within the temperature limits of iron titanate.

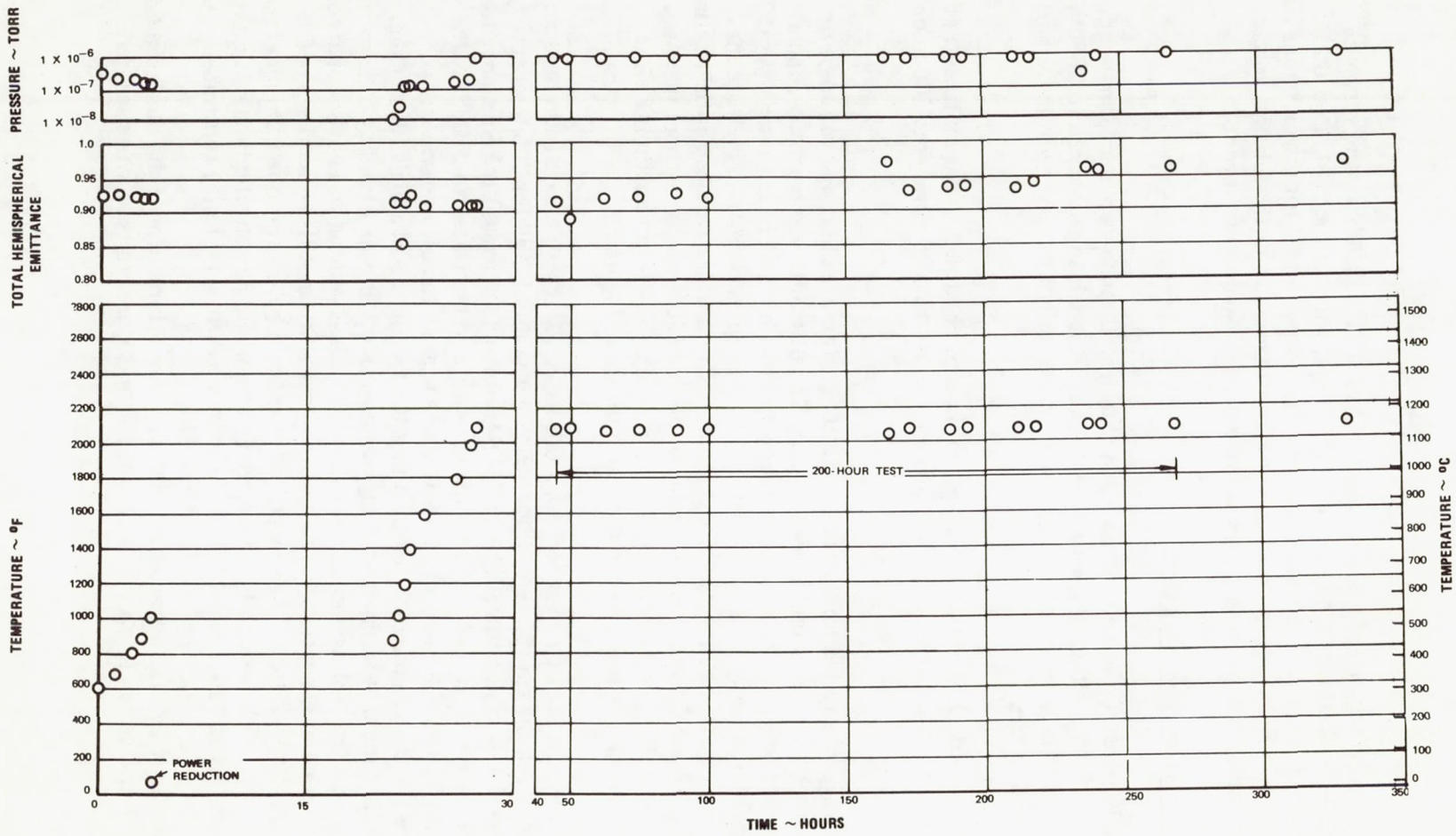


Figure 27 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate

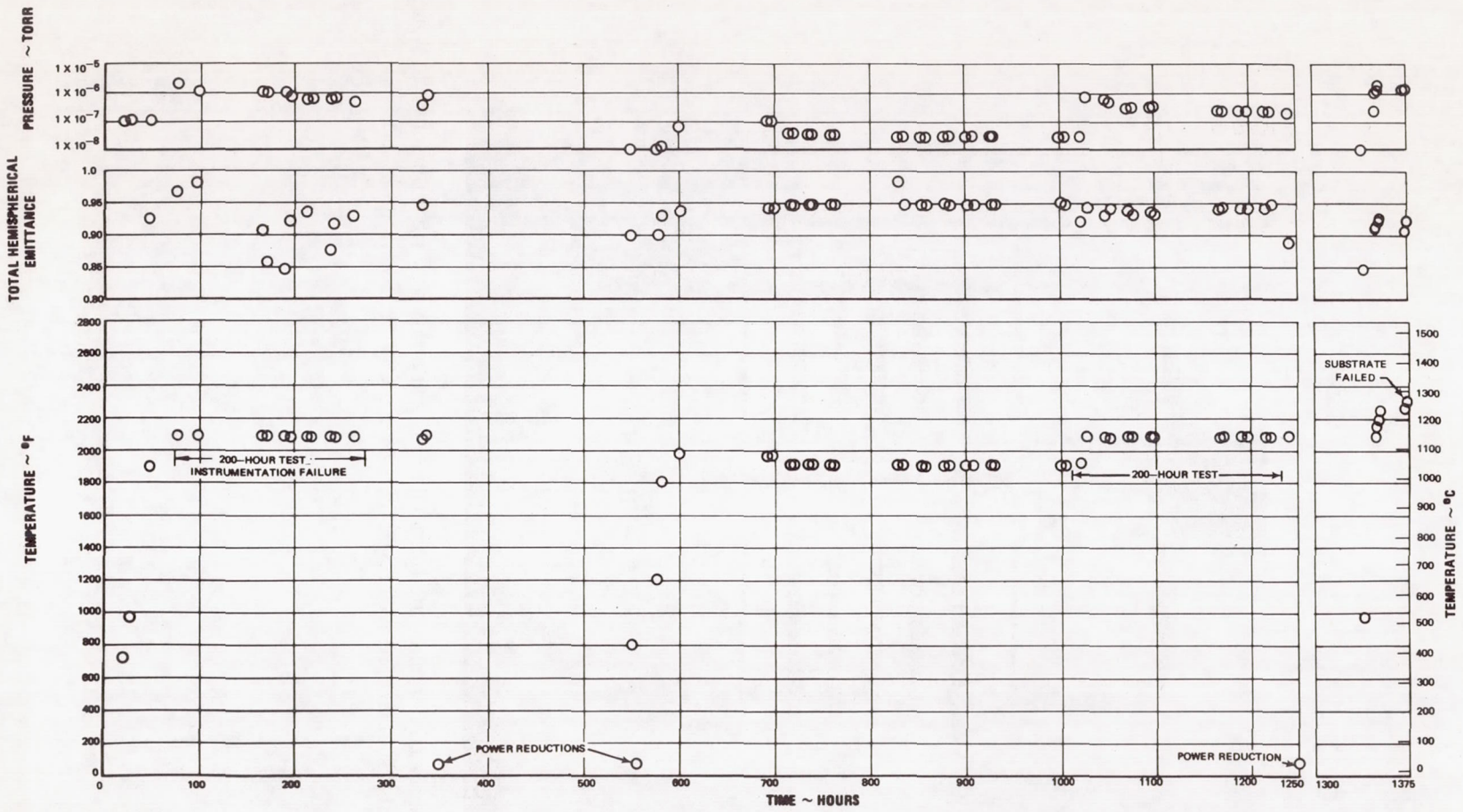


Figure 28 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate

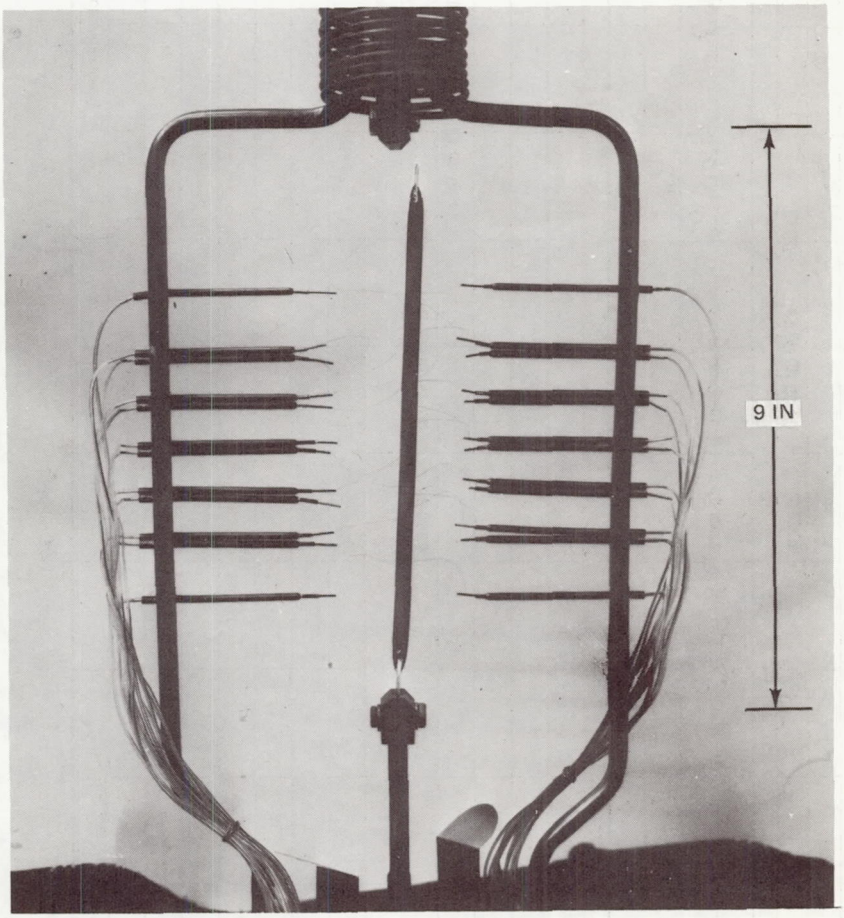


Figure 29 Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate Which Failed When Heated to 2300°F Following Over 1000 Hours at 2100°F
M-52064

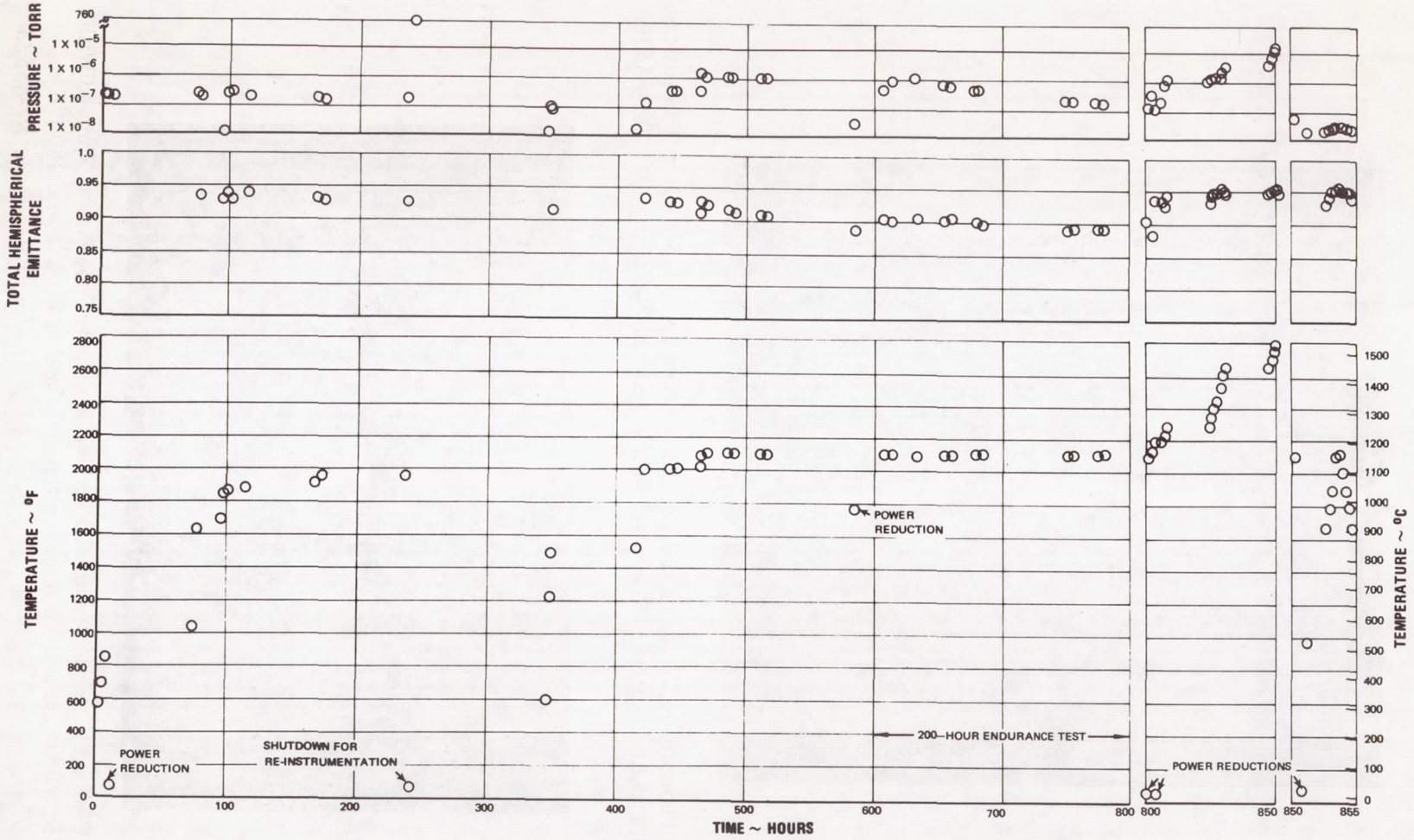


Figure 30 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate

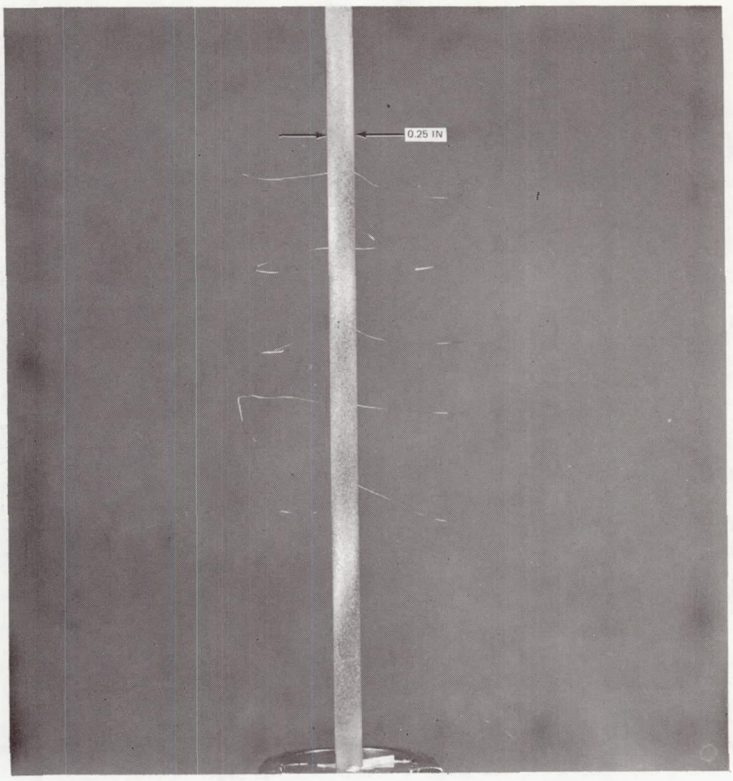


Figure 31 Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanante and Vacuum Emittance Tested at 2100°F and 2800°F XP-85520

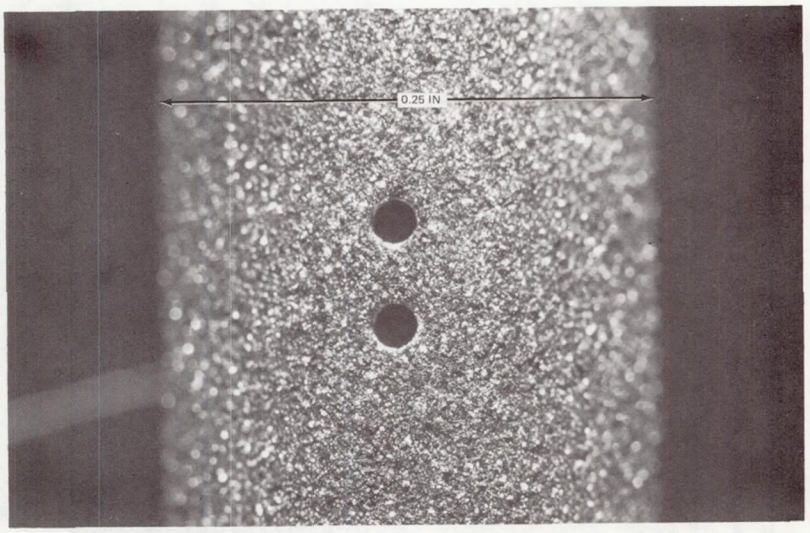


Figure 32 Closeup View of Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate and Vacuum Emittance Tested at 2100°F and 2800°F XP-85523

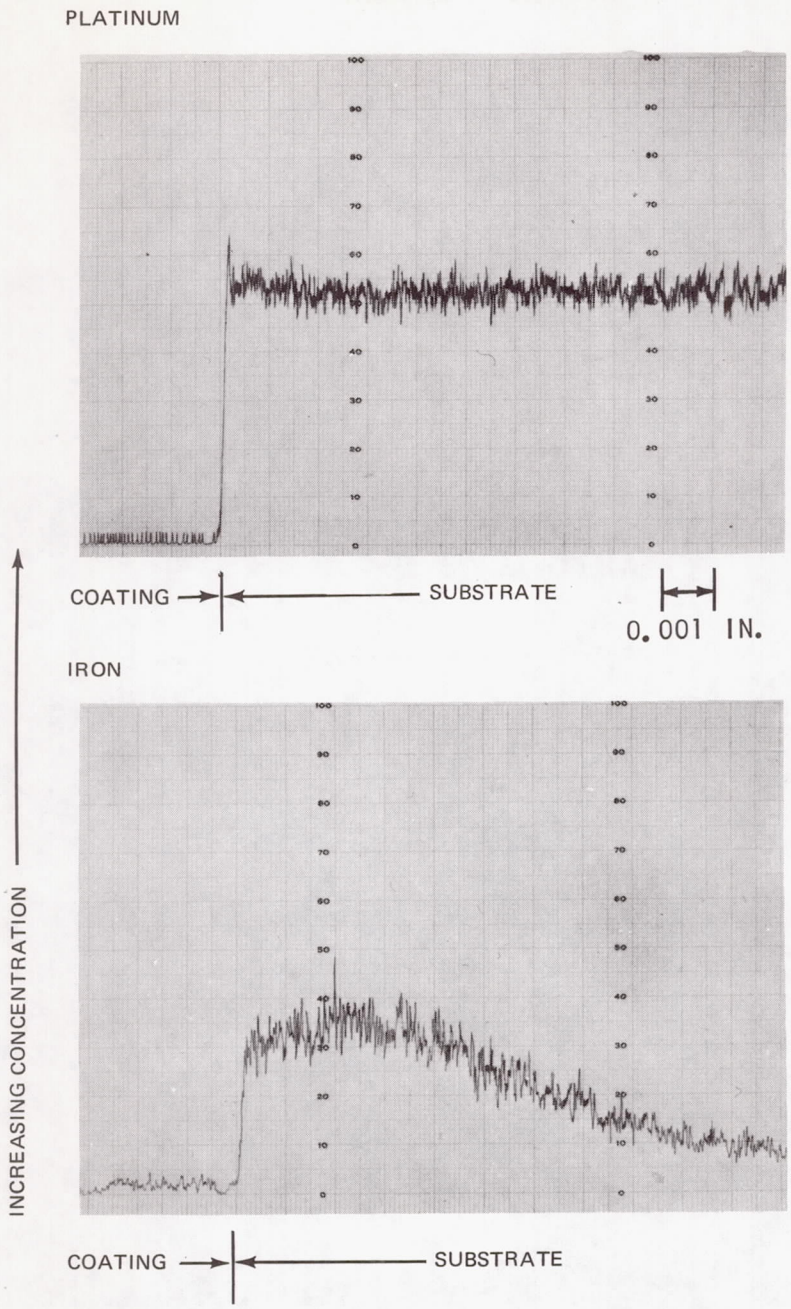


Figure 33 X-Ray Line Scan Intensities for Platinum and Iron Across Iron-Titanate-Coated Platinum-20 Percent Rhodium Tube After Vacuum Emittance Testing at 2100°F for 200 Hours and Heating to 2800°F. Note the Diffusion of Iron into the Substrate (An Area Immediately Adjacent Was Scanned for Iron in the Substrate; Up to 4 Percent of Iron Has Been Estimated at the Outside Diameter, and up to 1 Percent at the Inside Diameter)

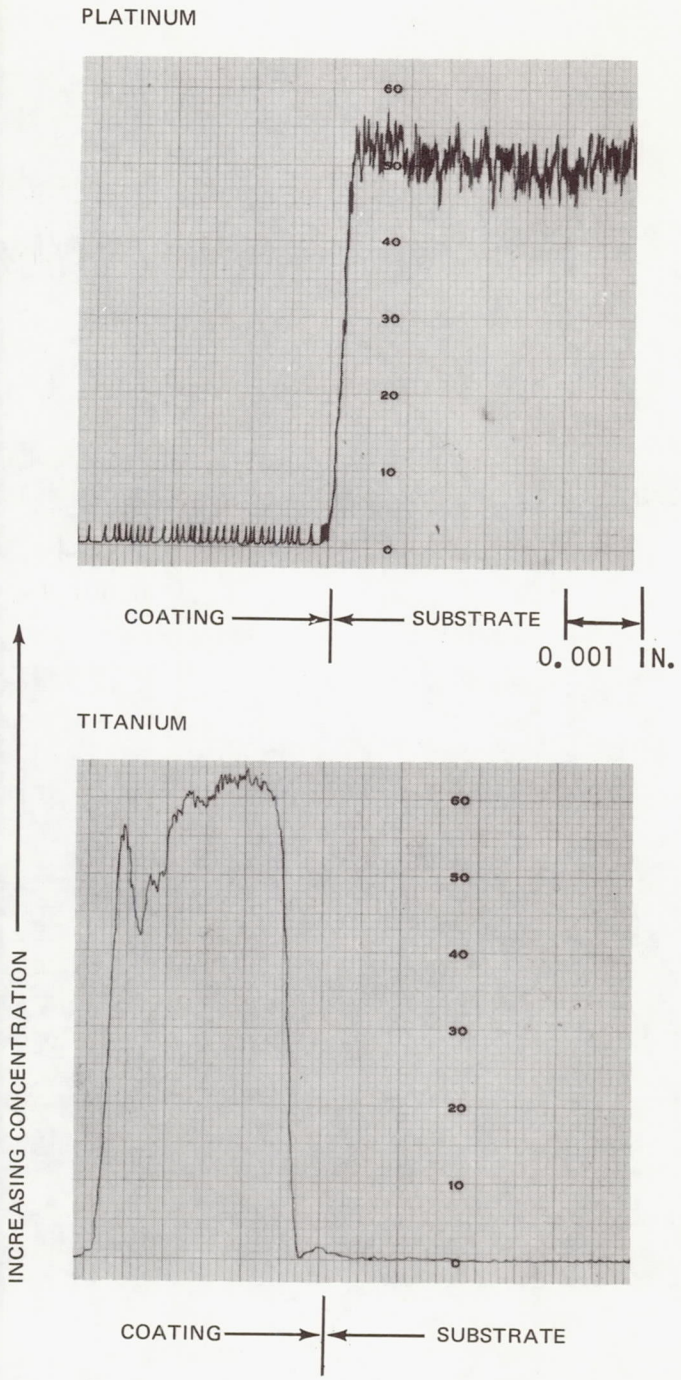


Figure 34 X-Ray Line Scan Intensities for Platinum and Titanium Across Iron-Titanate-Coated Platinum-20 Percent Rhodium Tube After Vacuum Emittance Testing at 2100°F for 200 Hours and Heating to 2800°F

c. Air-Aged Specimens

Three iron-titanate-coated platinum-20 percent rhodium specimens were aged in air at 1100°F for 1597 hours. Two of these were vacuum emittance tested for four hours at 2100°F, and the results are shown in Figures 35 and 36. As shown, the first of these demonstrated an emittance of 0.92, and the second demonstrated an emittane of 0.90.

The third specimen was vacuum emittance tested between 2100°F and 2800°F with emittance readings being taken at 25°F increments. The results, shown in Figure 37, indicate that the emittance varied between 0.90 and 0.87 between 2100°F and 2800°F.

d. Discussion of Results

The physical properties of iron titanate result in its being a very satisfactory coating material for platinum-20 percent rhodium with respect to structural capabilities. Because its coefficient of thermal expansion is close to that of the platinum-20 percent rhodium, the thermal stresses induced by heating the specimen to temperatures up to 2800°F are moderate, and none of the coatings separated or spalled from the substrate. Aging did not appear to have a detrimental effect on the coating, and in all cases, both before and after aging, the emittance was approximately 0.90 or slightly higher. Microprobe data indicate that a considerable amount of diffusion of iron into the platinum-20 percent rhodium occurs at the test times and temperatures considered here.

3. Hafnium Oxide Coating on Platinum-20 Percent Rhodium

a. Material Description

In accordance with the contract work statement, initial testing was performed on platinum-20 percent rhodium tubes coated with hafnia applied by the chemical vapor deposition process. The specimens were prepared by the San Fernando Laboratories. X-ray diffraction analysis of a chip of the coating removed from one of the specimens indicated that the predominant phase on the outer surface of the coating was HfO_2 (monoclinic), but the surface adjacent to the substrate was characterized by the diffraction pattern of platinum or a platinum alloy. The hafnium-oxide coated specimen was analyzed for traces of platinum in the coating, but none was found. Consequently, the X-ray data suggests that the initially deposited hafnium oxide grew epitaxially from the platinum-20 percent rhodium surface. Similar analyses performed on the coating after heating in vacuum detected only the presence of hafnium oxide (monoclinic), indicating that recrystallization occurred during the test. Emission spectrographic analyses were performed, and the impurities present in the coating were found to be iron, silicon, and magnesium.

Values for the thermal expansion characteristics of hafnia obtained from the literature indicate that large thermal stresses will be induced when this material is applied to platinum-20 percent rhodium and the temperature is varied from the temperature of application (see Figure 10). Assuming that the coating will be in equilibrium at the temperature of application, the coating will be in tension at temperatures above 1850°F and in compression at

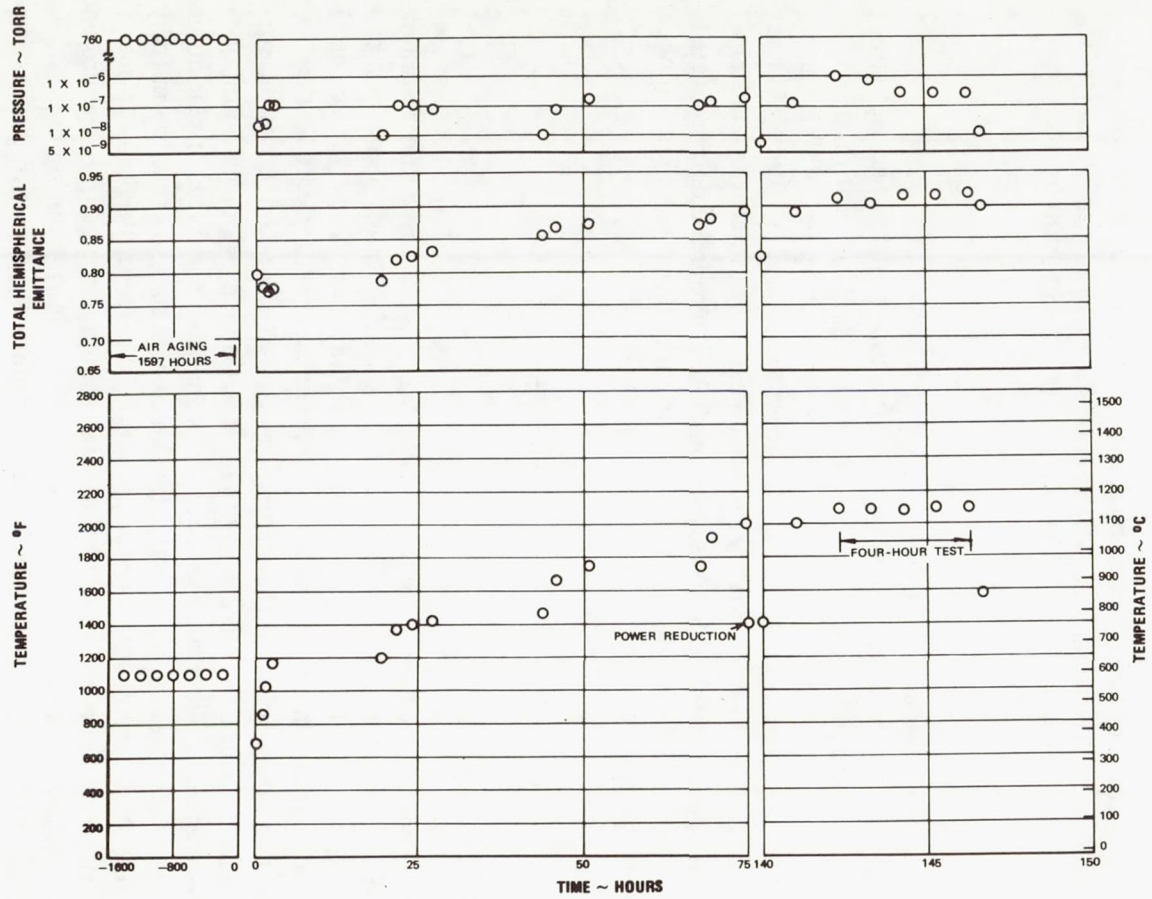


Figure 35 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate and Aged in Air at 1100°F for 1597 Hours

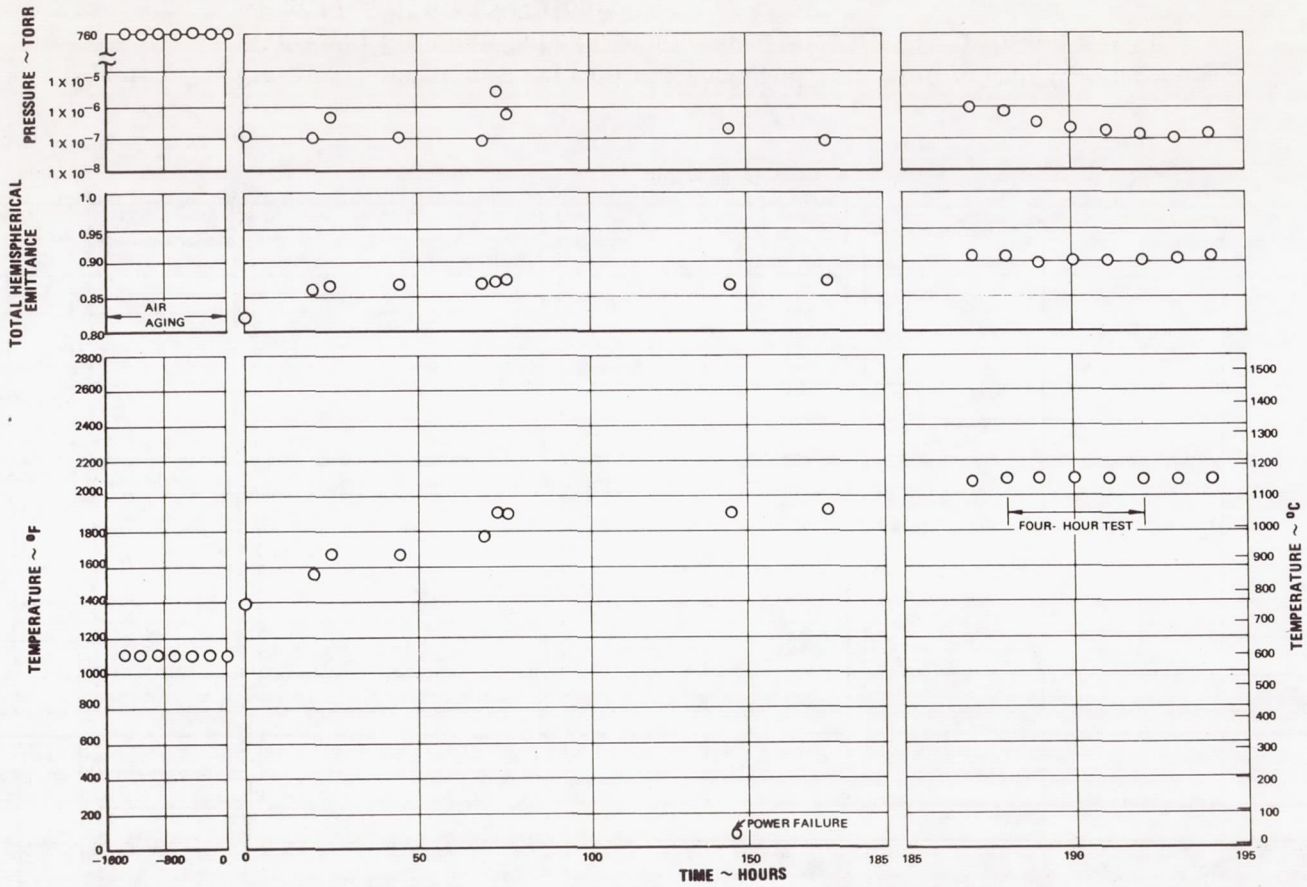


Figure 36 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate and Aged in Air at 1100°F for 1597 Hours

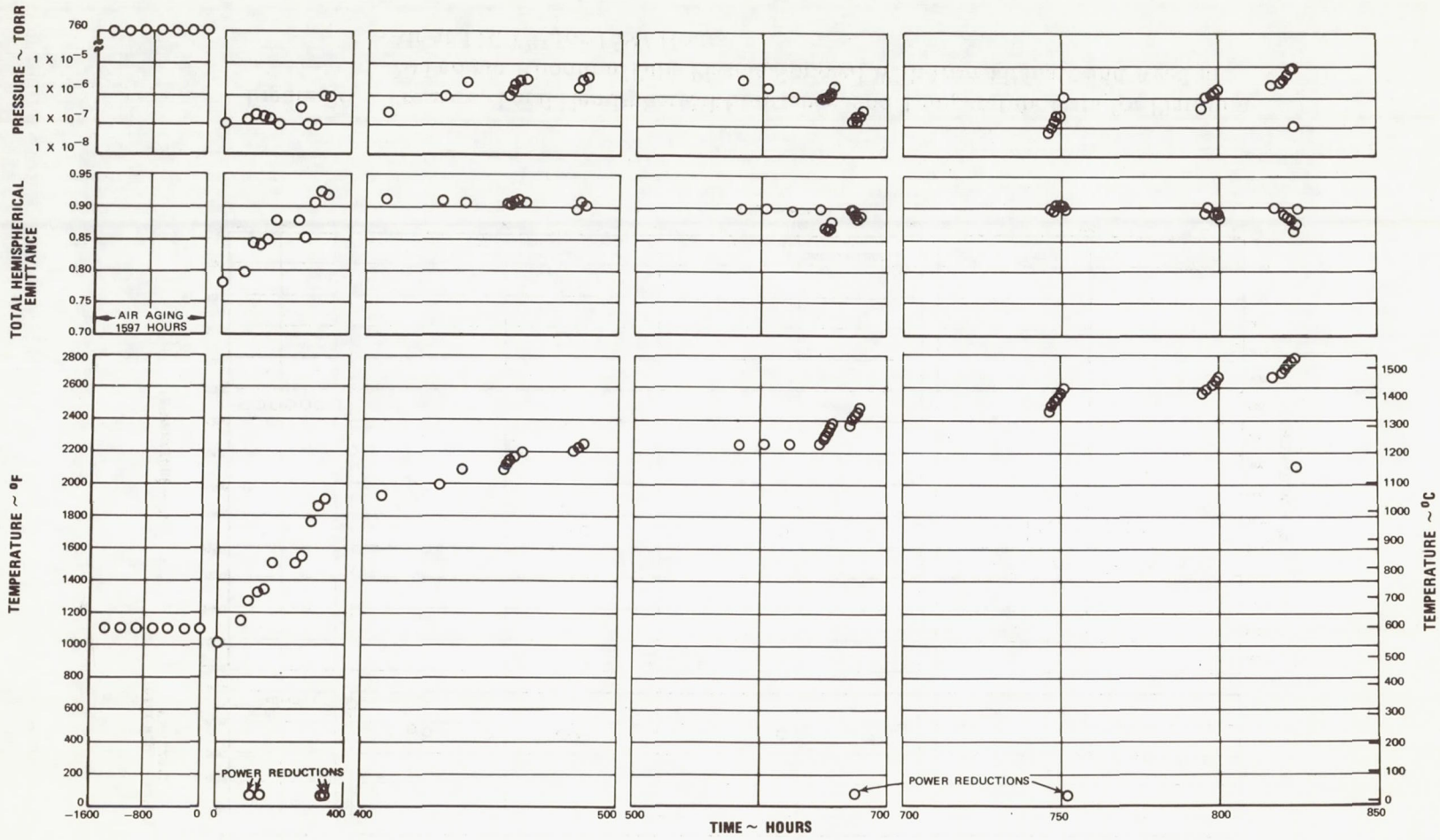


Figure 37 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Iron Titanate and Aged in Air at 1100°F for 1597 Hours

lower temperatures. Testing performed during this program indicated that the thermal stresses were excessive, since the coatings generally spalled from the substrate during cooling from the test temperature of 2100°F.

In an attempt to obtain a mechanically adherent hafnia coating for platinum-20 percent rhodium, two other hafnia coatings were tested. One of these was hafnia stabilized with 5 weight percent calcia, and the other was hafnia stabilized with 5 weight percent yttria. The literature indicated that both of the stabilizing compounds would shift the thermal expansion characteristic closer to that of platinum-20 percent rhodium, thereby reducing the thermal stresses. Both of these materials were applied by plasma spraying rather than chemical vapor deposition since plasma spraying results in a more porous coating which is more tolerant of differences in thermal expansion.

b. Two-Hundred-Hour Screening Tests

Four platinum-20 percent rhodium tubes coated with hafnia were vacuum emittance tested at 2100°F for 200 hours. Two of these had chemically vapor deposited hafnia coatings and two were stabilized with 5 weight percent calcia or yttria.

The first specimen had a chemically vapor deposited hafnia coating, and the test results are shown in Figure 38. The coating procedure used is presented on Page 11. The emittance during the 200-hour test was initially 0.86, but the level dropped rapidly to a value of about 0.66. Subsequently, the specimen's temperature was increased to 2800°F in 50°F increments. The emittance during this portion of the test ranged from 0.71 to 0.63. Following testing, the coating was very poorly bonded to the substrate with severe spalling occurring.

The second specimen, which also contained a chemically vapor deposited hafnia coating, was tested for 200 hours in vacuum at 2100°F, but the data indicated an emittance of only 0.2, which was obviously erroneous. However, over one weekend, optical pyrometer readings indicated that the temperature of the specimen increased from 2100°F to 2330°F without a change in the powerstat setting. Providing the electrical resistance of the specimen remained constant, the power radiated was the same at both temperatures, indicating a drop in emittance of approximately 30 percent. The drop was indicative of coating separation, and, in fact, at the conclusion of the test the condition of the specimen was found to be similar to that of the first hafnia-coated specimen tested.

The third specimen tested was coated with plasma-sprayed hafnia stabilized with 5 weight percent yttria. This specimen was subjected to a 200-hour vacuum emittance test, after which the temperature was increased in 50°F increments to 2800°F. The test results are shown in Figure 39. During the 200-hour test, the emittance decreased gradually from 0.64 to 0.51. When heated to 2800°F, the emittance increased from 0.51 to 0.57. Although the emittance behavior of this specimen was comparable to that of the chemically vapor deposited hafnia coated specimens, the coating following testing was very adherent, and no signs of lifting were observed.

The last specimen in this series was plasma sprayed with hafnia stabilized with 5 weight percent calcia. The substrate had previously been coated with hafnia by the chemical vapor

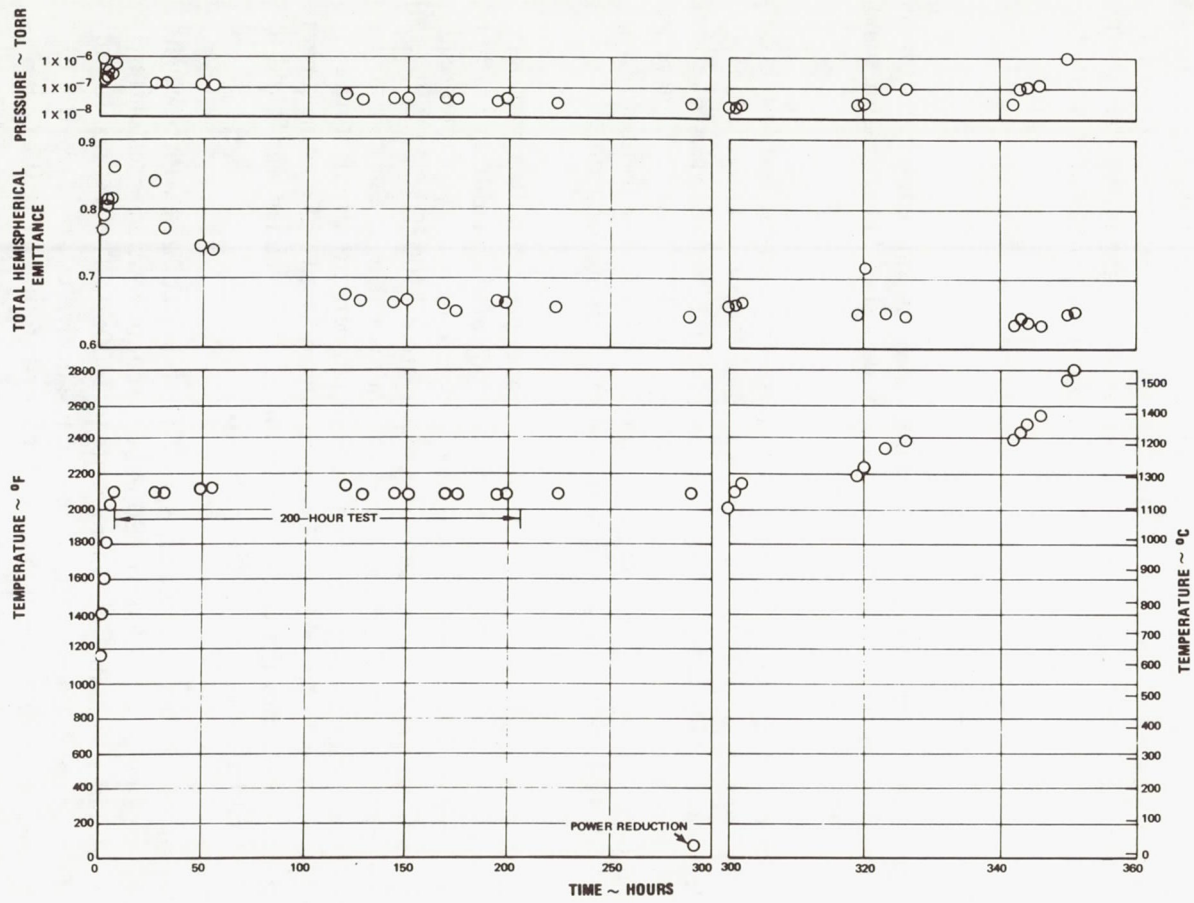


Figure 38 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Coated With Hafnia by Chemical Vapor Deposition

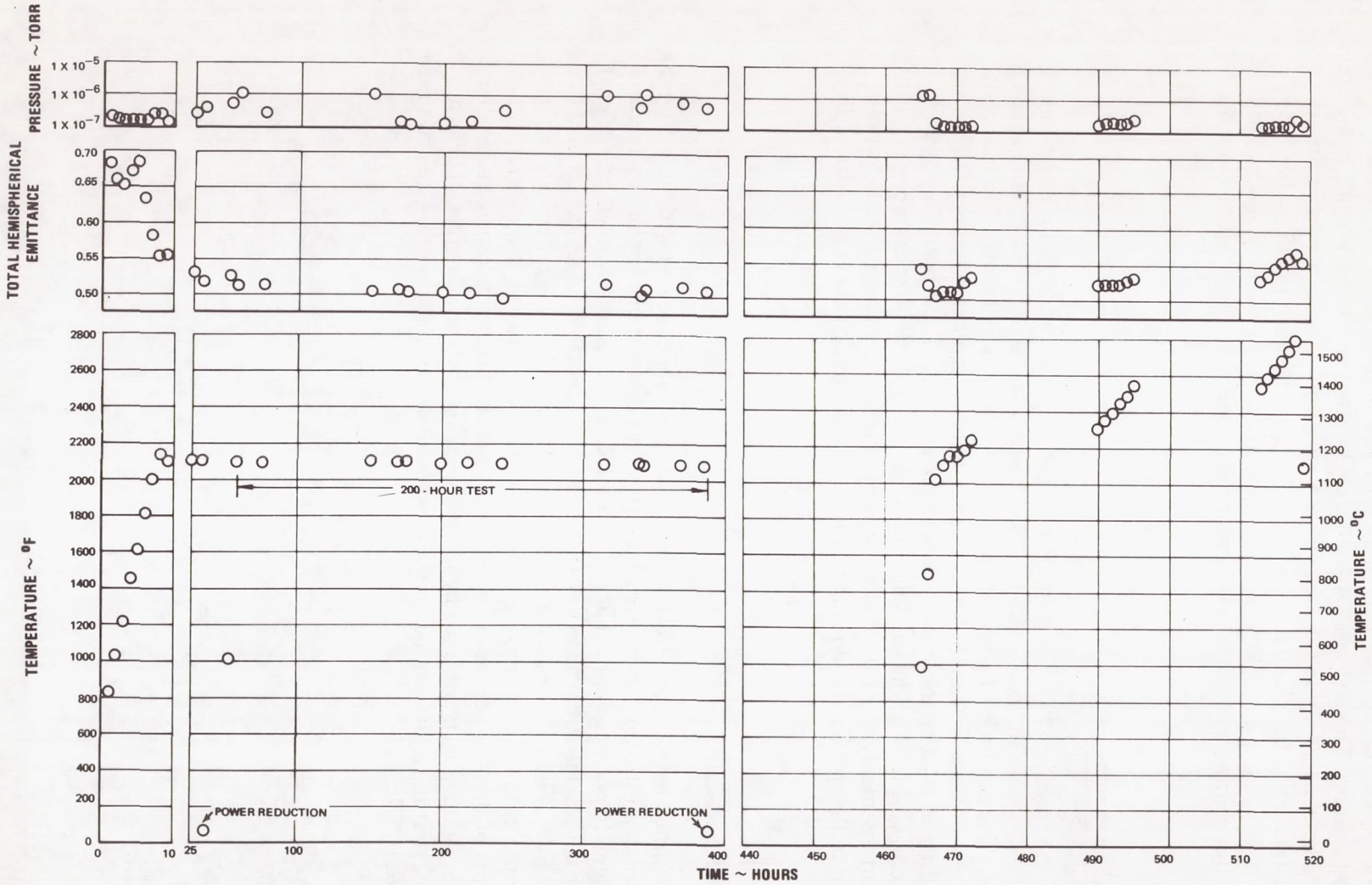


Figure 39 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Hafnia-5 Percent Yttria

deposition process, and this coating was removed by grit blasting before application of the plasma-sprayed coating. This specimen was subjected to the same test sequence as the other plasma-sprayed hafnia coating, and the results were very similar, as shown in Figure 40. The initial emittance was 0.58, and it dropped gradually to a value of 0.48 by the end of the 200-hour test. Heating to 2800°F in 50°F increments increased the emittance to 0.56. After testing, this coating was also very adherent with no indications of lifting from the substrate.

c. Air-Aged Specimens

Inspection of the platinum-20 percent rhodium tubes coated with hafnia by the chemical vapor deposition process and aged in air for 1597 hours at 1100°F revealed some cracking of the coating. The conditon of a typical specimen is shown in Figure 41. Vacuum emittance testing one of these specimens for four hours resulted in an emittance of 0.75 which decreased slightly to 0.74 by the end of the four-hour period. These results are shown in Figure 42. Following testing, the specimen was removed from the test chamber as gently as possible, but essentially all of the coating separated from the substrate in the process. The condition of the specimen following removal from the test chamber is shown in Figure 43.

d. Discussion of Results

The tests performed on platinum-20 percent rhodium specimens coated with hafnia by the chemical vapor deposition process clearly indicated that this material applied by this process to platinum-20 percent rhodium does not result in a satisfactory high-emittance coating. The emittance values were all below the minimum acceptable value, and all of the coatings prepared by this process separated from their substrates following thermal cycling, apparently because of the high thermal stresses induced by the relatively large differences in the coefficients of thermal expansion of the hafnia and the platinum-20 percent rhodium. More adherent coatings were achieved by plasma spraying coatings of hafnia stabilized with calcia or yttria, but the emittance values for these specimens were also below the minimum acceptable level.

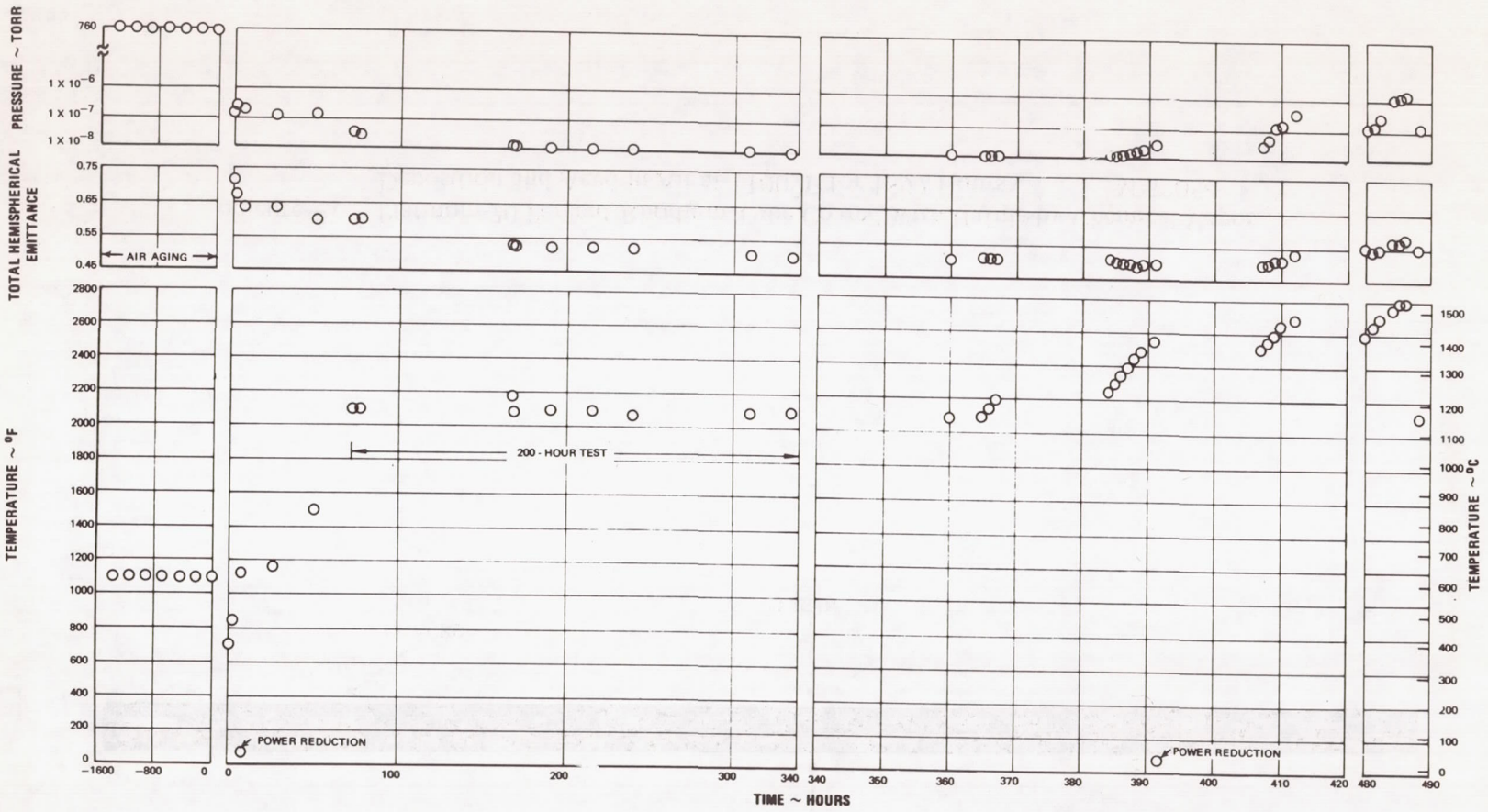


Figure 40. Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Plasma Sprayed With Hafnia-5 Percent Calcia

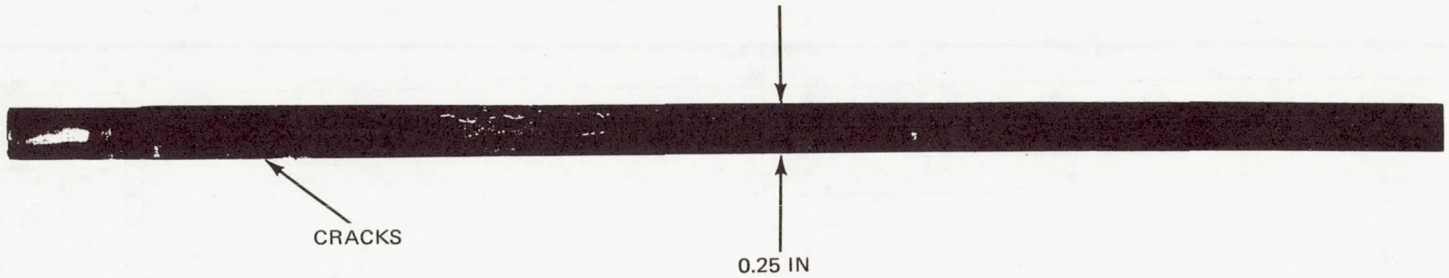


Figure 41 Platinum-20 Percent Rhodium Tube Coated With Hafnia by Chemical Vapor Deposition and Aged in Air at 1100°F for 1597 Hours M-52054

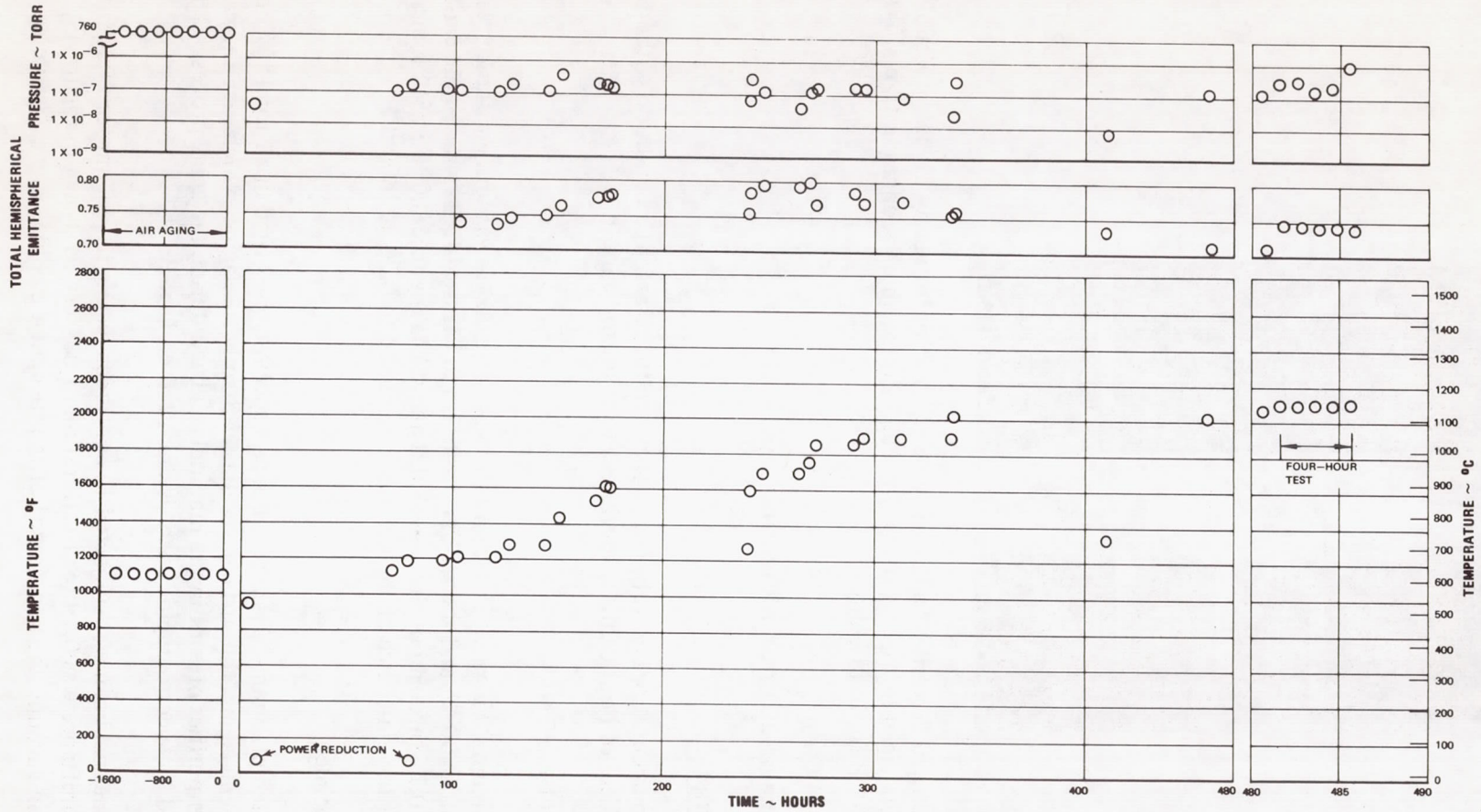


Figure 42 Pressure, Total Hemispherical Emittance, and Temperature Data for Platinum-20 Percent Rhodium Tube Coated With Hafnia by Chemical Vapor Deposition and Aged in Air at 1100°F for 1597 Hours

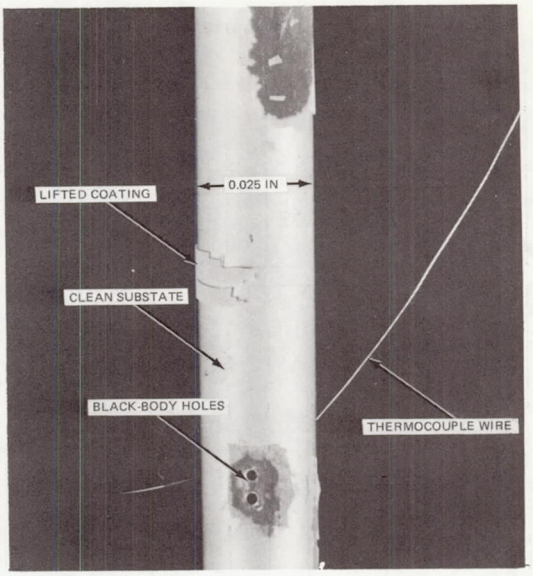


Figure 43 Platinum-20 Percent Rhodium Tube Coated With Hafnia by Chemical Vapor Deposition, Aged in Air at 1100°F for 1597 Hours, and Vacuum Emittance Tested at 2100°F for Four Hours M-52191

4. Uncoated Platinum-20 Percent Rhodium

a. Material Description

Two platinum-20 percent rhodium tubes were tested in the as-received condition without coatings. The surfaces of both of these specimens were mirror smooth.

b. Two-Hundred-Hour Test

One uncoated platinum-20 percent rhodium tube was subjected to vacuum emittance testing for 200 hours at 2100°F, and the results are shown in Figure 44. As shown, the emittance remained at 0.17 throughout the test. Subsequent heating to 2800°F in 50°F increments showed that the emittance of the specimen increased to 0.20 at 2800°F.

c. Air-Aged Specimen

The second uncoated platinum-20 percent rhodium specimen was aged in air for 1597 hours at 1100°F. Following aging, the surface was darker than before aging, which may indicate that some of the impurities present in the material oxidized during the aging process. The impurities detected by spectrographic analysis are listed on Page 3.

Following aging, the specimen was subjected to emittance testing in vacuum for 2000 hours at 2100°F. The emittance was 0.19 for the duration of the test, as shown in Figure 45. Following testing in vacuum, the appearance of the specimen was the same as before aging in air.

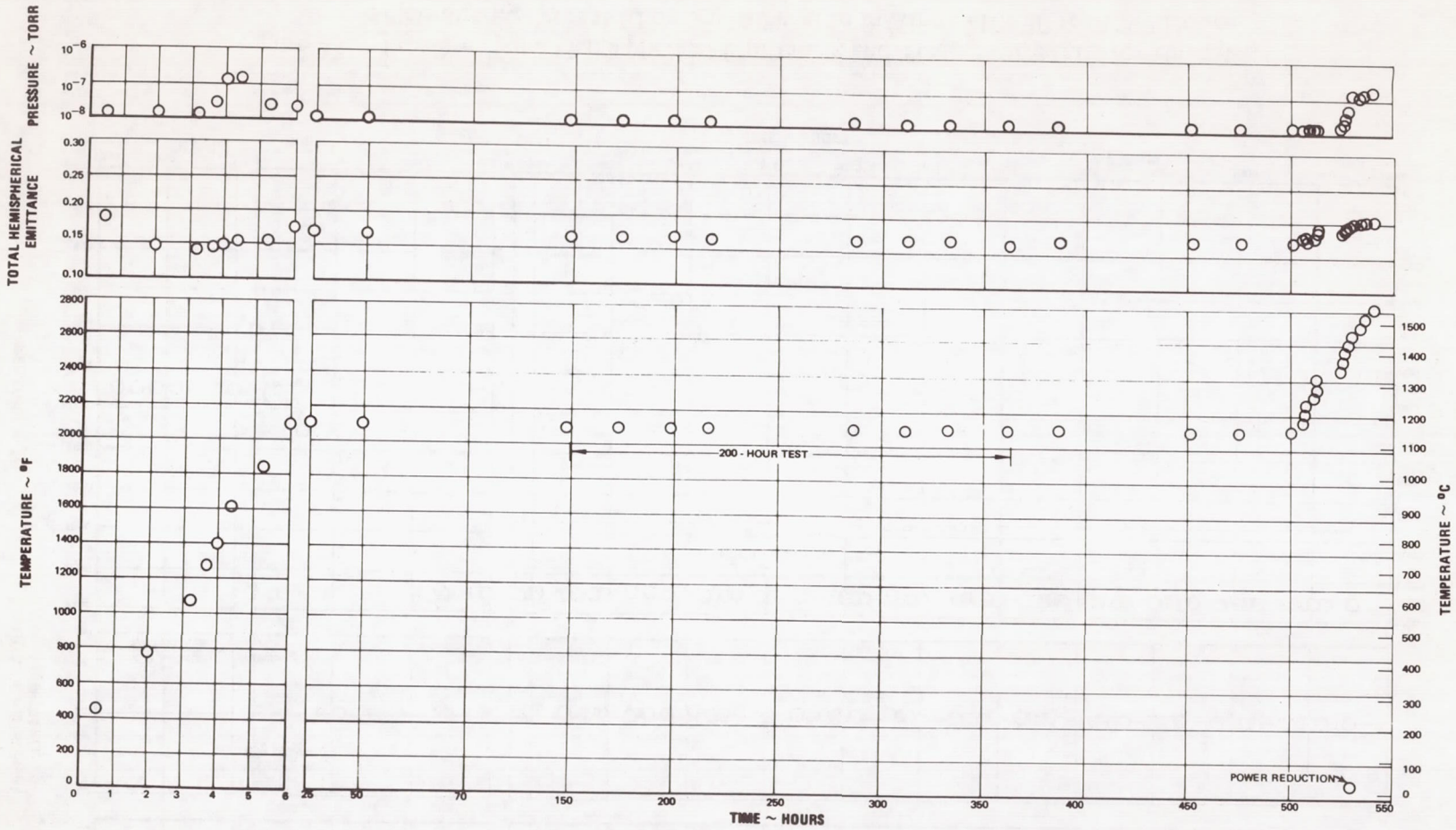


Figure 44 Pressure, Total Hemispherical Emittance, and Temperature Data for Uncoated Platinum-20 Percent Rhodium Tube

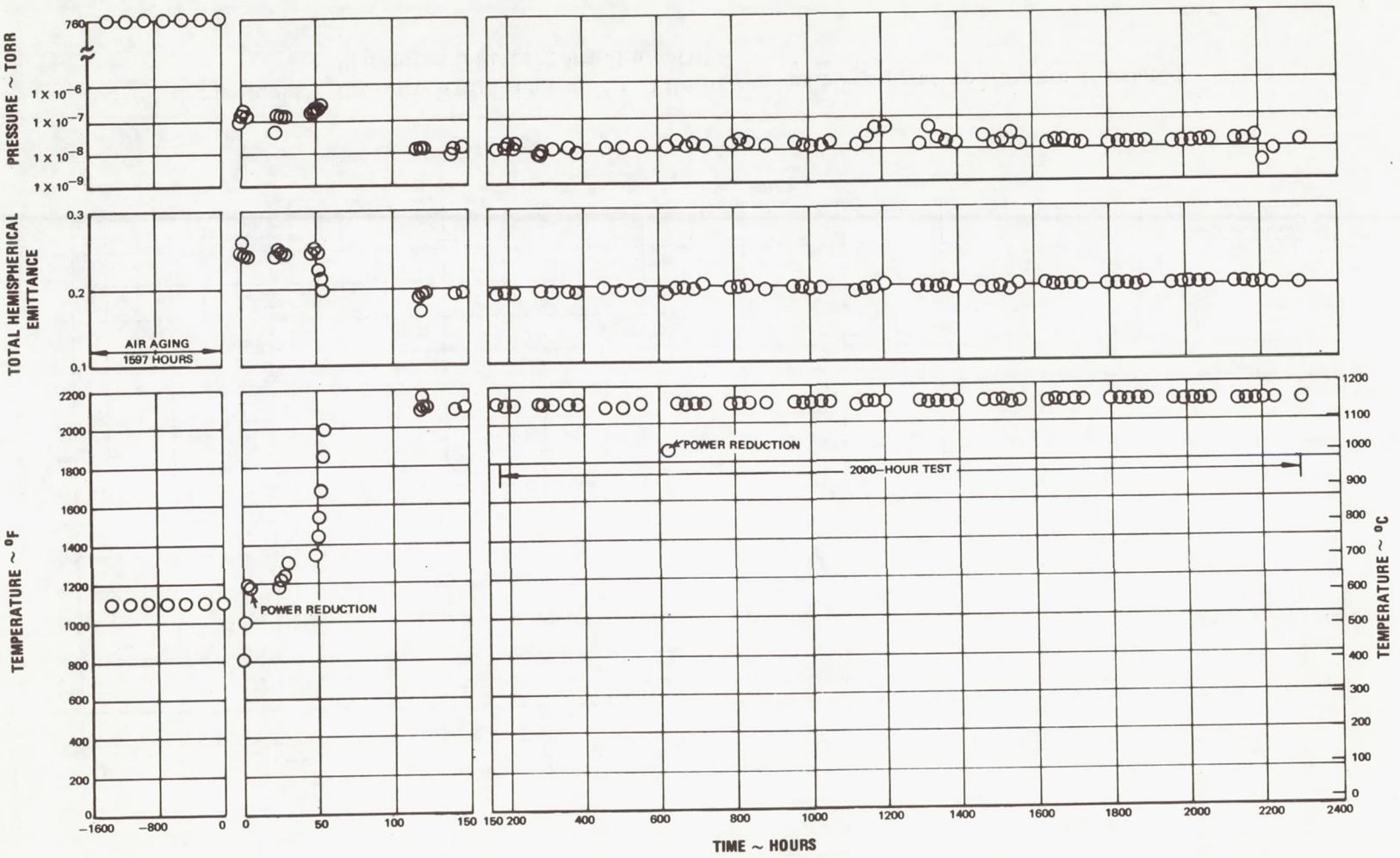


Figure 45 Pressure, Total Hemispherical Emittance, and Temperature Data for Uncoated Platinum-20 Percent Rhodium Tube Aged in Air at 1100°F for 1597 Hours

III. COATED COLUMBIUM-1 PERCENT ZIRCONIUM SUBSTRATES

A. INTRODUCTION

Previous tests of iron-titanate-coated columbium-1 percent zirconium (reported in NASA CR-1278, PWA-3278) have indicated that iron, titanium, and oxygen diffuse to a limited extent into the substrate after extended periods at elevated temperature in vacuum. The effect of this diffusion is an increase in the hardness of the columbium-1 percent zirconium, which may compromise the properties of the material.

In an effort to eliminate this diffusion, a specimen was prepared with a diffusion barrier layer under the iron titanate coating. This specimen, as well as a similar specimen without the diffusion barrier coating, were subjected to 1000-hour tests and subsequently analyzed to determine the extent to which the diffusion barrier coating actually limited diffusion.

B. ANALYSIS OF COLUMBIUM-1 PERCENT ZIRCONIUM

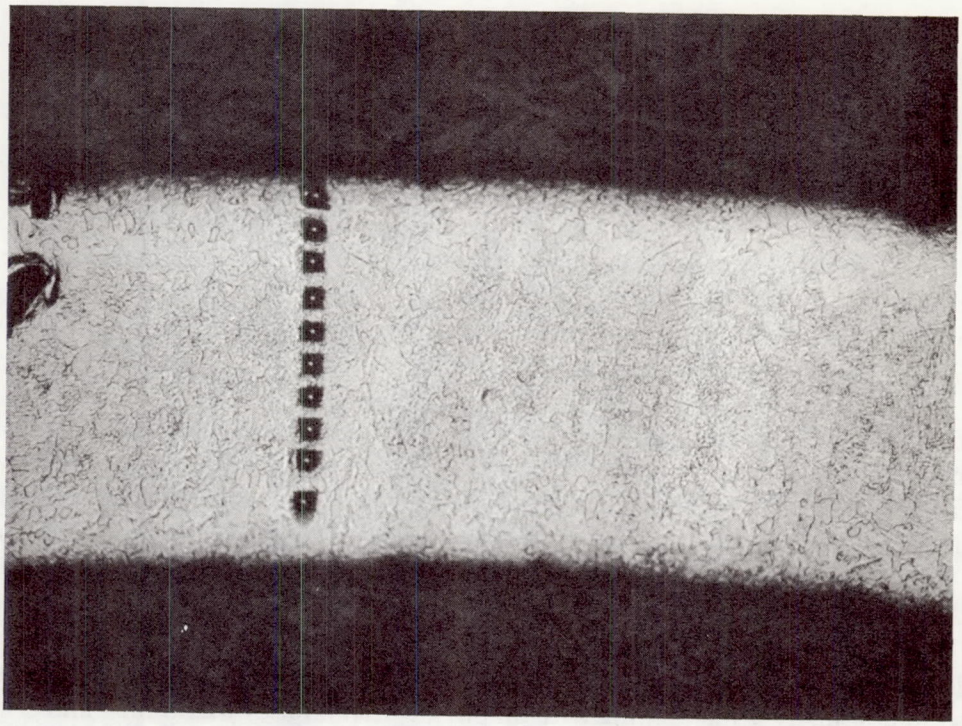
The columbium-1 percent zirconium substrates were obtained in the form of seamless tubes which were nominally 9 inches long with an outside diameter of 0.250 inch and a wall thickness of 0.010 inch. The material was purchased to CANEL Specification CS-1831F, revised December 4, 1964. The material contained 1 percent zirconium, 120 ppm carbon, 280 ppm oxygen, 7 ppm hydrogen, and 22 ppm nitrogen when received. The diamond pyramid hardness of the material ranged from 83 to 95 with the higher values being obtained near the center of the wall section. The microstructure of the material in the as-received condition is shown in Figure 46. X-ray line scans were made with an electron beam microprobe to determine the distribution of the zirconium in the substrate. The results are shown in Figure 47.

C. COATING SELECTION AND SPECIMEN PREPARATION

The iron titanate material used to coat the specimens for this test series was obtained from the Continental Coatings Corporation and was designated FCT-11H. The properties of this material are described in Section II-E-2-a of this report.

Tungsten was selected for the barrier coating material because it possesses properties which tend to limit diffusion and because the bond of tungsten to the substrate was expected to be better than that of candidate ceramic materials.

Two specimens were prepared, one with the barrier coating and one without. Both were prepared by the plasma spray process, and the plasma spray parameters are presented in the appendix.



Mag: 200X

Figure 46 Photomicrograph of Columbium-1 Zirconium in As-Received Condition

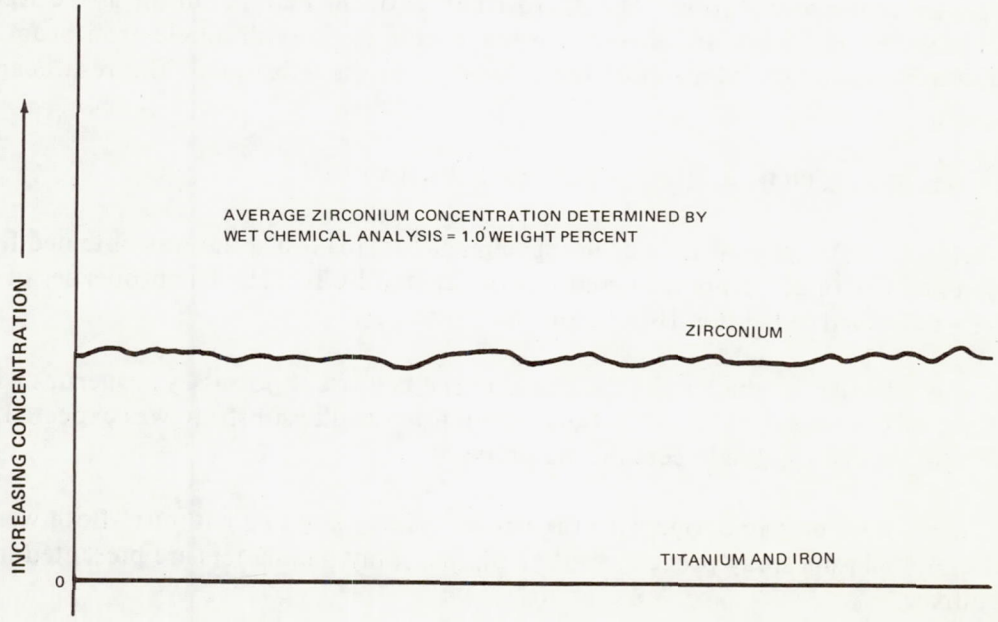


Figure 47 X-Ray Line Scan Intensities for Zirconium Across Columbium-1 Percent Zirconium Tube in As-Received Condition

D. TEST APPARATUS AND PROCEDURES

The test program for both specimens involved an initial heating to 1500°F in vacuum followed by thermal cycling between 1500°F and 1700°F. During each cycle, the specimens were held at 1500°F for 36 minutes, heated to 1700°F over a period of one minute, held at 1700°F for 60 minutes, and then cooled to 1500°F over a period of one minute.

The thermal cycling was performed automtically by an electromechanical device consisting of a multiswitch timer, a 250-rpm DC motor, and a number of microswitches. The motor drove the powerstat through a speed-reducing gear train. The direction of rotation and the starting time for changing the powerstat setting was controlled by the timer. The drive motor was stopped at the powerstat control positions corresponding to the desired specimen temperatures by microswitches mounted on the back of the powerstat. Safety microswitches were also provided to prevent the powerstat control from being rotated either above the maximum temperature or below the minimum temperature in the event that one of the other switches failed. Opening the microswitch at the upper limit deactivated the circuit for increasing the powerstat setting, but still permitted the setting to be reduced by the timer circuit. Opening the microswitch at the lower limit deactivated the entire control circuit. Consequently, failure of any of the control microswitches would result in the specimen temperature being reduced to and maintained at 1500°F. The cycling operation was continuously monitored by recording the specimen heating current on a strip chart recorder.

E. EMITTANCE TEST RESULTS

The emittance test results for the iron-titanate-coated columbium-1 percent zirconium tubes with and without a tungsten barrier coating are shown in Figures 48 and 49, respectively. As shown, both specimens exhibited an emittance of approximately 0.90 throughout the 1000-hour cyclic test.

F. POST–TEST ANALYSES

1. Introduction

Both specimens were subjected to detailed post-test analyses to determine both the general condition of the specimens and to determine the effectiveness of the tungsten diffusion barrier coating. The analyses included a qualititative determination of the coating bond strengths, X-ray diffraction and semiquantitative spectrographic analyses of the coatings, vacuum fusion and hardness traverses of the substrate, and electron-beam microprobe analyses of both the coatings and the substrates. In general, the results indicated that the tungsten diffusion barrier coating both increased the coating bond strength and reduced the amount of diffusion across the coating-substrate interface, although both specimens possessed good bond strengths and only very little diffusion occurred in either specimen during the 1000 hours of testing.

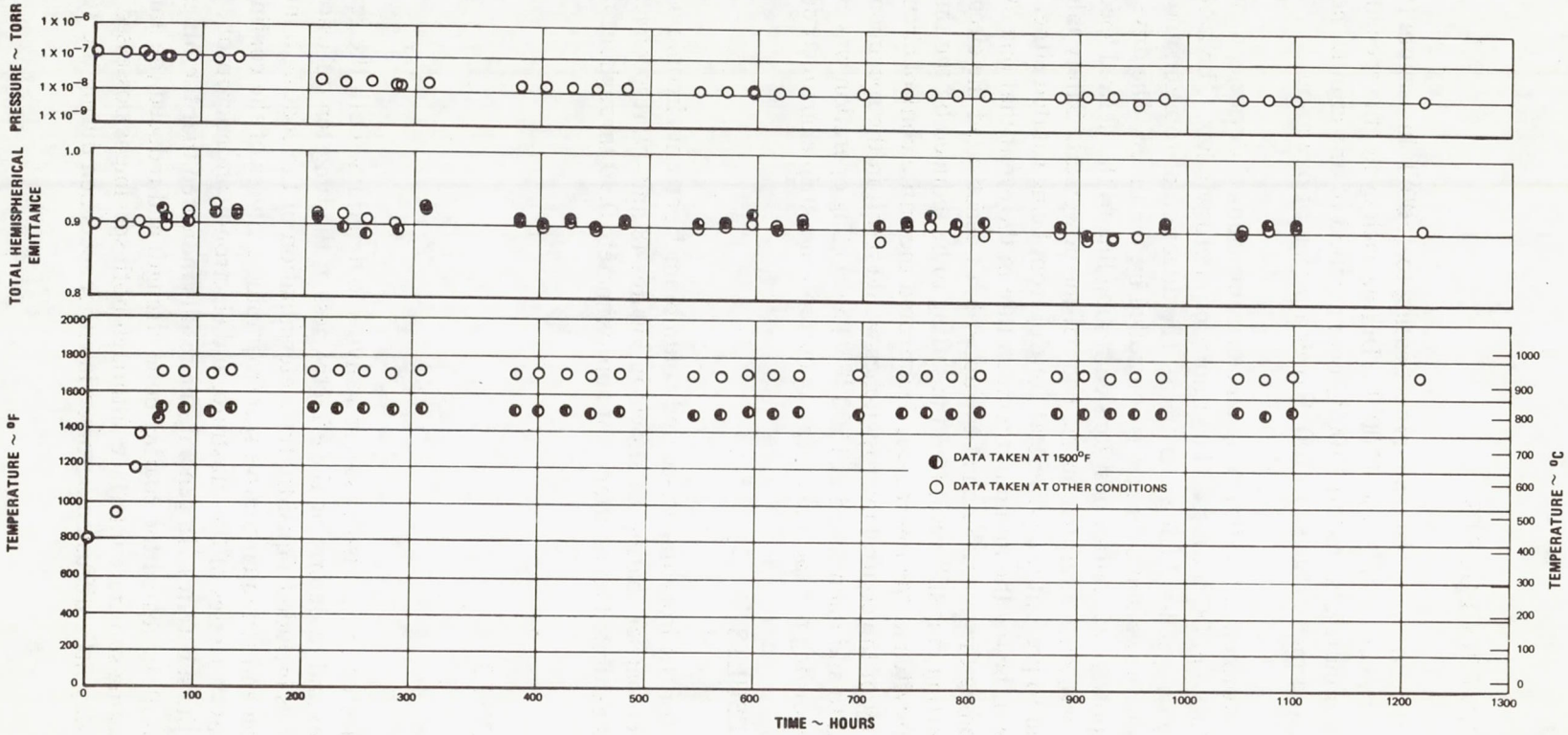


Figure 48 Pressure, Total Hemispherical Emittance, and Temperature Data for Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating and Iron Titanate

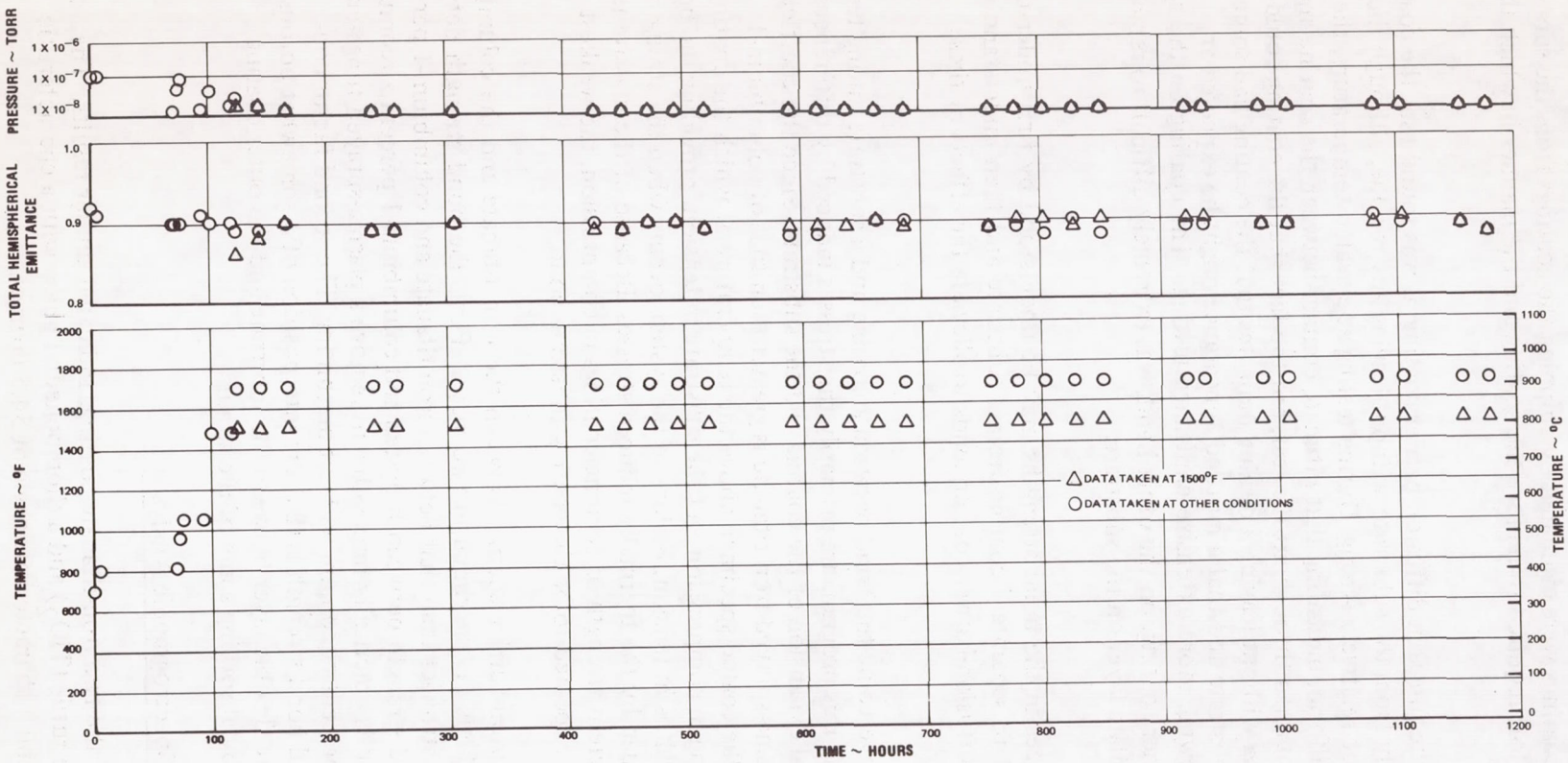


Figure 49 Pressure, Total Hemispherical Emittance, and Temperature Data for Columbium-1 Percent Zirconium Tube Coated With Iron Titanate

2. Bond-Strength Evaluation

The bond strengths of the coatings were evaluated by chipping the coatings from the substrates and observing the effort required to remove the coating and the manner in which the coating separated.

For the specimen without the tungsten diffusion-barrier coating, it was found that the coating could be removed cleanly from the substrate without leaving any residue, although the bond strength appeared to be relatively strong. During testing at elevated temperature, the specimen color had been uniform, indicating that intimate contact between the coating and the substrate had been maintained throughout the test, but the fact that the coating could be removed following testing without leaving a residue indicates that the coating had some tendency to lift from the substrate and that a mottled appearance might be expected at elevated temperatures following more extensive emittance testing. The coating on the specimen with the diffusion-barrier coating, on the other hand, was extremely difficult to remove without leaving an intermediate layer on the substrate.

The reason for the differences in the bond strengths may be understood by first understanding the mechanisms which tend to separate a coating from a substrate and then understanding the way in which the tungsten diffusion-barrier coating tends to alleviate the effects of these mechanisms.

The stresses which tend to overcome the bond between a coating and a substrate during testing of the type performed during this program are primarily the stresses induced by differences in the coefficients of thermal expansion of the coating and the substrate. Since the coefficient of thermal expansion of plasma-sprayed iron titanate is greater than that of columbium-1 percent zirconium, heating the coated specimen above the temperature at which the coating was applied places the coating in compression and the substrate in tension, providing the bond remains intact. The bond itself is in tension. Failure of the system occurs when the strength of the weakest part is exceeded by the thermally induced stresses. Because of the massiveness of the substrate and the inherent strength of ceramic coatings in compression, the weakest part of the system would be expected to be the coating-substrate bond.

Introducing a tungsten diffusion-barrier coating between the iron titanate and the columbium-1 percent zirconium strengthens the specimen in two ways. First, the bond strength between iron titanate and tungsten is stronger than that between iron titanate and columbium-1 percent zirconium, and the bond strength between tungsten and columbium-1 percent zirconium is extremely strong. In fact, it is practically impossible to remove a plasma-sprayed tungsten coating from columbium-1 percent zirconium without machining. The second factor contributing to the higher overall bond strength is that the interposition of a somewhat porous and, therefore, softer or more flexible layer between the substrate and the outer coating tends to reduce the stresses by absorbing some of the strains.

3. X-ray Diffraction and Spectrographic Analyses

X-ray diffraction analysis of the two iron-titanate coatings indicated similar results. The major phases identified were rutile (TiO_2) and a rhombohedral phase with a characteristic spacing of 5.52 Angstroms and a characteristic angle of 54.5 degrees.

The results of the semiquantitative spectrographic analyses are shown in the appendix and indicate no substantial changes from the results obtained with untested FCT-11H iron titanate.

4. Vacuum Fusion Analyses and Microhardness Test Results

The coatings of both specimens were stripped from the substrates, and the substrates were then subjected to vacuum fusion analyses to determine the overall concentrations of oxygen, hydrogen, and nitrogen in the columbium-1 percent zirconium. The results are shown in Table 3.

TABLE 3

VACUUM FUSION ANALYSIS RESULTS FOR COLUMBIUM-1 PERCENT ZIRCONIUM TUBES COATED WITH FCT-11H IRON TITANATE WITH AND WITHOUT A TUNGSTEN DIFFUSION BARRIER AND THERMAL CYCLED IN VACUUM FOR 1000 HOURS BETWEEN 1500°F AND 1700°F

	Concentration (Weight Percent)		
	Oxygen	Hydrogen	Nitrogen
Specimen Without Diffusion Barrier	0.370	0.001	0.005
Specimen With Diffusion Barrier	0.034	0.002	0.006

Microhardness traverses were made across the substrates of both specimens, and the results are shown in Figure 50. In both substrates, the hardness was higher near the outer surface than near the inner surface, but the gradient was considerably less in the substrate which had been tested with the diffusion barrier coating than that tested without the diffusion barrier coating. This result may be indicative of less contamination in the substrate with the duplex coating. Etched photomicrographs of both substrates showing the locations where the microhardness tests were made are presented in Figures 51 and 52. Unetched photomicrographs are shown in Figures 53 and 54.

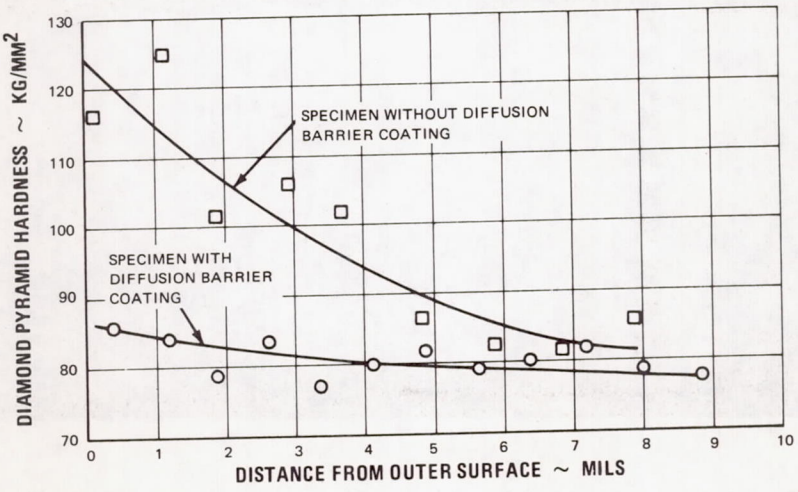
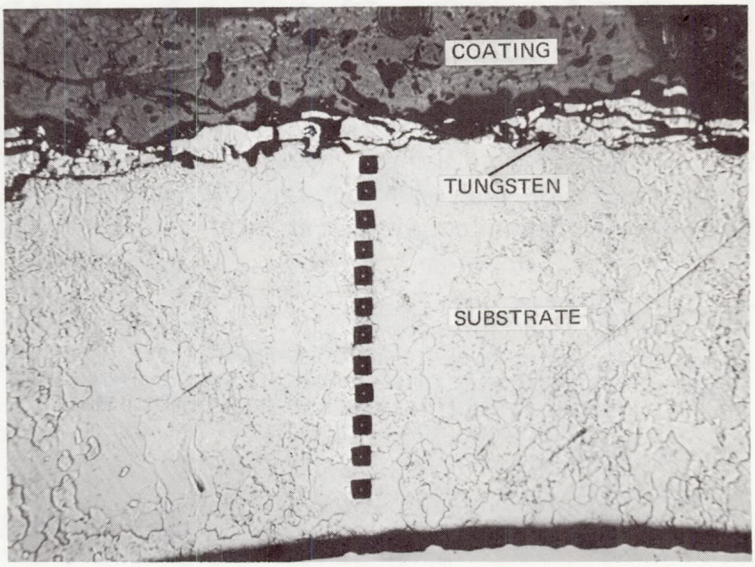
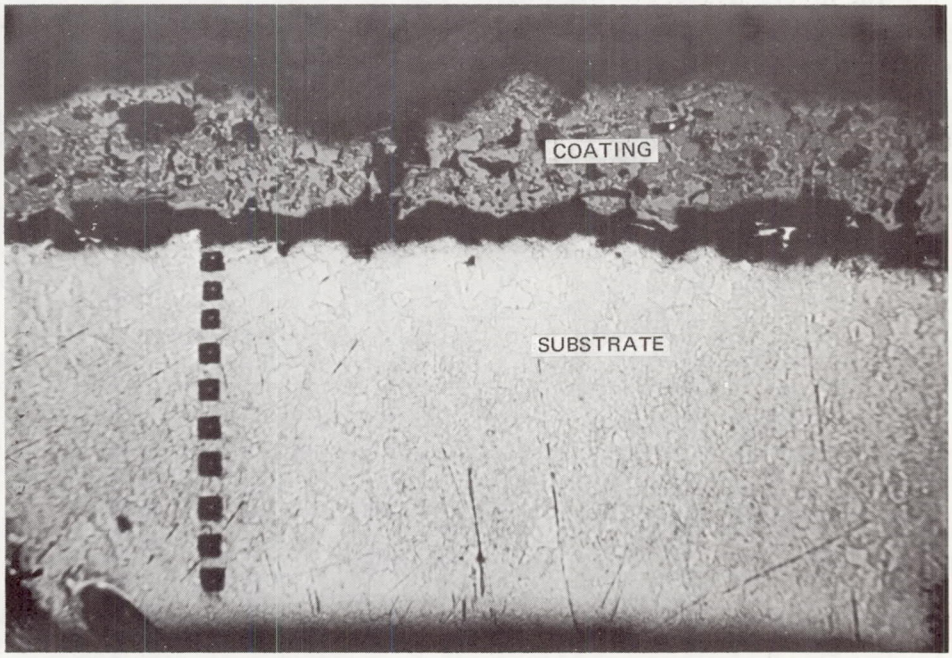


Figure 50 Microhardness Test Results for Columbium-1 Percent Zirconium Tube Coated With Iron Titanate With and Without Tungsten Diffusion Barrier Coating



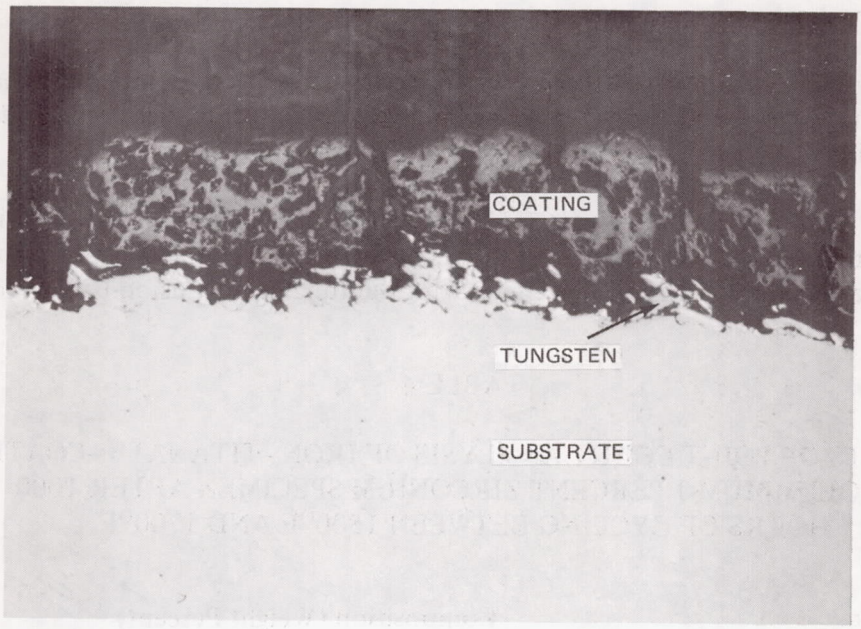
Mag: 200X

Figure 51 Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating and Iron Titanate and Cycled Between 1500°F and 1700°F in Vacuum for 1000 Hours Showing Points Where Hardness Data Were Taken



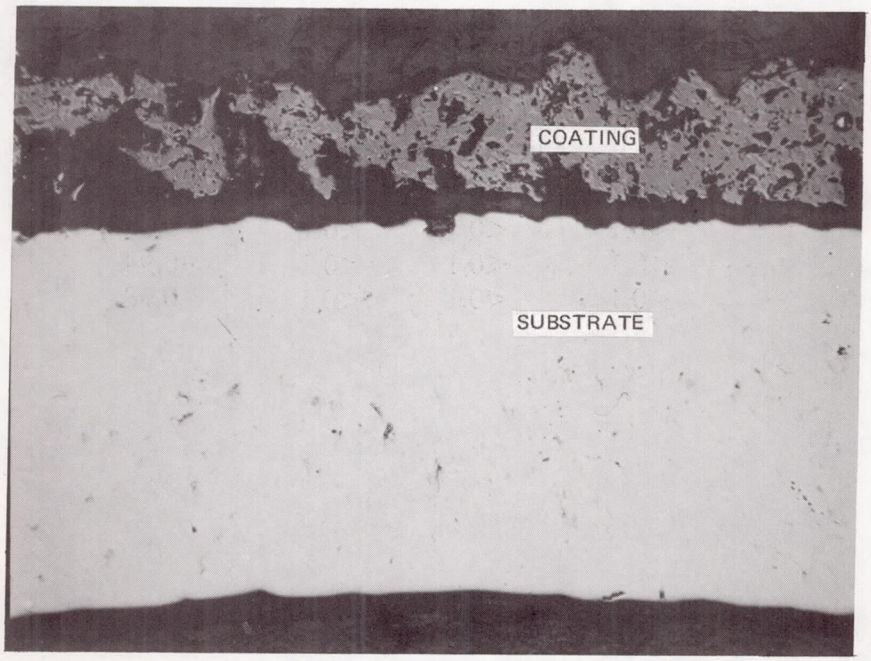
Mag: 200X

Figure 52 Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Cycled Between 1500°F and 1700°F in Vacuum for 1000 Hours Showing Points Where Hardness Data Were Taken



Mag: 200X

Figure 53 Unetched Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating and Iron Titanate and Cycled Between 1500°F and 1700°F in Vaccum for 1000 Hours



Mag: 200X

Figure 54 Unetched Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Cycled Between 1500°F and 1700°F in Vacuum for 1000 Hours

5. Microprobe Analyses

The microprobe analyses involved three types of tests. These were point-count analyses, X-ray line scan analyses, and X-ray beam scan analyses. The techniques used are described in the appendix.

The results of the point count analyses are shown in Tables 4 and 5. In both specimens, small concentrations of the coating constituents were detected in the substrate, but the concentrations are generally less in the specimen with the tungsten diffusion-barrier coating.

TABLE 4

RESULTS OF POINT COUNT ANALYSIS OF IRON–TITANATE–COATED COLUMBIUM-1 PERCENT ZIRCONIUM SPECIMEN AFTER 1000 HOURS OF CYCLING BETWEEN 1500°F AND 1700°F

Distance From Coating-Substrate Interface (Mils)	Composition (Weight Percent)				
	Fe	Ti	O	Zr	Cb
Center of Coating	49	23	26	<0.1	<0.1
0.4	0.2	0.1	0.1	0.93	Bal
1.2	<0.1	<0.1	<0.1	0.92	Bal
2.0	<0.1	<0.1	<0.1	0.82	Bal
2.8	<0.1	<0.1	<0.1	0.99	Bal
3.5	<0.1	<0.1	<0.1	1.01	Bal
4.5	<0.1	<0.1	<0.1	0.90	Bal
5.4	<0.1	<0.1	<0.1	0.90	Bal
6.7	<0.1	<0.1	<0.1	0.88	Bal
7.3	<0.1	<0.1	<0.1	0.94	Bal
8.3	<0.1	<0.1	<0.1	0.98	Bal

TABLE 5

RESULTS OF POINT–COUNT ANALYSIS OF IRON–TITANATE COATED COLUMBIUM–1 PERCENT ZIRCONIUM SPECIMEN WITH TUNGSTEN DIFFUSION BARRIER COATING AFTER 1000 HOURS OF CYCLING BETWEEN 1500°F AND 1700°F

Distance from Coating Substrate Interface (Mils)	Composition (Weight Percent)				
	Fe	Ti	O	Zr	Cb
(Coating)	43.0	23.0	High	0.05	0.05
(Tungsten)	0.1	0.1	----	0.05	0.05
0.3	0.05	< 0.1	0.13	1.3	Bal
1.0	< 0.1	< 0.1	0.10	1.2	Bal
1.7	< 0.1	< 0.1	<0.1	1.4	Bal
2.7	< 0.1	< 0.1	<0.1	1.1	Bal
3.7	< 0.1	< 0.1	<0.1	1.3	Bal
4.7	< 0.1	< 0.1	<0.1	1.3	Bal
5.6	< 0.1	< 0.1	<0.1	1.2	Bal
6.7	< 0.1	< 0.1	<0.1	1.0	Bal
7.7	< 0.1	< 0.1	<0.1	1.4	Bal
8.7	< 0.1	< 0.1	<0.1	1.3	Bal

X-ray line scans were made across both substrates for the elements of interest with the emission of titanium being recorded in all cases to indicate the coating-substrate interface. The results obtained for the specimen with the tungsten diffusion-barrier coating are shown in Figures 55 through 58. No detectable diffusion of columbium occurred out of the substrate. Detectable concentrations of zirconium were found in both the tungsten and the iron titanate, but the data do not indicate a gradient in either the tungsten or the iron titanate, so it is not certain that the zirconium detected diffused from the substrate. No iron was detected in the substrate, but a small uniform concentration of iron was detected in the tungsten layer. In the iron-titanate coating, the iron concentrations are irregular with the regions which are rich in iron being low in titanium, indicating the inhomogeneous nature of the coating. The X-ray line scan for tungsten indicated a small but definite gradient of tungsten in the iron-titanate coating, indicating that some diffusion of the tungsten into the iron-titanate coating did occur. No tungsten was detected in the substrate. None of the line scans for titanium indicated any diffusion of the titanium out of the iron-titanate coating. The X-ray beam scan results for the specimen with the tungsten-barrier coating are shown in Figure 59. In these oscilloscope photographs, the light intensity in the specimen current photograph is indicative of the atomic number of the chemical constituent on the surface of the sample. In the remaining photographs, the light intensity is indicative of the concentration of the particular element for which the scan was performed. These photographs show trends similar to those shown in the X-ray line scan data.

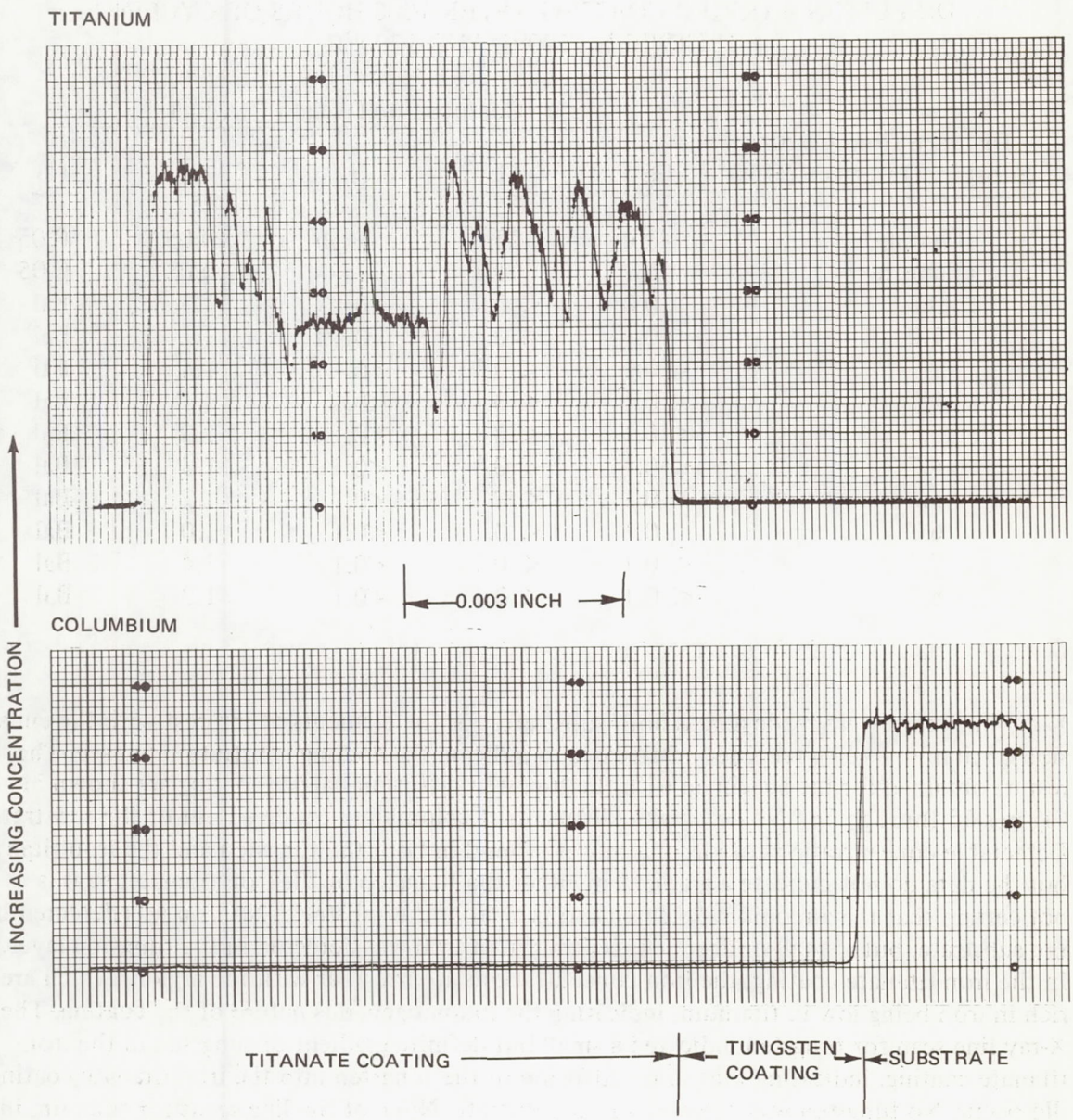


Figure 55 X-Ray Line Scan Intensities for Titanium and Columbium Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube With Tungsten Diffusion-Barrier Coating After 1000 Hours of Cycling Between 1500°F and 1700°F

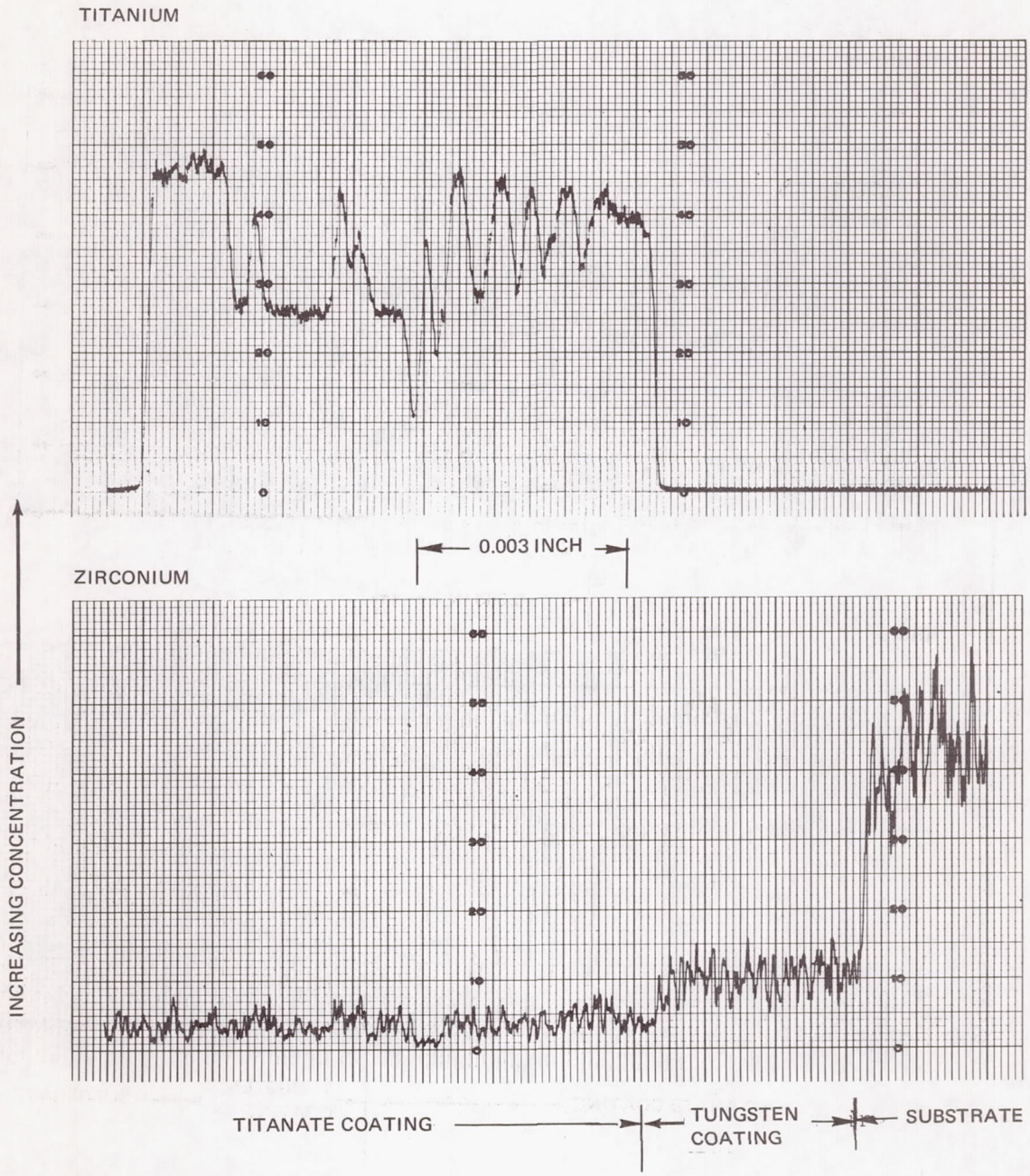


Figure 56 X-Ray Line Scan Intensities for Titanium and Zirconium Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube With Tungsten Diffusion-Barrier Coating After 1000 Hours of Cycling Between 1500°F and 1700°F

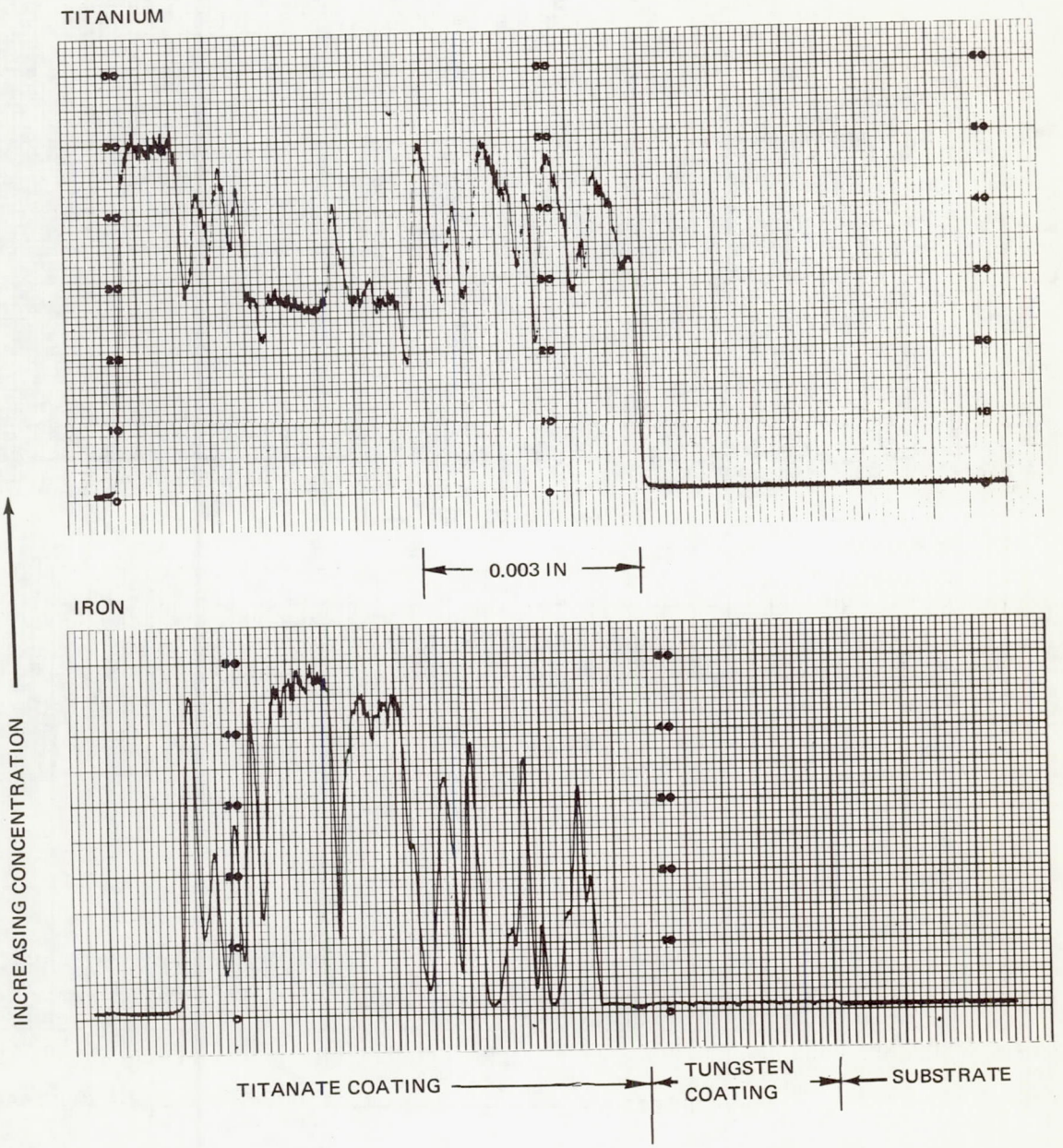


Figure 57 X-Ray Line Scan Intensities for Titanium and Iron Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating After 1000 Hours of Cycling Between 1500°F and 1700°F

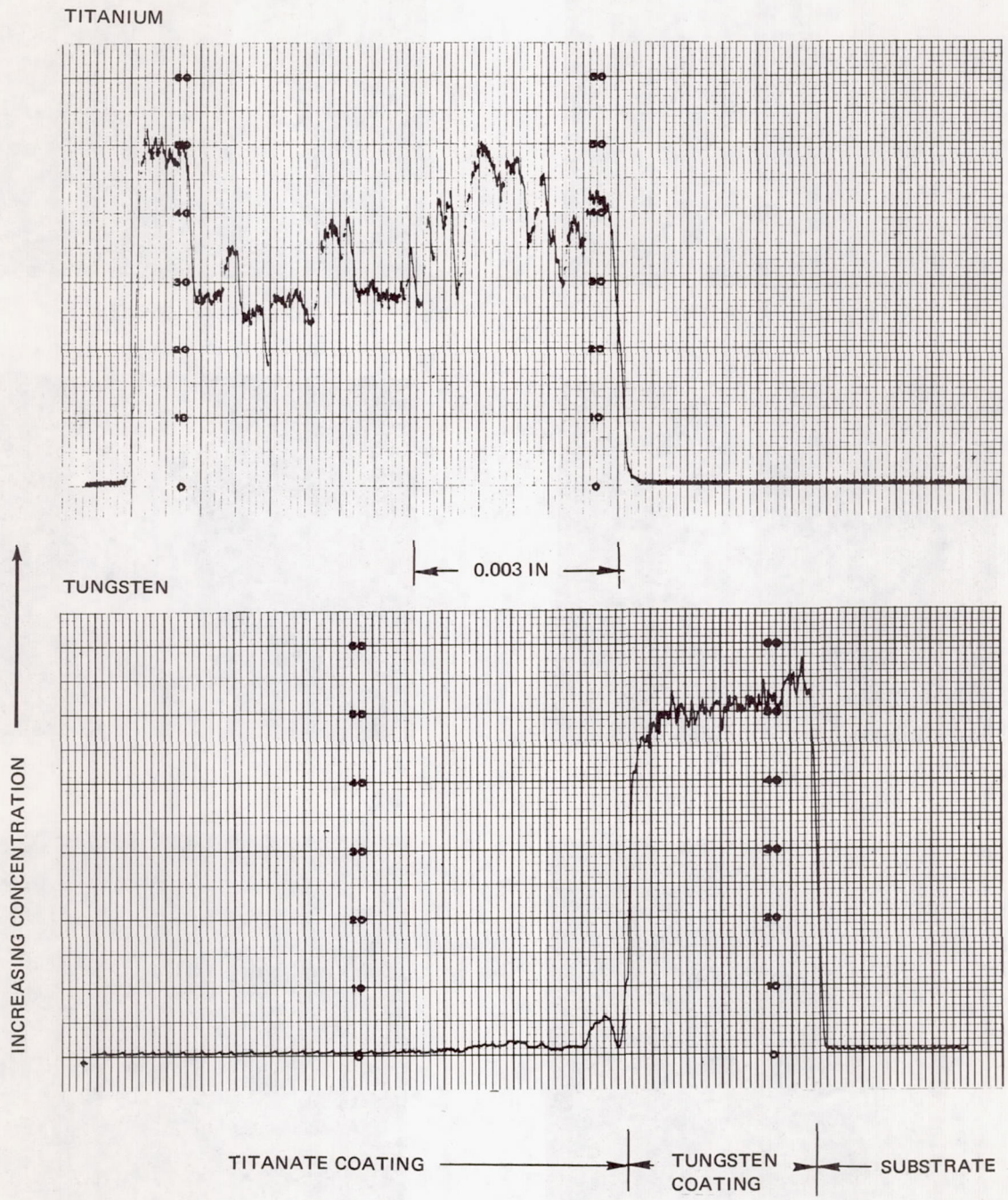
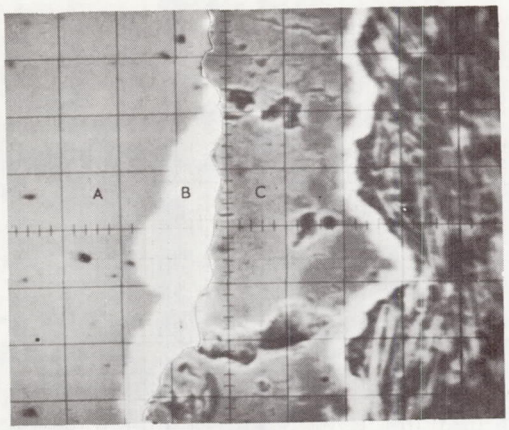
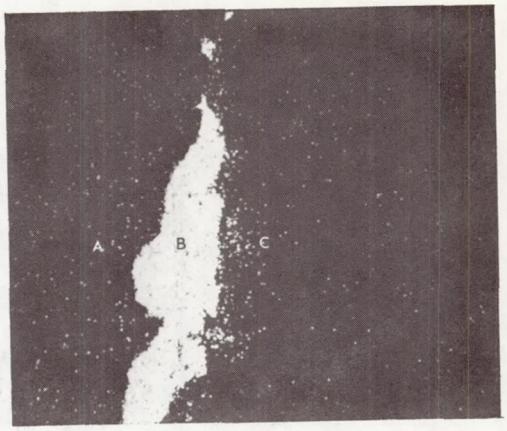


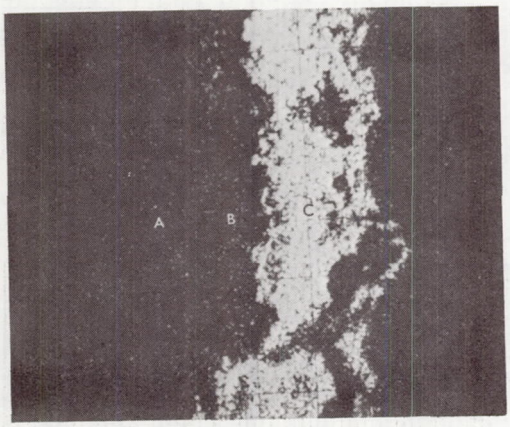
Figure 58 X-Ray Line Scan Intensities for Titanium and Tungsten Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating After 1000 Hours of Cycling Between 1500°F and 1700°F



SPECIMEN CURRENT



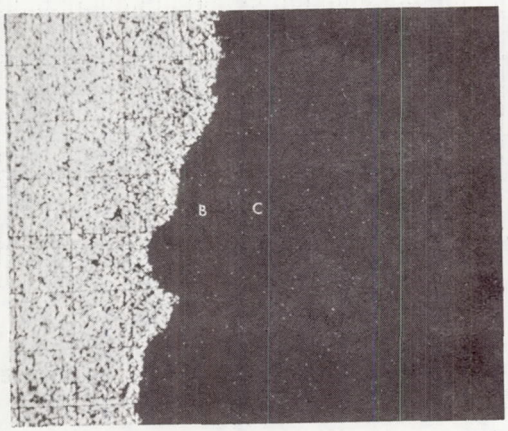
TUNGSTEN X-RAYS



IRON X-RAYS



TITANIUM X-RAYS



COLUMBIUM X-RAYS



ZIRCONIUM X-RAYS

Mag: 280X

Figure 59 X-Ray Beam Scan Photographs of Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube Coated With Tungsten Diffusion-Barrier Coating After 1000 Hours of Cycling Between 1500°F and 1700°F

A. Substrate B. Tungsten C. Coating

The X-ray line scan results for the specimen without the tungsten diffusion-barrier coating are shown in Figures 60, 61, and 62. Again, no diffusion of the columbium occurred. The scan for zirconium is similar to that for the other specimen with a relatively uniform concentration of zirconium in the iron titanate coating. This scan also shows a region of extremely low zirconium concentration in the vicinity of the coating-substrate interface, indicating a gap between the coating and the substrate. The scan for iron was made in a region where a small piece of the coating material remained adherent to the substrate, as indicated by the small peak in both the iron and titanium scans. Both of these scans show clearly identifiable concentration gradients extending into the substrate for a short distance, indicating that diffusion did occur. The X-ray beam scan results are shown in Figure 63 and verify the results of the X-ray line scan data, including the slight gradients of both iron and titanium into the substrate.

6. Conclusions

The data obtained from analyzing the iron-titanate-coated columbium-1 percent zirconium specimens with and without a tungsten-barrier coating indicate that the tungsten barrier coating improves the bond strength of the coating to the substrate and that it retards the rate of diffusion of the various constituents across the coating-substrate interface. However, because of the short duration of the test, even without the diffusion-barrier coating, the amount of diffusion was barely detectable, making a realistic evaluation of the value of the tungsten-barrier coating extremely difficult. Determination of diffusion rates over longer periods and at isothermal conditions would provide more quantitative data which would be valuable for engineering design purposes.

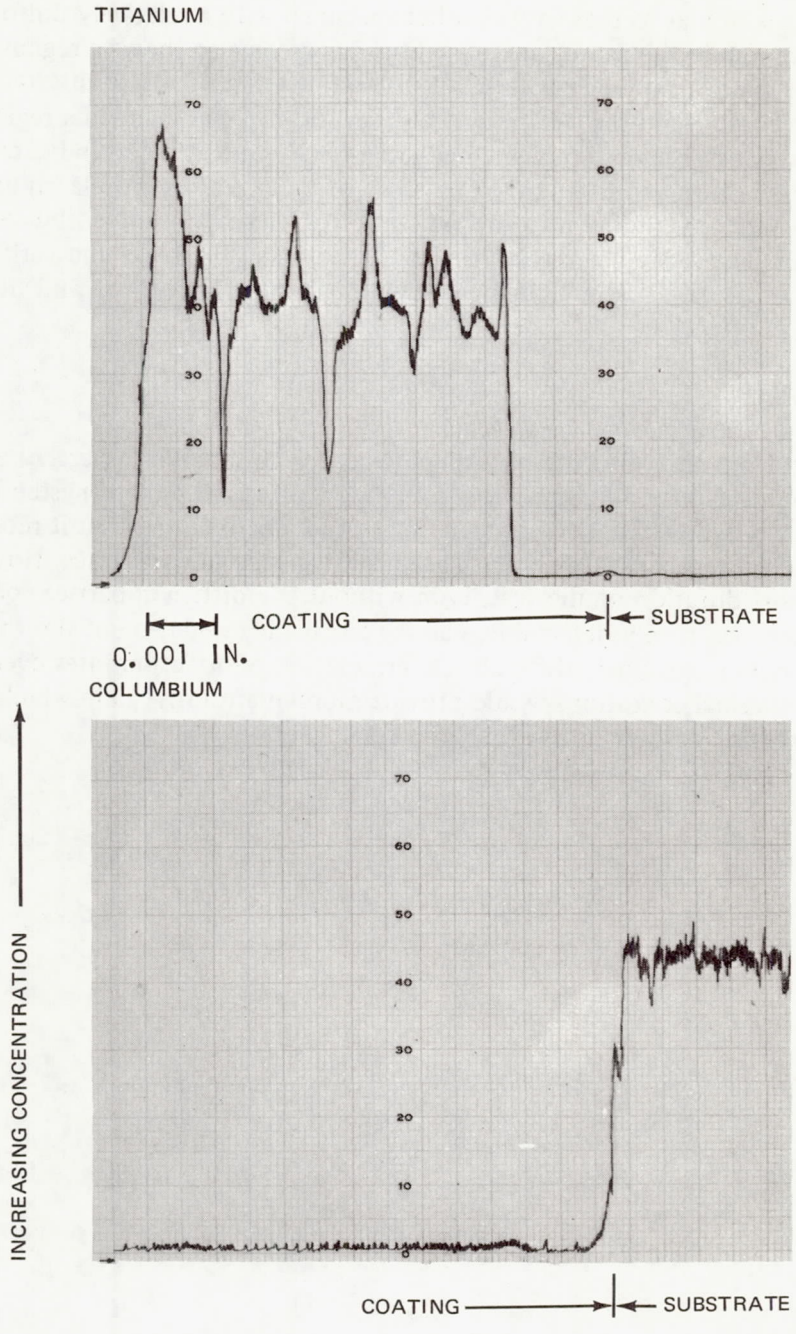


Figure 60 X-Ray Line Scan Intensities for Titanium and Columbium Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After 1000 Hours of Cycling Between 1500°F and 1700°F

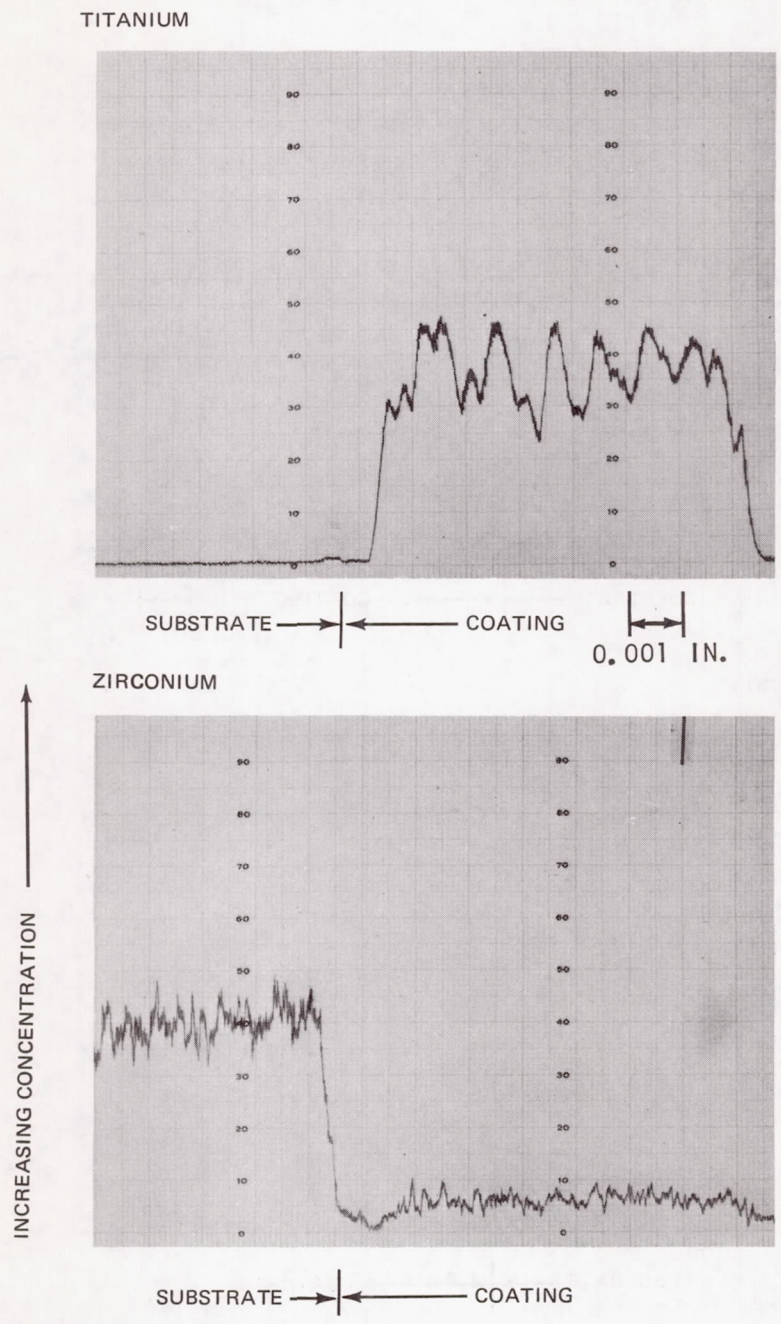


Figure 61 X-Ray Line Scan Intensities for Titanium and Zirconium Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After 1000 Hours of Cycling Between 1500°F and 1700°F

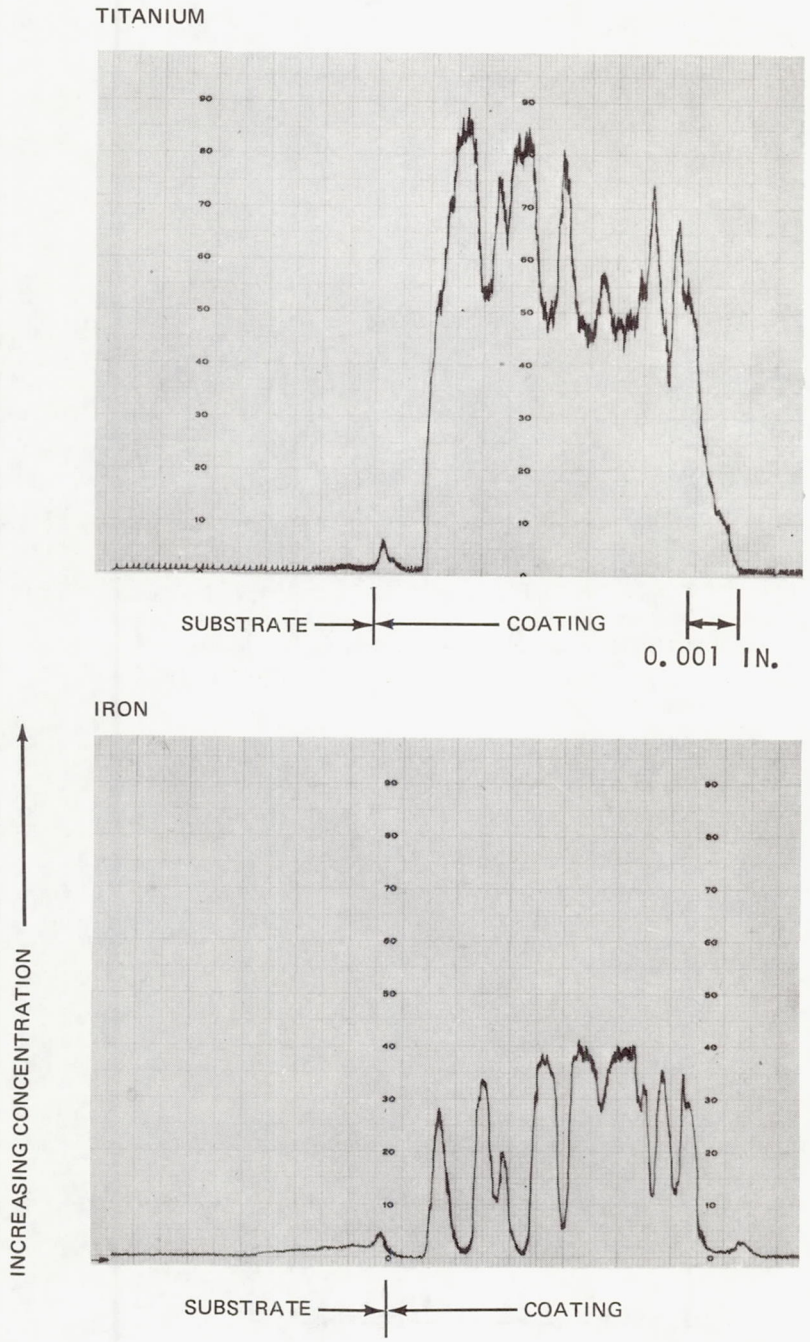
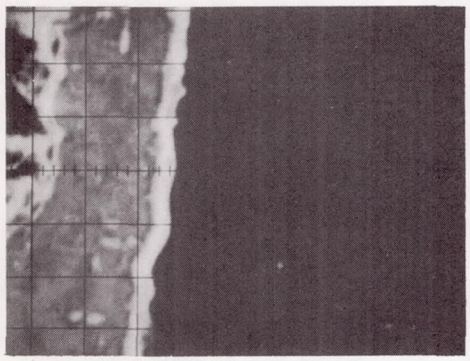
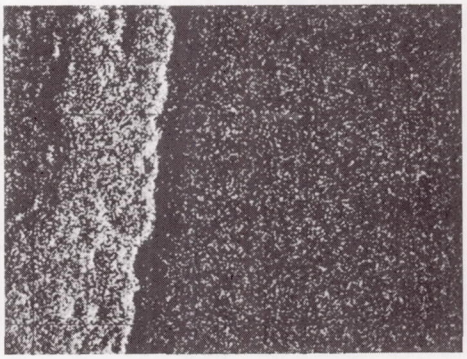


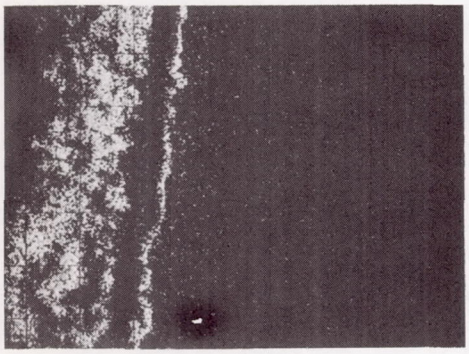
Figure 62 X-Ray Line Scan Intensities for Titanium and Iron Across Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After 1000 Hours of Cycling Between 1500°F and 1700°F



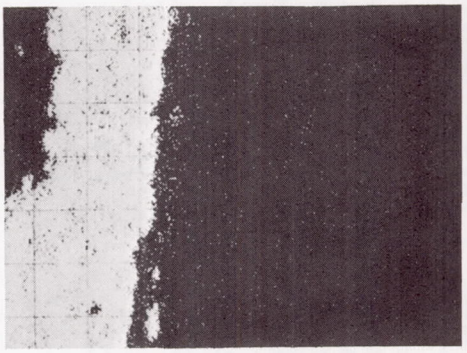
SPECIMEN CURRENT



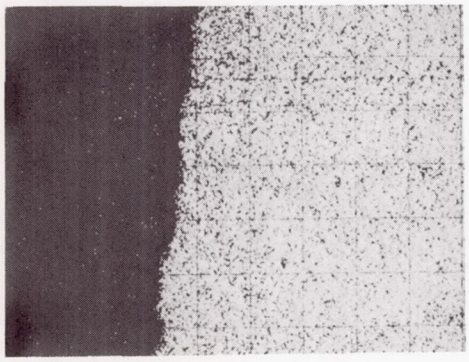
OXYGEN X-RAYS



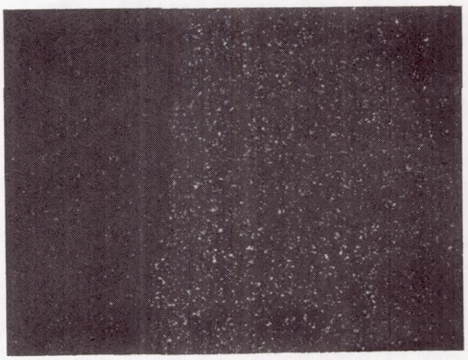
IRON X-RAYS



TITANIUM X-RAYS



COLUMBIUM X-RAYS



ZIRCONIUM X-RAYS

Mag: 280X

Figure 63 X-Ray Beam Scan Photographs for Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After 1000 Hours of Cycling Between 1500°F and 1700°F

IV. COATED AISI-310 STAINLESS STEEL

A. INTRODUCTION

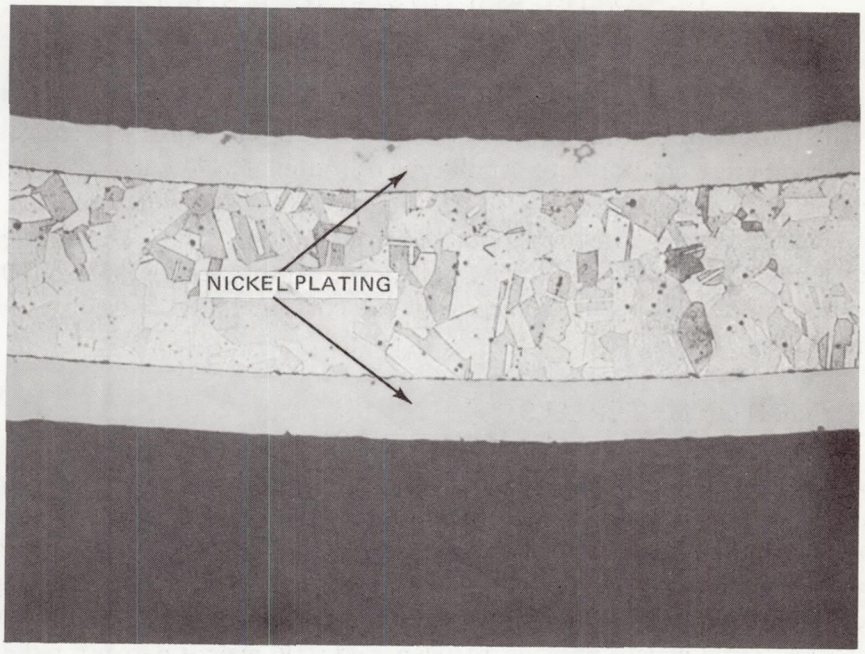
To evaluate the sources of natural iron titanate reviewed in Section II-E-2-a, tests were performed to determine the emittance of samples of iron titanate obtained from two different sources. One batch of material was FCT-11H obtained from the Continental Coatings Corporation, and the second batch was obtained from duPont. The materials were plasma sprayed onto AISI-310 stainless-steel tubes and vacuum emittance tested for 1000 hours at 1350°F. Following the vacuum emittance tests, the coatings and substrates were subjected to detailed metallurgical analyses.

B. DESCRIPTION OF MATERIALS

The AISI-310 stainless steel tubing was seamless and was nominally 9 inches long with an outside diameter of 0.25 inch and a wall thickness of 0.010 inch. Wet chemical analysis indicated the presence of 1.63 weight percent manganese, 0.45 weight percent silicon, 25.26 weight percent chromium, 19.42 weight percent nickel, 0.27 weight percent molybdenmum, and 0.04 weight percent copper. In addition, 0.027 weight percent oxygen, 0.002 weight percent hydrogen, 0.194 weight percent nitrogen, and 0.06 weight percent carbon were detected. A representative photomicrograph of the etched AISI-310 stainless-steel substrate in the as-received condition is shown in Figure 64, and an unetched photomicrograph is shown in Figure 65. Diamond pyramid hardness values were obtained at random locations. The hardness ranged from 187 to 206 mg/mm^2, with an average value of 196 mg/mm^2. X-ray line scans of the AISI-310 stainless steel before testing showed a uniform distribution of iron and no detectable titanium, as expected.

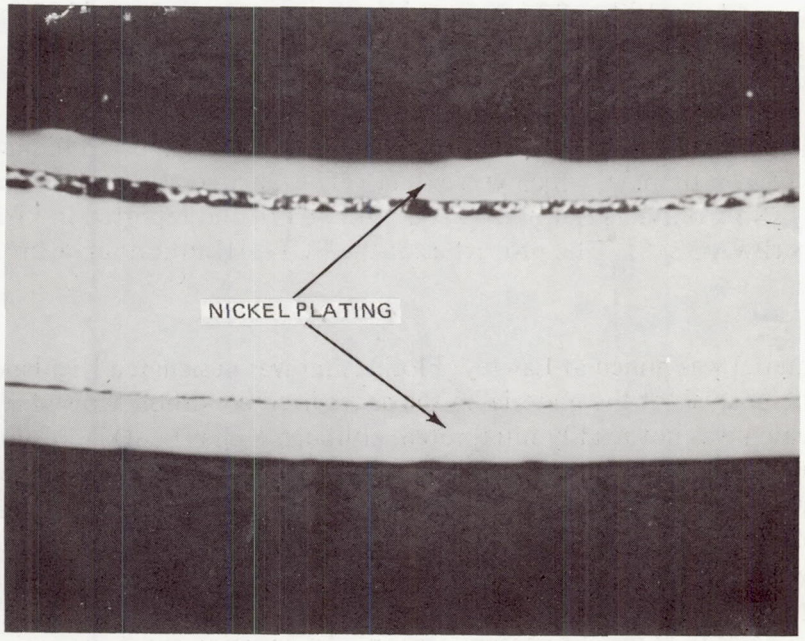
The FCT-11H iron titanate material was selected because it was expected to have properties similar to FCT-11 iron titanate, which was extensively evaluated as a part of the work performed under NASA Contracts NASw-104 and NAS3-4174 and reported in PWA-2206 and NASA CR-1278 (PWA-3278). The properties of the FCT-11H iron titanate are described in Section II-E-2-a.

The duPont material was mined at Lawtey, Florida and was designated Highland Ilmenite. X-ray diffraction analysis of the material in the as-received condition showed a poorly defined pattern which was not readily interpreted, although alpha (Fe_2O_3), rutile (TiO_2), and pseudobrookite (Fe_2TiO_5) phases were identified. After plasma spraying, a clear pattern was obtained which showed the major constituent to be pseudobrookite (Fe_2TiO_5) with an indication of the presence of rutile (TiO_2). A wet chemical analysis detected the presence of 63.52 weight percent TiO_2, 25.91 weight percent Fe_2O_3, 4.26 weight percent FeO, 1.66 weight percent Al_2O_3, and 0.98 weight percent SiO_2. Additional analysis detected the presence of 0.23 weight percent carbon. An emission spectrographic analysis was performed, and the impurities detected by this analysis are listed in the appendix. A screen analysis was performed to determine the particle size distribution, and the results are presented in Table 6.



Mag: 100X

Figure 64 Photomicrograph of AISI-310 Stainless Steel Tube as Received



Mag: 100X

Figure 65 Photomicrograph of Unetched AISI-310 Stainless Steel Tube As Received

TABLE 6

PARTICLE SIZE DISTRIBUTION OF DUPONT IRON TITANTE AS-RECEIVED

Weight Percent	Size Range (Microns)	(Mesh Size)
8.8	Greater than 177	Smaller than 80
30.4	177 to 149	80 to 100
29.2	149 to 125	100 to 120
27.9	125 to 88	120 to 170
3.0	88 to 74	170 to 200
0.7	74 to 44	200 to 325

The material was ground in a steel-ball mill to reduce the particles to a size more suitable for plasma spraying. The material was subsequently screened and those between the 200 and 325 mesh sizes were used for spraying. Plasma spraying was performed at ambient temperature using the plasma spray parameters listed in the appendix.

C. EMITTANCE TEST RESULTS

The specimens were subjected to 1000-hour vacuum emittance tests using the equipment and procedures described in Section II-D-3. Both tests were performed at 1350°F.

The emittance test results for the FCT-11H iron-titanate-coated specimen are shown in Figure 66, and the results for the duPont iron-titanate-coated specimen are shown in Figure 67. The emittance of the FCT-11H material was 0.89 at the beginning of the test and 0.93 at the end at 1350°F. The emittance of the duPont material was 0.93 at the beginning of the test and decreased slightly to 0.92 by the end. Testing produced no visible changes to either of the specimens, and both coatings remained adherent to the substrates.

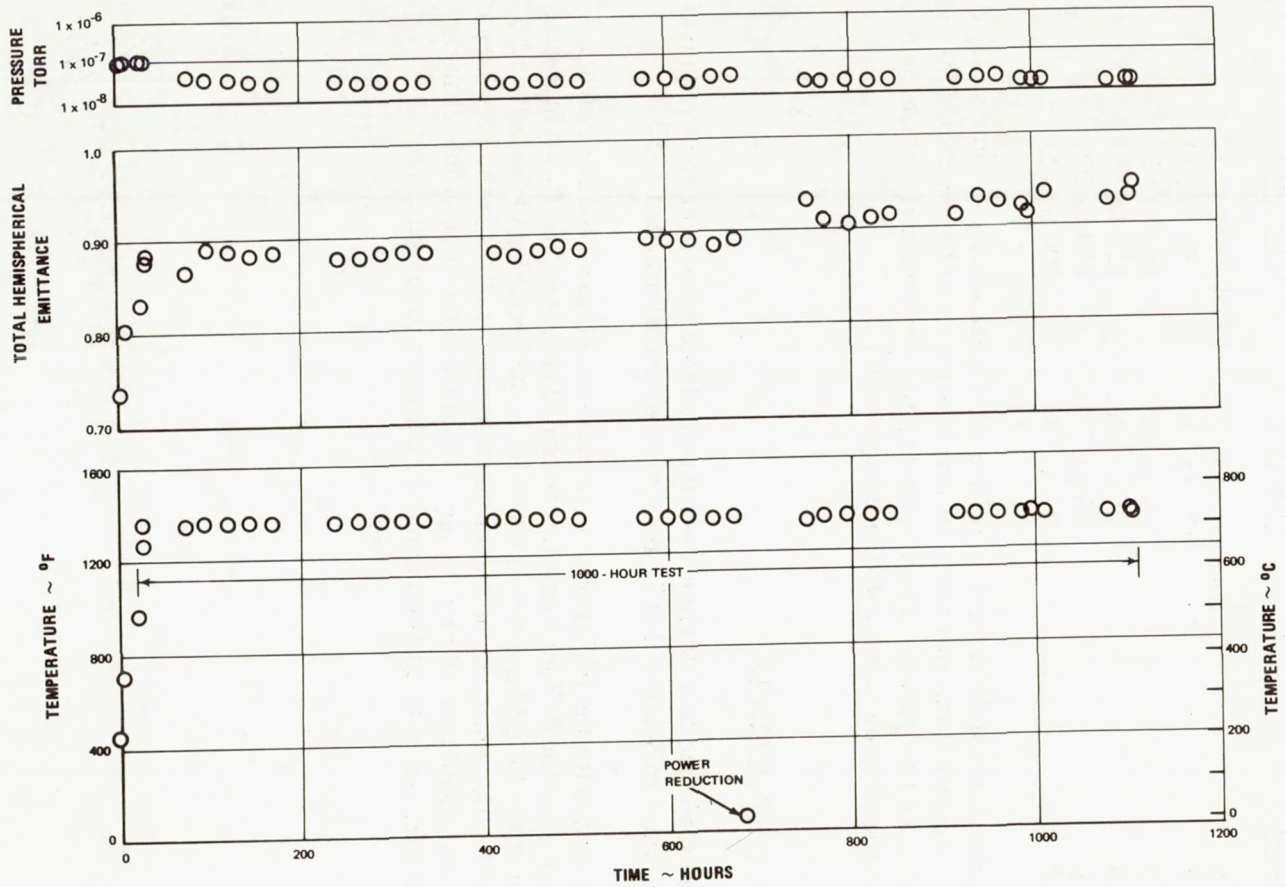


Figure 66 Pressure, Emittance, and Temperature Data for AISI-310 Stainless-Steel Tube Coated with FCT-11H Iron Titanate

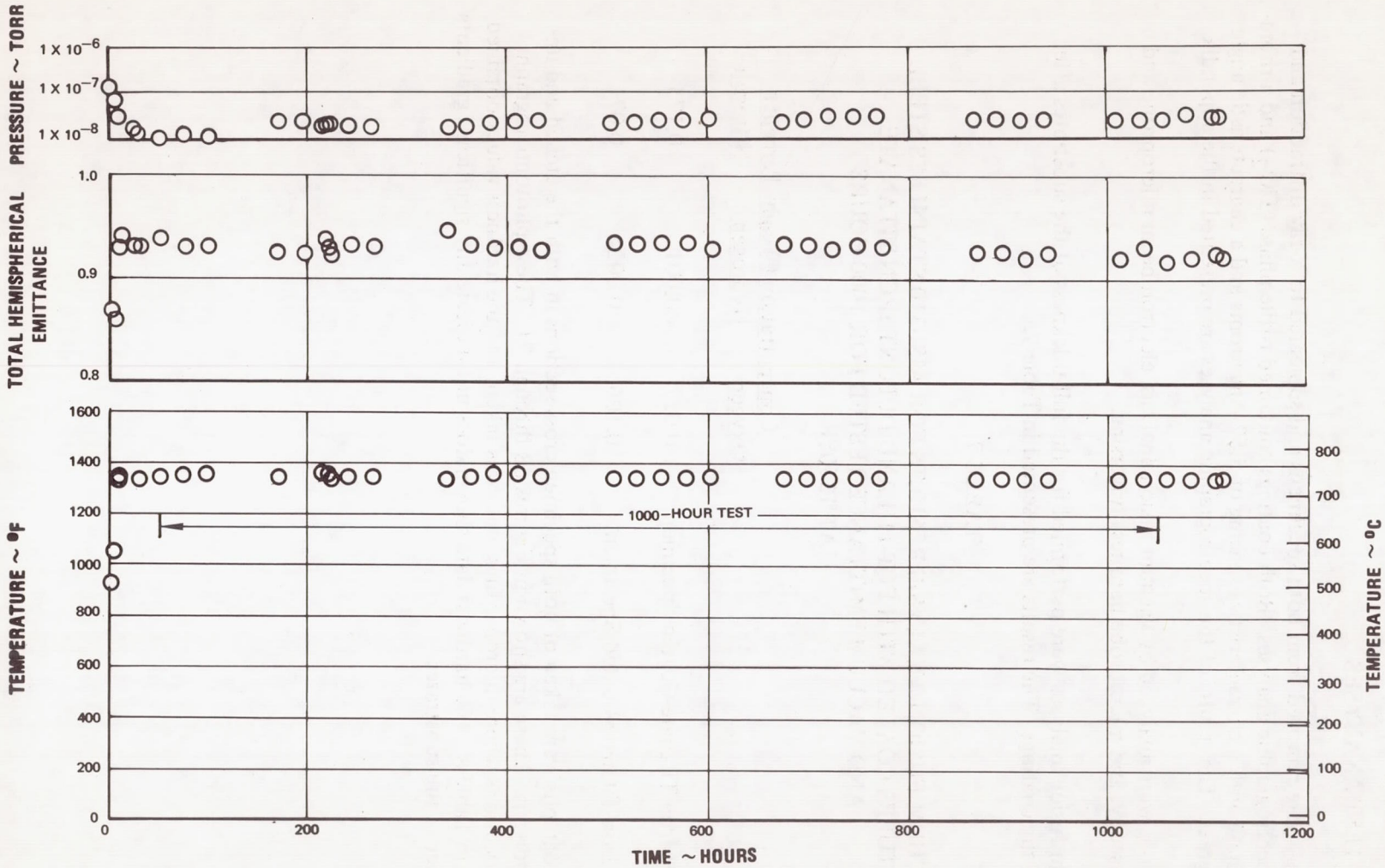


Figure 67 Pressure, Emittance, and Temperature Data for AISI-310 Stainless-Steel Tube Coated with DuPont Iron Titanate

D. POST-TEST ANALYSES

The coatings were removed from both specimens and subjected to X-ray diffraction and emission spectrographic analyses. Both coatings contained rutile phase (TiO_2) and a rhombohedral phase with a characteristics spacing of 5.52 Angstroms and a characteristic angle of 54.5 degrees. The results of the spectrographic analyses are presented in the appendix.

The substrates were analyzed by vacuum fusion analysis, electron beam microprobe and light microscopy, and microprobe hardness traversing.

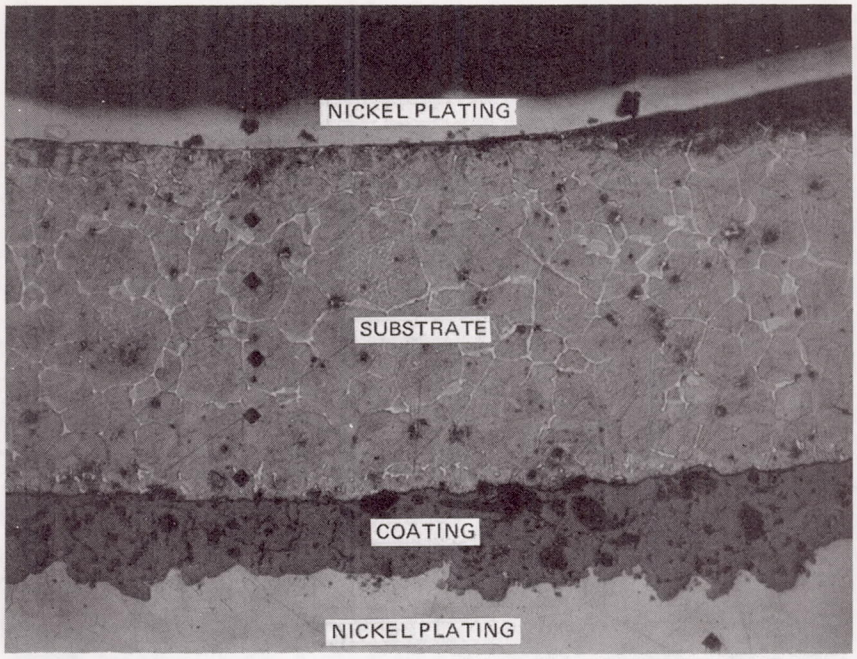
The vacuum fusion analyses were performed for the full thickness of the substrates after removal of the coatings. The results are presented in Table 7.

TABLE 7

VACUUM FUSION ANALYSIS RESULTS FOR AISI-310 STAINLESS STEEL TUBES COATED WITH FCT-11H AND DUPONT IRON TITANATE AND VACUUM EMITTANCE TESTED FOR 1000 HOURS AT 1350°F

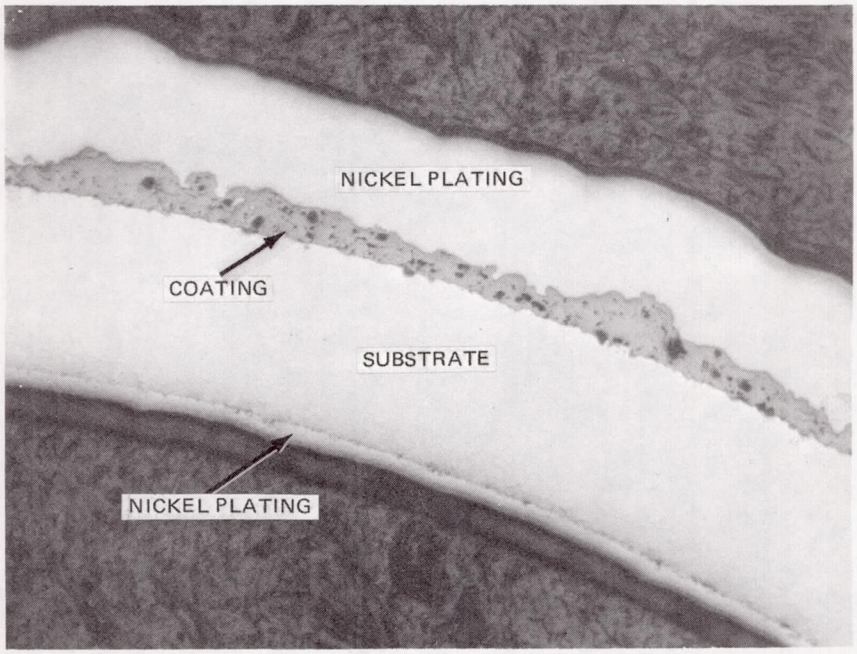
	Concentration (Weight Percent)		
	Oxygen	Hydrogen	Nitrogen
FCT-11H Iron Titanate-Coated Specimen	0.027	<0.001	0.175
DuPont Iron-Titanate-Coated Specimen	0.106	0.002	0.071

Photomicrographs were taken of both specimen cross sections in both the etched and unetched conditons. These are shown in Figures 68 through 71. These photomicrographs show the locations where microhardness data was taken, and the hardness values obtained are shown in Table 8. The hardness data shown does not indicate any significant gradients across either of the substrates.



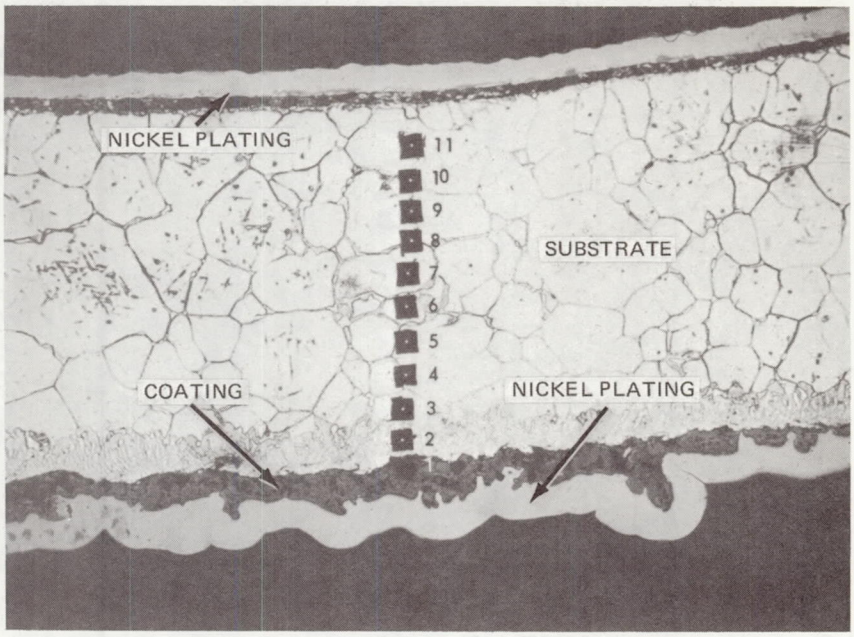
Mag: 180X

Figure 68 Photomicrograph of FCT-11H Iron-Titanate-Coated AISI-310 Stainless-Steel Tube After Vacuum Emittance Testing for 1000 Hours at 1350°F



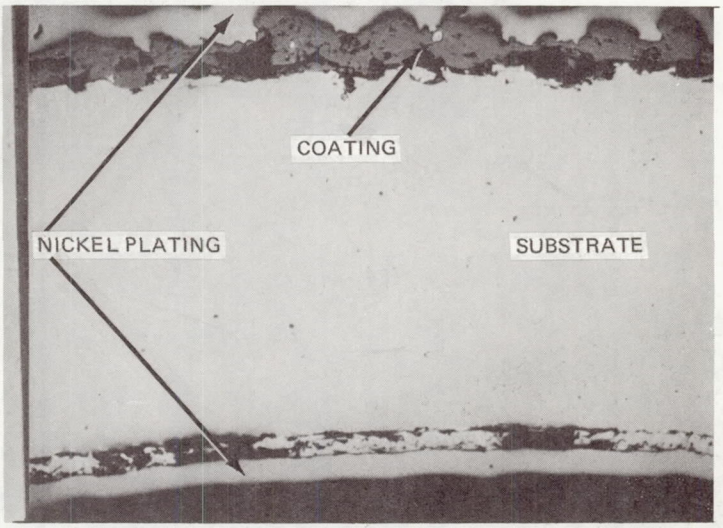
Mag: 100X

Figure 69 Photomicrograph of Unetched FCT-11H Iron-Titanate-Coated AISI-310 Stainless Steel Tube After Vacuum Emittance Testing for 1000 Hours at 1350°F



Mag: 180X

Figure 70 Photomicrograph of duPont Iron-Titanate-Coated AISI-310 Stainless-Steel Tube After Vacuum Emittance Testing for 1000 Hours at 1350°F



Mag: 180X

Figure 71 Photomicrograph of Unetched duPont Iron-Titanate-Coated AISI-310 Stainless-Steel Tube After Vacuum Emittance Testing for 1000 Hours at 1350°F

TABLE 8

DIAMOND PYRAMID HARDNESS VALUES FOR AISI-310 STAINLESS STEEL TUBES COATED WITH FCT-11H AND DUPONT IRON TITANATE AND VACUUM EMITTANCE TESTED FOR 1000 HOURS AT 1350°F

DuPont Iron-Titanate-Coated Specimen		FCT-11H Iron-Titanate-Coated Specimen	
Depth Below Coating-Substrate Interface (Microns)	Diamond Pyramid Hardness (mg/mm^2)	Depth Below Coating-Substrate Interface (Microns)	Diamond Pyramid Hardness (mg/mm^2)
Coating	307	0.5	200
0.32	224	2.3	200
1.3	213	3.9	200
2.3	213	6.1	200
3.2	190	7.8	230
4.3	228	8.9	240
5.2	228		
6.1	190		
6.9	213		
7.9	228		
8.9	187		

X-ray line scans were taken for manganese, titanium, iron, chromium, and nickel for both substrates, and the results are presented in Figures 72 through 76. Little if any diffusion of titanium was detected from either coating into the substrates. The coatings themselves appear very similar with high varying concentrations of titanium and with the higher concentrations of titanium being associated with lower concentrations of iron.

Figure 72 shows that the FCT-11H iron-titanate coating contains two titanium concentration plateaus suggesting the presence of two titanium-rich phases in the coating. In addition, at point 2 in Figure 72, a large globular phase rich in aluminum and silicon was detected, and at point 4 a region rich in aluminum was detected. The aluminum-rich region at point 4 is attributed to polishing compound imbedded in a large pore in the coating. There also appears to be a reaction zone below the coating that is slightly richer in chromium and iron and lower in manganese, and there is metallographic evidence that some precipitation occurred in this region. The compositions given in Figure 72 are approximate.

The regions in the FCT-11H iron-titanate coating which were rich in silicon and aluminum were glassy in appearance. A photomicrograph of one of these regions is shown in Figure 77 together with the location of the trace for which data is shown in Figure 72.

Point count analyses were performed at the points shown in Figure 78 on the duPont iron-titanate-coated specimen, and the results are shown in Table 9. This data shows a small amount of titanium diffusion across the coating-substrate boundary into the substrate. X-ray beam scan photographs for this specimen are shown in Figure 79.

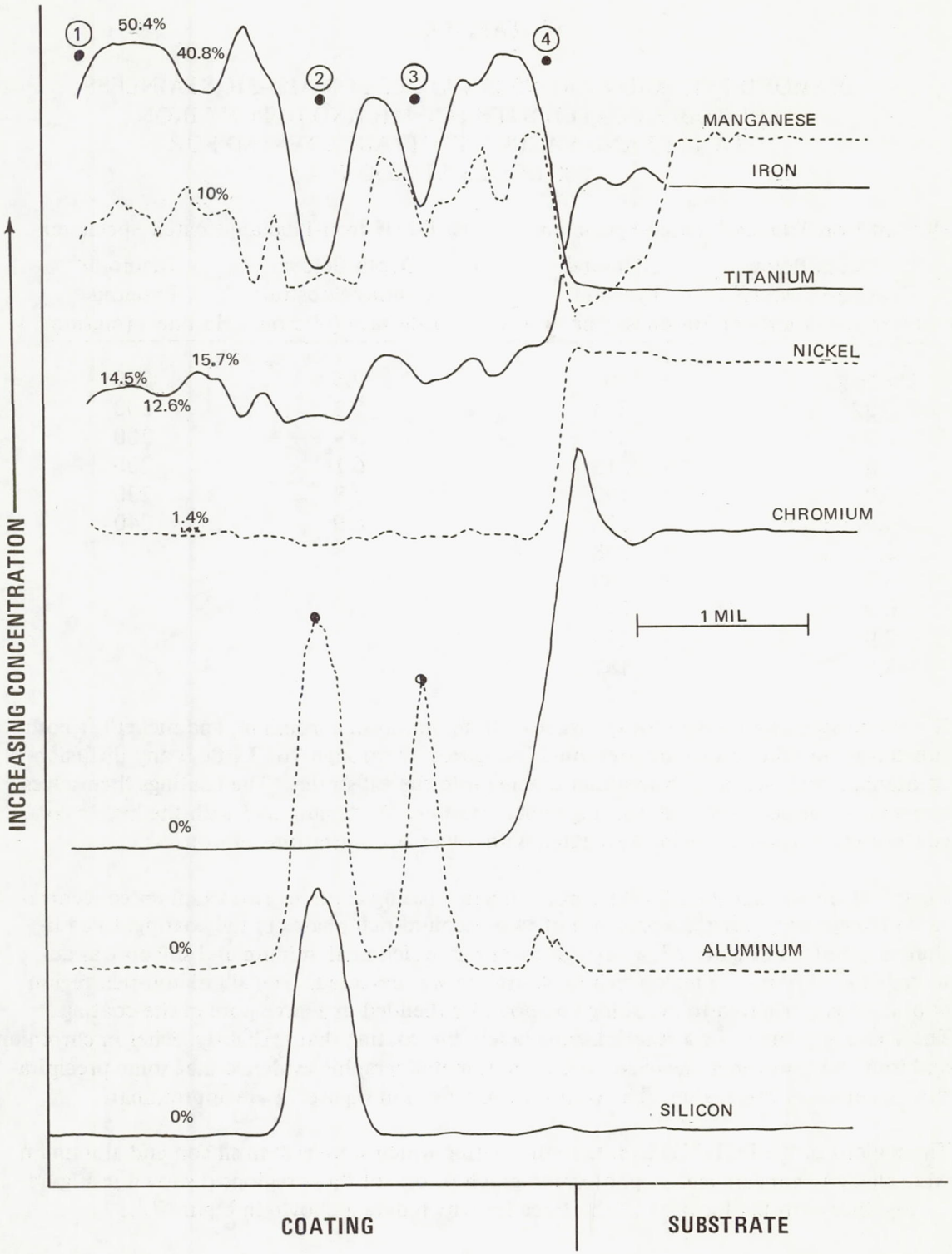


Figure 72 X-Ray Line Scan Intensities for Manganese, Titanium, Iron, Chromium, and Nickel Across AISI-310 Stainless-Steel Tube Coated With FCT-11H Iron Titanate After 1000 Hours at 1350°F

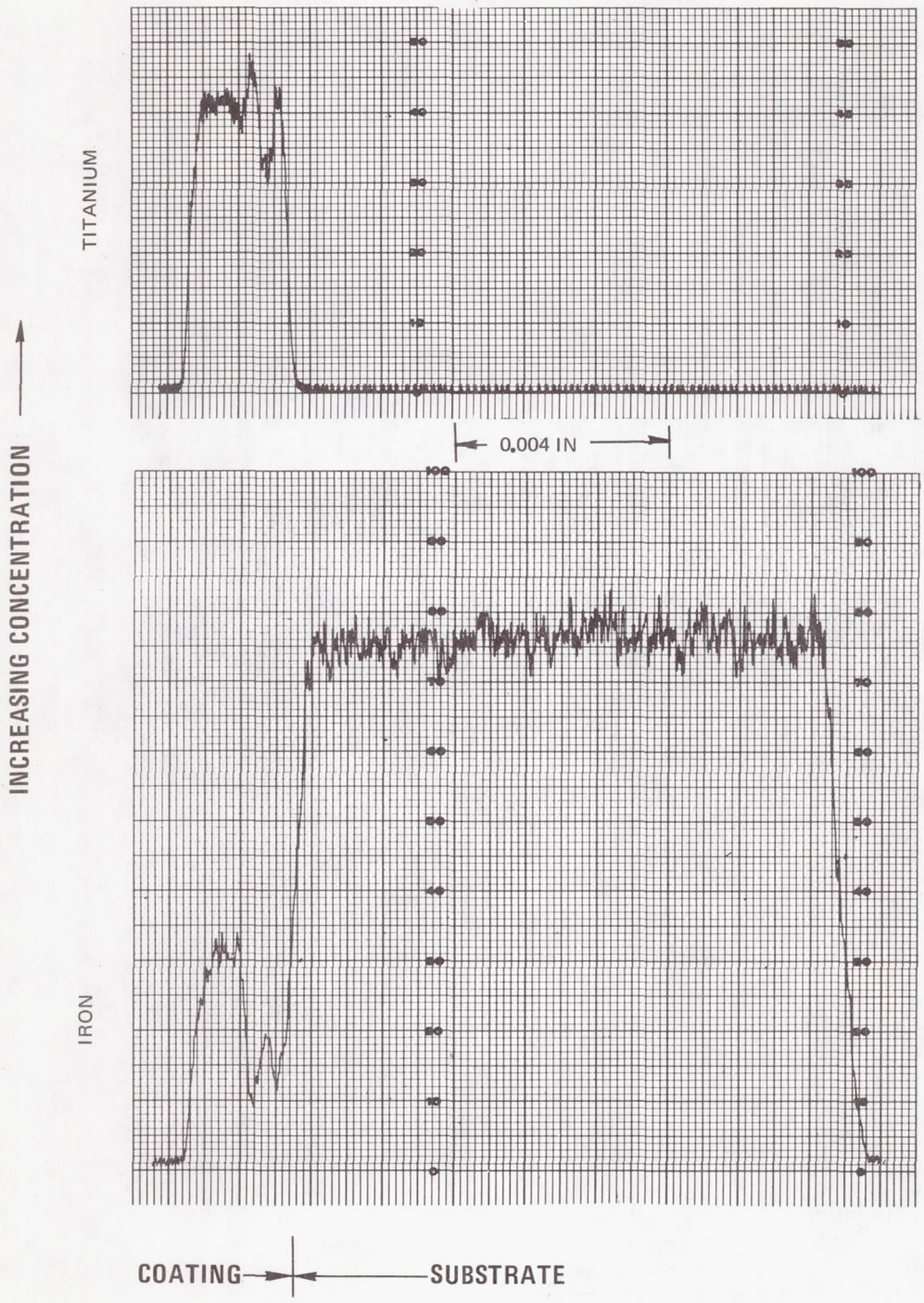


Figure 73 X-Ray Line Scan Intensities for Titanium and Iron Across AISI-310 Stainless-Steel Tube Coated With duPont Iron Titanate After 1000 Hours at 1350°F

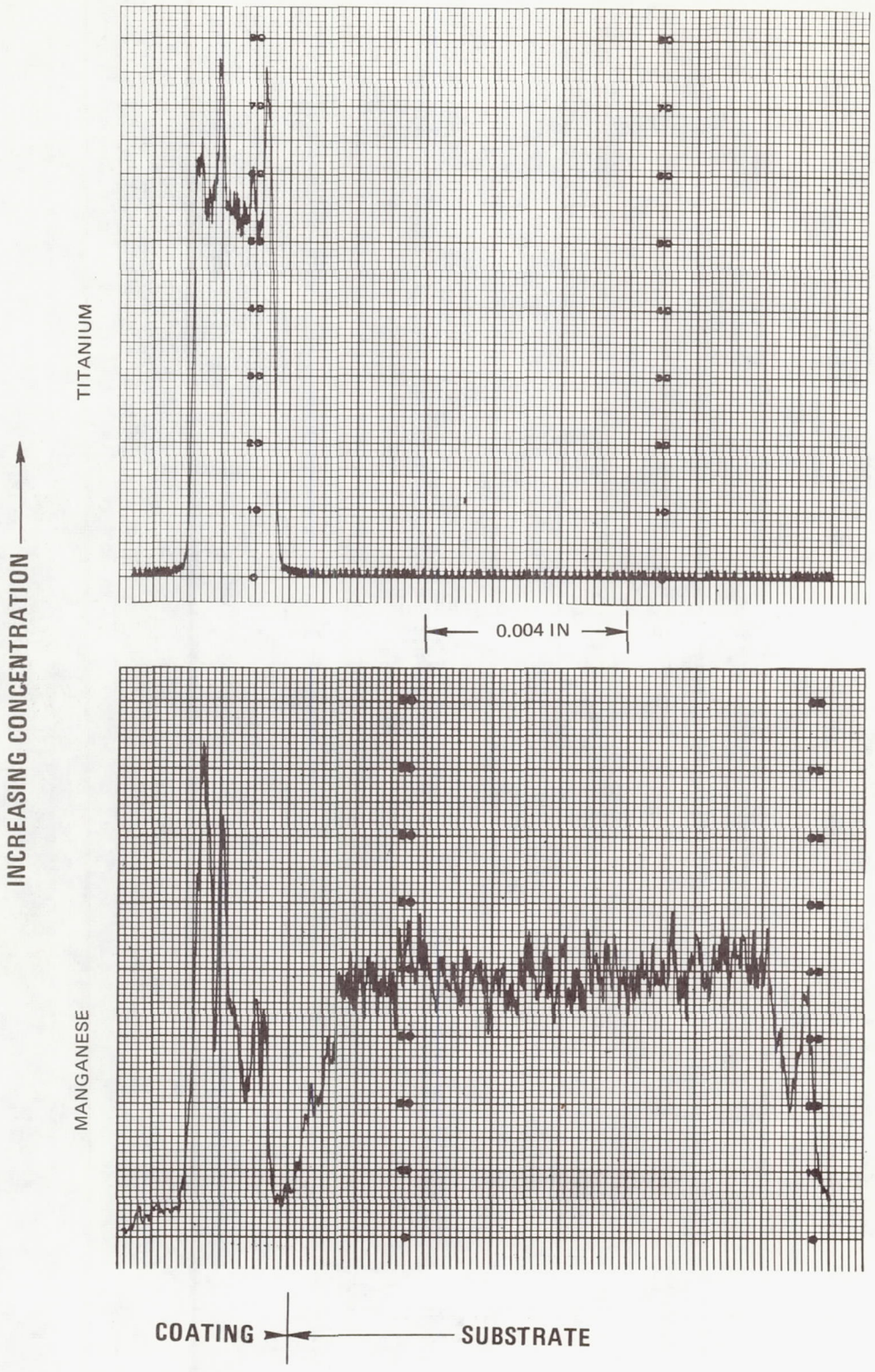


Figure 74 X-Ray Line Scan Intensities for Titanium and Manganese Across AISI-310 Stainless-Steel Tube Coated With duPont Iron Titanate After 1000 Hours at 1350°F

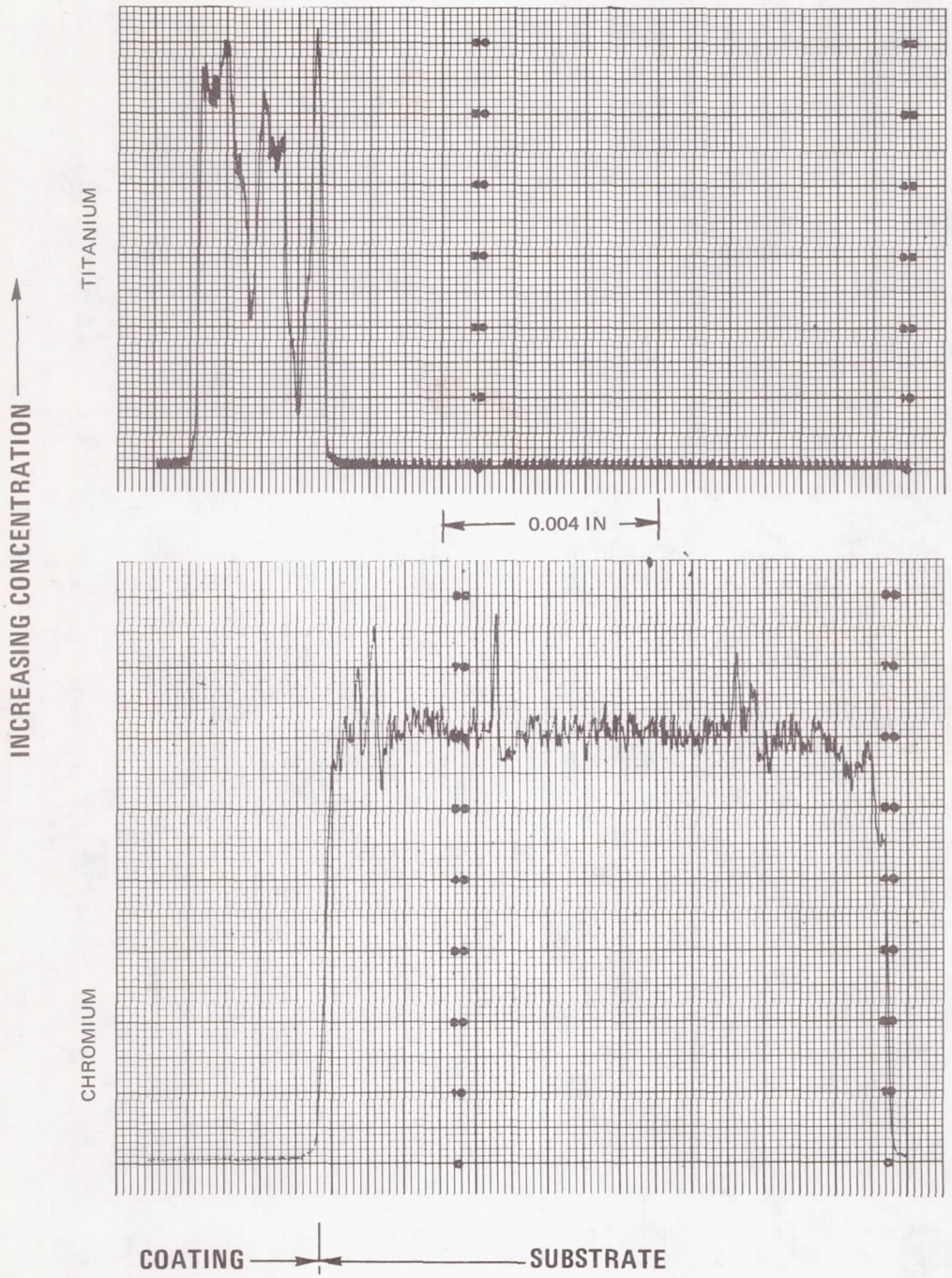


Figure 75 X-Ray Line Scan Intensities for Titanium and Chromium Across AISI-310 Stainless-Steel Tube Coated With duPont Iron Titanate After 1000 Hours at 1350°F

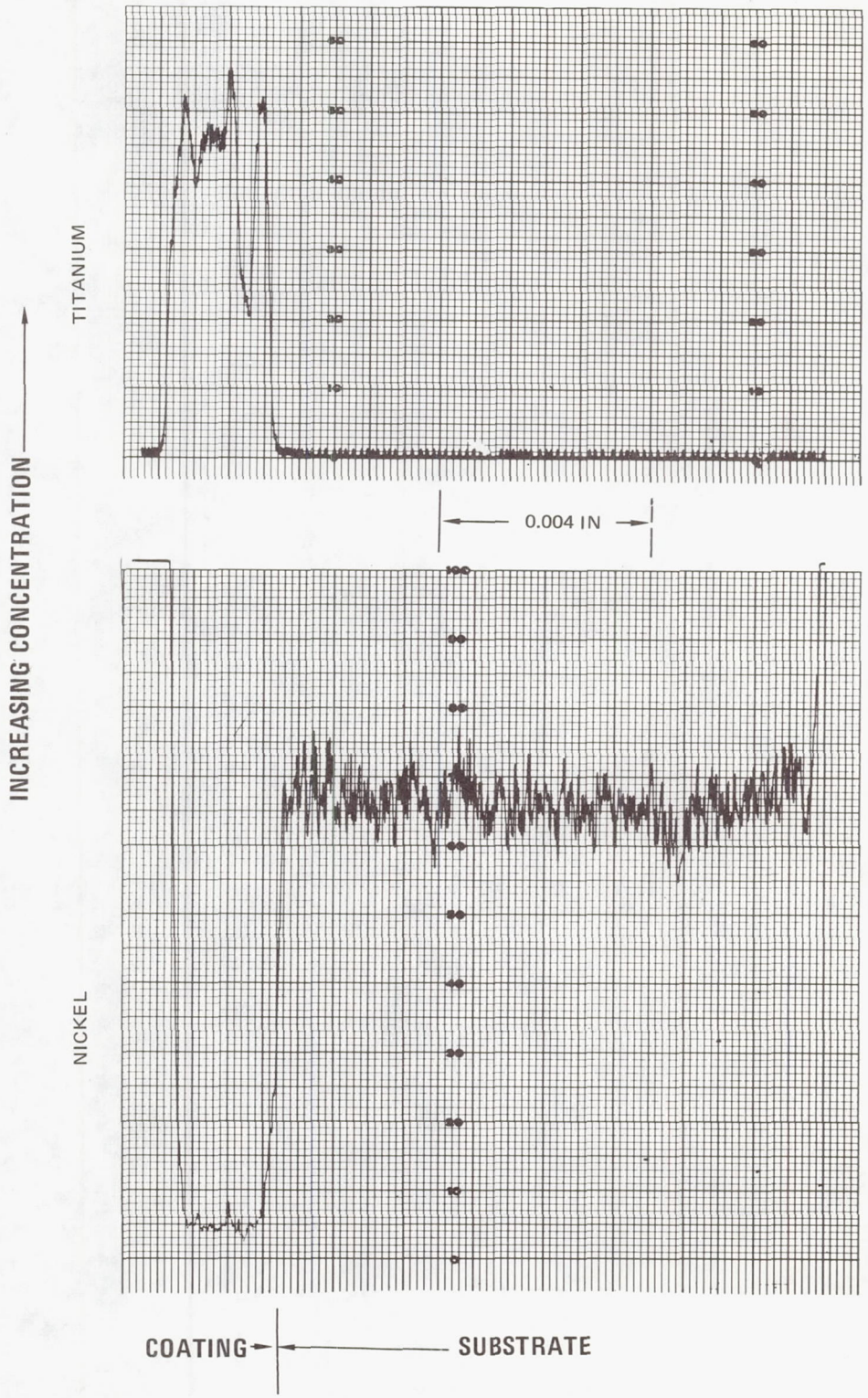
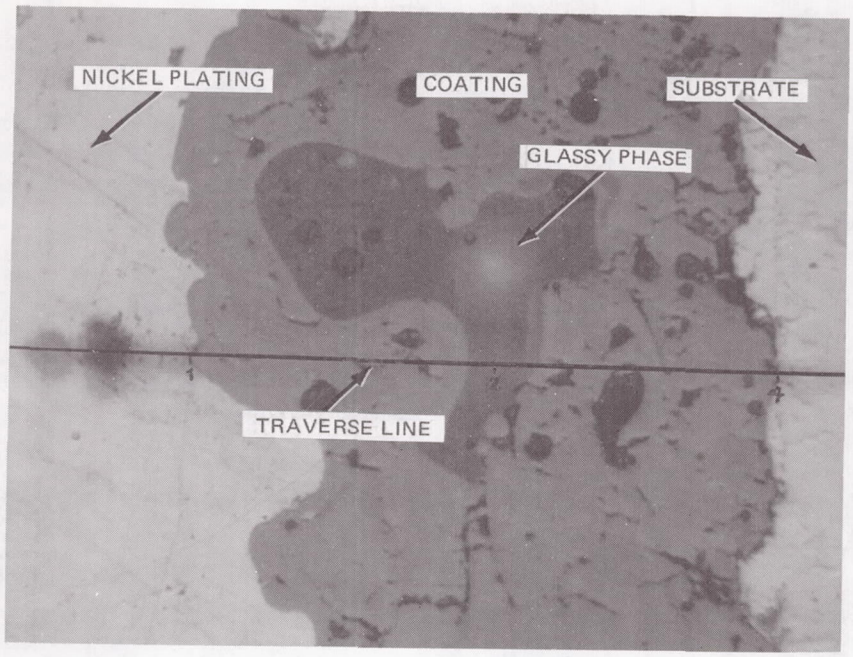
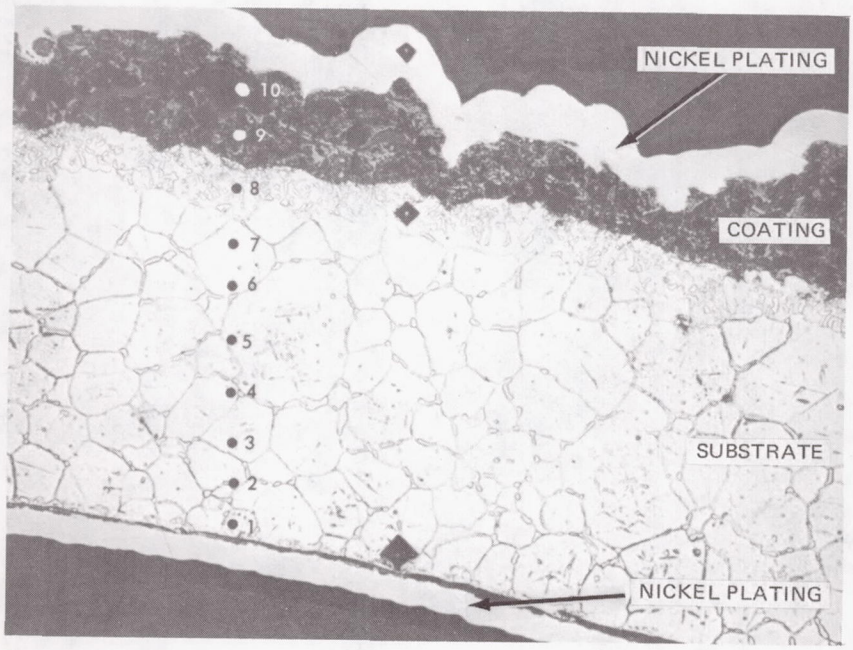


Figure 76 X-Ray Line Scan Intensities for Titanium and Nickel Across AISI-310 Stainless-Steel Tube Coated With duPont Iron Titanate After 1000 Hours at 1350°F



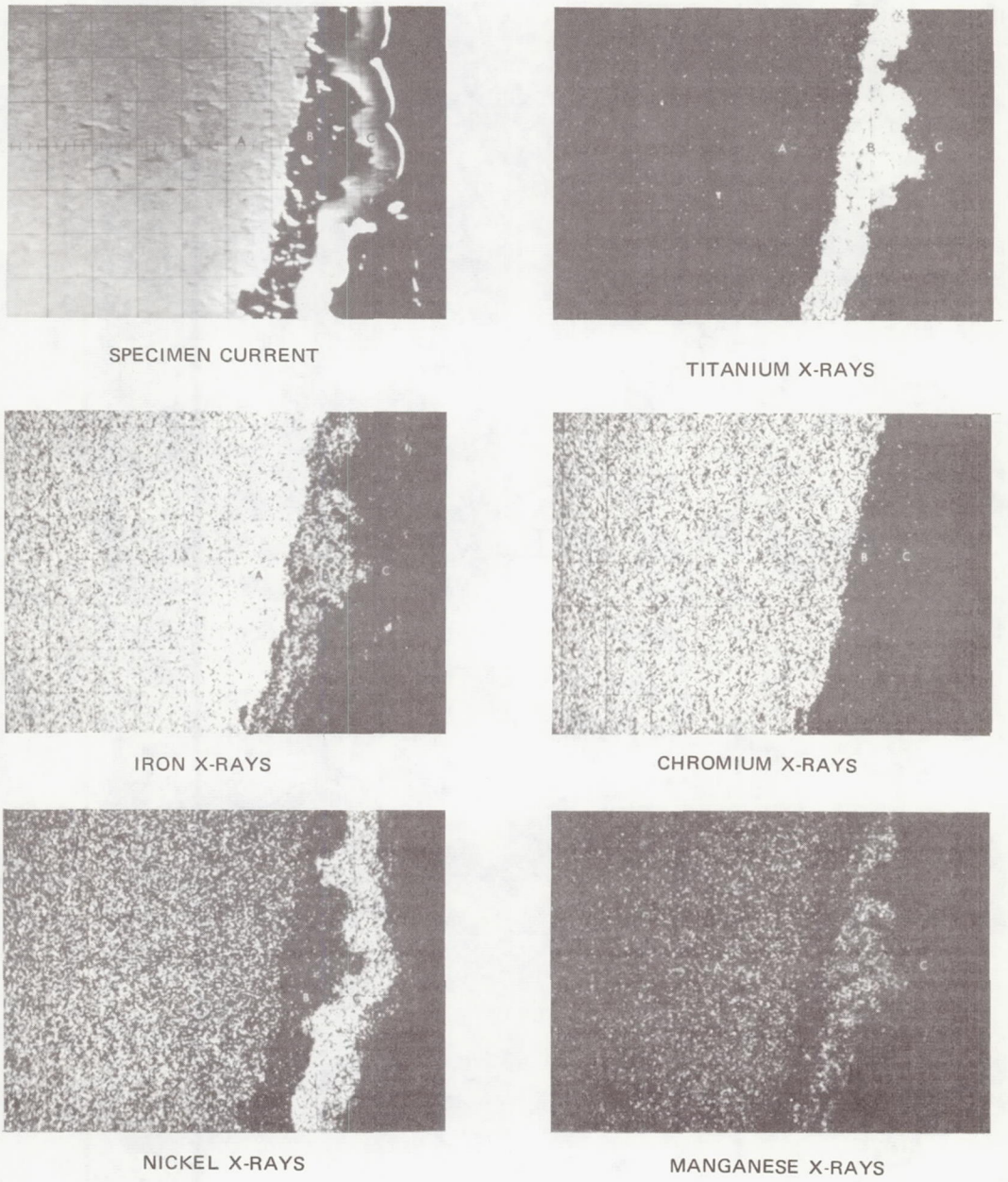
Mag: 670X

Figure 77 Photomicrograph of Silicon and Aluminum-Rich Region of FCT-11H Iron Titanate Coating After 1000 Hours at 1350°F



Mag: 220X

Figure 78 Photomicrograph of duPont Iron-Titanate-Coated AISI-310 Stainless-Steel Tube Showing Locations Where Point-Count Analyses Were Performed After 1000 Hours at 1350°F



Mag: 220X

Figure 79 Electron Beam Scan Photographs of duPont Iron-Titanate-Coated AISI-310 Stainless-Steel Tube After 1000 Hours at 1350°F

TABLE 9

RESULTS OF POINT-COUNT ANALYSIS OF AISI-310
STAINLESS STEEL SPECIMEN COATED WITH DUPONT IRON TITANATE

Distance form Coating-Substrate Interface (Mils)	Composition (Weight Percent) Fe	Ti	Ni	Cr	Mn
Coating	48.0	19.0	0.1	0.1	1.4
Coating	44.0	26.0	0.1	0.3	2.9
0.4	Bal	0.08	20.9	25.1	0.1
1.9	Bal	< 0.05	21.2	24.3	1.4
3.1	Bal	--	20.5	25.7	1.6
4.5	Bal	--	20.4	24.4	1.4
6.0	Bal	--	20.3	34.7	1.7
7.4	Bal	--	20.7	25.8	1.5
8.5	Bal	--	19.8	25.0	1.6
9.6	Bal	--	20.9	24.8	1.5
As-Received Material	Bal	<0.05	20.1	25.8	1.8

E. DISCUSSION OF RESULTS

The vacuum emittance tests and the post-test analyses performed on the two AISI-310 stainless-steel tubes coated with FCT-11H iron titanate and duPont iron titanate indicate that these two coating materials have extremely similar emittance properties and respond to exposure to vacuum conditions at 1350°F for 1000 hours similarly.

ANALYSIS OF IRON TITANATES

by

Sigmund L. Smith

The following material has been extracted from the Phase III Report entitled "Microscopic, Quantitative, Qualitative, and X-Ray Diffraction Analysis Investigation of Three Titanium Materials to be Used for Plasma Sprayed Coatings." The work was performed by Sigmund L. Smith under NASA Order No. C-32376-B.

RESULTS:

Samples 1(FCT-11SP) special powder ± 5 grams received 12/1/67 and 1HS (head sample) (FCT-11) ± 1,000 grams received 4/5/68, and 2(FCT-11H) ± 5 grams received 12/1/67 and 2HS(FCT-11H) ± 4,500 grams received 4/6/68, and 6 (DuPont,Fla.) ± 5 grams received 12/1/67 and 6 HS (DuPont,Fla.) ± 2,000 grams received 4/4/68 all originated from the same general geological deposit and have under proper conditions the same chemical, microscopic and x-ray diffraction analysis.

Sample 1(FCT-11SP & 11) originated by heat treating to about 900°C a titanium beach sand concentrate and then ground to about 0.1% plus 100 mesh (0.147 mm) by the Continental Coatings Corporation. Sample 1(FCT-11SP) was a fraction screened from the original lot (FCT-11) analyzing about 48% minus 140 mesh (0.10 mm) plus 300 mesh (0.046 mm) and 52% minus 300 mesh. Other fractions were scalped from the original (FCT-11) heat treated and ground material for other purposes, such as welding flux, etc. This of course makes any investigation very difficult to correlate.

Samples 2(FCT-11H) and 6(DuPont,Fla.) are raw titanium beach sand concentrates originating from different concentrators as the size range varies slightly between the two samples, for example 2(FCT-11H) has 56% plus 100 mesh and 6(DuPont,Fla.) has only 42% plus 100 mesh. This can be accounted for by the difference in milling technics of the two concentrators. Sample 2 (FCT-11H) appears to be the better of the two.

ANALYSIS (chemical and microscopic analysis can still be considered in a state of flux) :

CHEMICAL

	% Ti	% Fe^{++}	% Fe^{+++}	% Al	% Zr	% Cb	% Mg
1 (FCT-11SP or 11)	40.80	3.50	19.18	1.00	0.90	0.220	0.106
2 (FCT-11H)	43.75	3.00	20.50	1.10	0.70	0.240	0.124
6 (DuPont,Fla.)	42.60	2.10	20.52	1.05	0.60	0.115	0.112

MICROSCOPIC

1 (FCT-11SP or 11), 2 (FCT-11H) and 6 (DuPont,Fla.) all contain the same minerals, to wit:

Pseudobrookite (Fe_2TiO_5)	45%	Garnet ($Mg_3Al_2(SiO_4)_3$)	Trace
Rutile (TiO_2)	39%	Andalusite ($Al_2O_3 \cdot SiO_2$)	Trace
Leucoxene ($TiO_2 \cdot xFe_2O_3$)	11%	Gahnite ($ZnMgFeO \cdot Al_2O_3$)	Trace
Staurolite($FeAl_4Si_2O_{10}(OH)_2$)	3%	Sphene ($CaTiSiO_5$)	Trace
Zircon ($ZrSiO_4$)	1.2%	Corundum (Al_2O_3)	Trace
Hematite (Fe_2O_3)	0.2%	Tourmaline (complex)	Trace
Free quartz (SiO_2)		Hornblende (complex)	Trace
(may be a contaminant)	0.05%	Chlorite (complex) ?	Trace

X - RAY DIFFRACTION

Pseudobrookite	± 50%	Zircon	present
Rutile	± 50%	Hematite	present
Staurolite	present	Magnetite	present

Poor quality X-ray diffraction patterns as shown in Figure 4 can be obtained on unheat-treated samples.

DATA:

Because of the confusion and misinterpretation of x-ray patterns in Phase II perhaps an explanation of the crystal and lattice structure peculiar for pseudobrookite and rutile will help the reader understand why the as received material 1 (FCT-11 or 11SP) gave reliable patterns and 2 (FCT-11H) and 6 (DuPont,Fla.) gave ambiguous results. Also an explanation why 1 (FCT-11SP or 11) was heat treated.

From Figure 3A (figure numbers are the same as page numbers) shows a unit cell of pseudobrookite and rutile. Also the 110 planes, which are very important as they have the highest number of atoms and consequently are more susceptible to slip or dislocations. Figure 3B shows excellent x-ray diffraction patterns from the various planes of the two minerals listed in Table 3. Excessive unorganized or unparallel slip along the 110 planes and others will result in: (1) A diffused x-ray pattern. The 110 planes have preference over others as they are high density planes and (2) Where the scrambled or unorganized 110 planes exists the area has high brittleness and is susceptible in forming an excess amount of slimes (less than 1 micron) by grinding. Fracture now takes place along multi-billion directions and can only be relieved by annealing or normalizing before the grinding operation. Annealing or normalizing relocates the planes so they are more parallel and consequently less slimes are produced. Items 1 and 2 can best be explained by Angstro Structures developed by the author.

ANGSTRO STRUCTURES (imaginary arrangement of atoms)

Legend: **Sphere** of Influence in Angstroms

	Solid Ident.	Liquid Identification
Titanium atom	2.95	3.03
Titanium solid metal is hexagonal and has metallic bonding		
Iron atom	2.86	2.92
Iron solid metal is body centered cubic and has metallic bonding		
Oxygen atom	6.83	7.02 molecules of two atoms
Columbium atom	3.29	3.36 and when solid is BCC

PSEUDOBROOKITE (Fe_2TiO_5)
Ti = 20.1%, Fe = 46.5%, O_2 = 33.4%
Titanium and iron can vary widely. Hematite and rutile crystals can occur as inclusions.

RUTILE (TiO_2)
Ti = 60% and O_2 = 40%
Iron atoms can substitute for titanium up to 10%. Hematite crystals can occur as inclusion in the rutile.

IDENTIFICATION

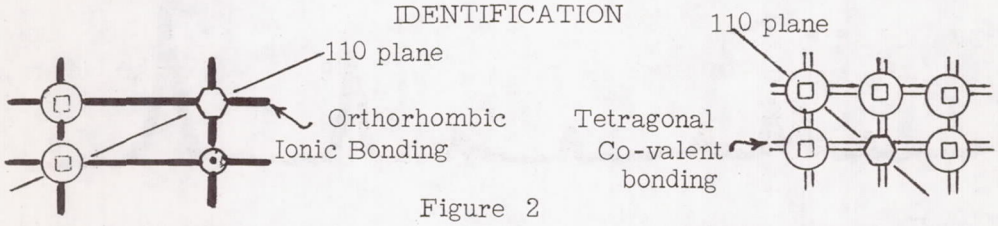


Figure 2

It should be noted at this time that the lattice of pseudobrookite, particularly along the 110 planes, can be distorted more easily than the 110 planes of rutile. Consequently everything being equal a better diffraction pattern will be obtained from the 110 planes of rutile than pseudobrookite. To distinguish between the bonding of the atoms in the two minerals pseudobrookite will be labeled ionic and rutile co-valent. In general co-valent is stronger than ionic bonding.

Table 3

PSEUDOBROOKITE			RUTILE		
Crystallographic Planes					
Plane	Intensity	Distance	Plane	Intensity	Distance
200	3	4.86 A	110	10	3.24 A
220(110)	10	3.48	011	5	2.49
230	8	2.75	111	3	2.18
002	4	1.86	121	7	1.68
Unit Cells					
Orthorhombic unit cell			Tetragonal unit cell		
Density = 4.4 to 5.0			Density = 4.18 to 5.25		

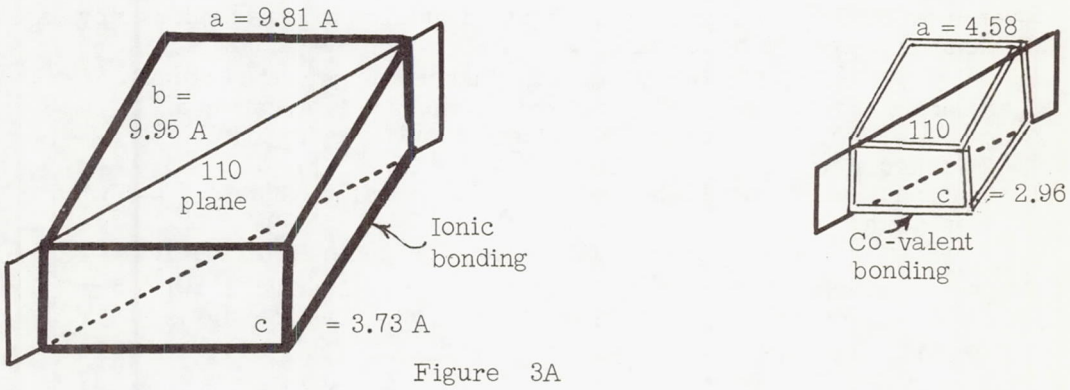


Figure 3A

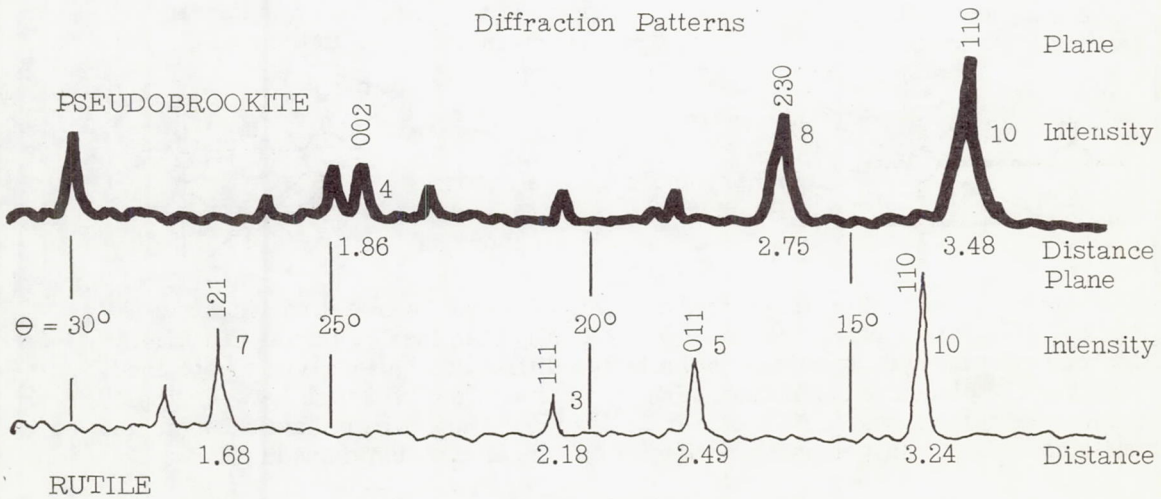


Figure 3B

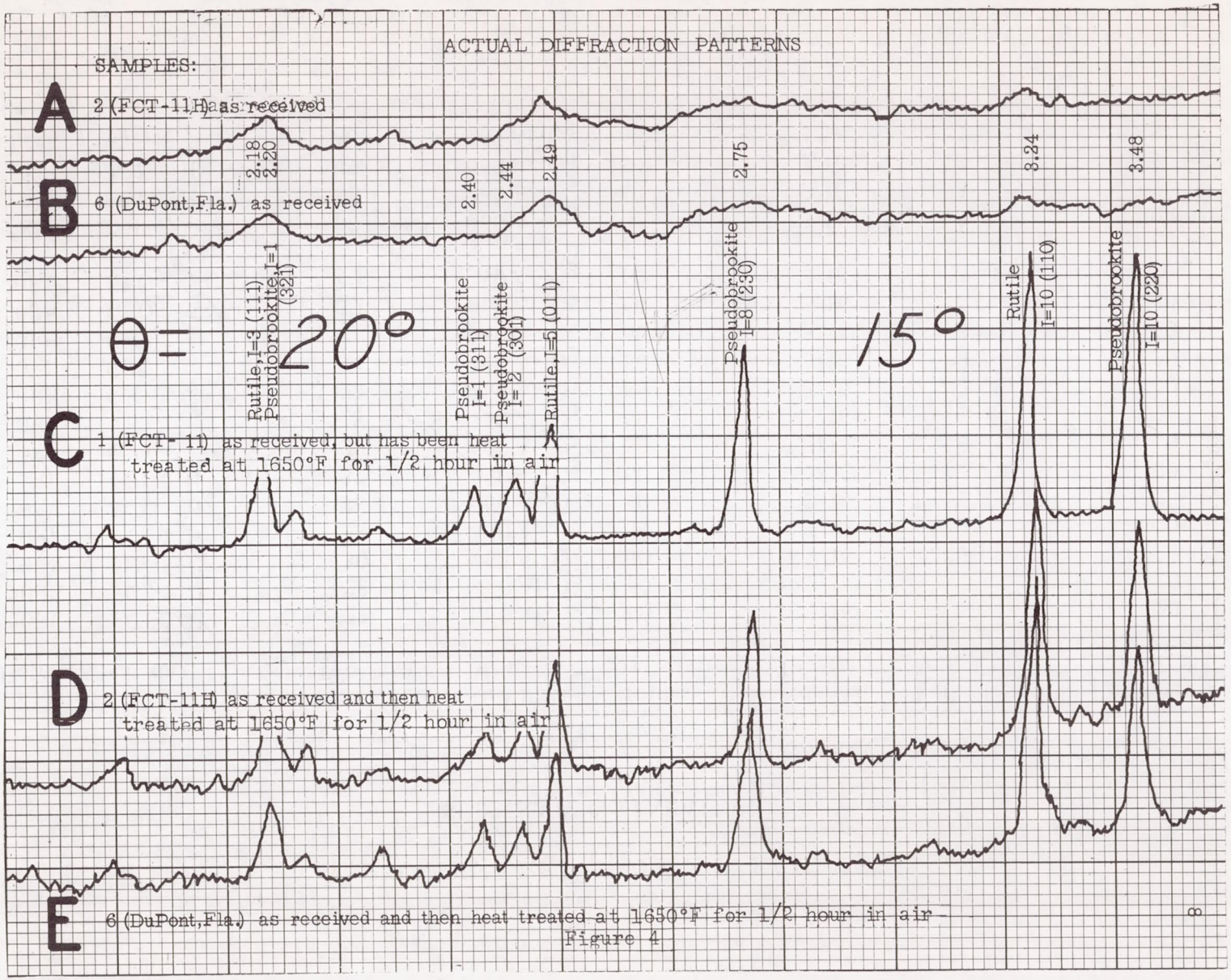

ACTUAL DIFFRACTION PATTERNS
SAMPLES:
A 2 (FCT-11H) as received
B 6 (DuPont,Fla.) as received
C 1 (FCT-11) as received, but has been heat treated at 1650°F for 1/2 hour in air
D 2 (FCT-11H) as received and then heat treated at 1650°F for 1/2 hour in air
E 6 (DuPont,Fla.) as received and then heat treated at 1650°F for 1/2 hour in air
θ= 20°
15°
2.18
2.20
2.40
2.44
2.49
2.75
3.24
3.48
Rutile, I=3 (111)
Pseudobrookite, I=1 (321)
Pseudobrookite I=1 (311)
Pseudobrookite I=2 (301)
Rutile, I=5 (011)
Pseudobrookite I=8 (230)
Rutile I=10 (110)
Pseudobrookite I=10 (220)

Figure 4

SPECIMEN PREPARATION PARAMETERS

SUBSTRATE PREPARATION

Substrate	Coating	Figure Number for Test Data	Grit Blast Media	Grit Blast Gas Pressure	Grit Blast Orifice Nominal Dia. (in.)	Nozzle Distance from Work Piece (in.)	Surface Roughness (Microinches)
Pt-20Rh	FCT-11H	27	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	FCT-11H	28	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	FCT-11H	30	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	FCT-11H	35	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	FCT-11H	36	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	FCT-11H	37	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	CeO_2	20	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	CeO_2	18	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	CeO_2	23	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	CeO_2	24	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	CeO_2	21	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	HFO_2 +5 Y_2O_3	39	#60 Al_2O_3	60	3/16	3	120
Pt-20Rh	HFO_2 +5 CaO	40	#60 Al_2O_3	60	3/16	3	120
310 S/S	DuPont	67	#60 Al_2O_3	60	3/16	3	90 to 100
310 S/S	FCT-11H	66	#60 Al_2O_3	60	3/16	3	65
Cb-1Zr	FCT-11H	49	#60 Al_2O_3	60	3/16	3	65
Cb-1Zr	W/FCT-11H	48	#60 Al_2O_3	60	3/16	3	65

POWDER FEED PARAMETERS

Substrate	Coating	Figure Number for Test Data	Gas Composition	Pressure (psi)	Flow Rate (ft^3/hr)	Powder Feed Rate (lb/hr)
Pt-20Rh	FCT-11H	27	Ar	15	10	3½
Pt-20Rh	FCT-11H	28	Ar	15	10	3½
Pt-20Rh	FCT-11H	30	Ar	15	10	3½
Pt-20Rh	FCT-11H	35	Ar	15	10	3½
Pt-20Rh	FCT-11H	36	Ar	15	10	3½
Pt-20Rh	FCT-11H	37	Ar	12	10	3
Pt-20Rh	CeO_2	20	Ar	15	10	3
Pt-20Rh	CeO_2	18	Ar	15	10	3
Pt-20Rh	CeO_2	23	Ar	15	10	3
Pt-20Rh	CeO_2	24	Ar	15	10	3
Pt-20Rh	CeO_2	21	Ar	15	10	3
Pt-20Rh	$HFO_2 + 5Y_2O_3$	39	Ar	15	7	3
Pt-20Rh	$HFO_2 + 5CaO$	40	Ar	15	7	3
310 S/S	DuPont	67	Ar	20	10	4
310 S/S	FCT-11H	66	Ar	20	8	4
Cb-1Zr	FCT-11H	49	Ar	20	8	4
Cb-1Zr	W	48	Ar	20	8	4
Cb-1Zr	FCT-11H	48	Ar	20	8	4

COATING APPLICATION PARAMETERS

Figure Number for Test Data	Substrate	Coating	Arc Gas Composition	Arc Gas Pressure (psi)	Arc Voltage (Volts)	Arc Current (Amperes)	Substrate Coating Temperature (^{o}F)	Gun Distance From Substrate (inches)	Arc Gas Flow Rate (lb/hr)	Coating Thickness (inch)
27	Pt-20Rh	FCT-11H	Ar	11	30	500	1000 ± 50	3	52	0.003 to 0.004
28	Pt-20Rh	FCT-11H	Ar	11	30	500	1000 ± 50	3	52	0.003 to 0.004
30	Pt-20Rh	FCT-11H	Ar	11	30	500	1000 ± 50	3	52	0.003 to 0.004
35	Pt-20Rh	FCT-11H	Ar	11	30	500	1000 ± 50	3	52	0.003 to 0.004
36	Pt-20Rh	FCT-11H	Ar	11	30	500	1000 ± 50	3	52	0.003 to 0.004
37	Pt-20Rh	FCT-11H	100% Ar	14	30	700	1000 ± 50	3	64	0.004
20	Pt-20Rh	CeO_2	90% Ar + 10% H_2	16	50	500	1000 ± 80	3	70	0.004 to 0.006
18	Pt-20Rh	CeO_2	90% Ar + 10% H_2	16	50	500	1000 ± 80	3	70	0.004 to 0.006
23	Pt-20Rh	CeO_2	90% Ar + 10% H_2	16	50	500	1000 ± 80	3	70	0.004 to 0.006
24	Pt-20Rh	CeO_2	90% Ar + 10% H_2	16	50	500	1000 ± 80	3	70	0.004 to 0.006
21	Pt-20Rh	CeO_2	90% Ar + 10% H_2	16	50	500	1000 ± 80	3	70	0.004 to 0.006
39	Pt-20Rh	$HFO_25Y_2O_3$	90% Ar + 10% H_2	15	50	500	Ambient	3	68	
40	Pt-20Rh	HFO_25CaO	90% Ar + 10% H_2	15	50	500	Ambient	3½	68	
67	310 S/S	DuPont	Ar	14	30	700	Ambient	3	64	0.004 to 0.005
66	310 S/S	FCT-11H	Ar	11	29.5	700	Ambient	3½	50	0.004
49	Cb-1Zr	FCT-11H	Ar	11	29	700	Ambient	3½	50	0.004
48	Cb-1Zr	W	Ar	11	29.5	500	Ambient	2	52	0.0015
48	Cb-1Zr	FCT-11H	Ar	11	30	700	Ambient	3	52	0.004

X-RAY DIFFRACTION ANALYSIS RESULTS FOR IRON TITANATES

Vendor	Condition		Fe_2TiO_5	$Fe_2(TiO_3)_3$	$FeTiO_3$	TiO_2	Fe_2O_3	Fe_3O_4
AstroMet	As Received	First Sample	Major				2	
AstroMet	As Received	Second Sample	Major		2		3	
Cerac	As Received	First Sample	2	Indication		3	Major	
Cerac	As Received	Second Sample	Major			2		
Continental	As Received	FCT-11CP	2	Indication		3	Major	
Continental	After Spraying	FCT-11CP				2		Major
Continental	As Received	FCT-11H	Indication			Major		
Continental	After Spraying	FCT-11H	Major			Indication		
DuPont	As Received	Highland Ilmenite	Indication				Major	
	After Spraying	Highland Ilmenite	Major			Indication		

Numbers denote order of predominance.

RESULTS OF SPECTROGRAPHIC ANALYSES OF COATING MATERIALS

Composition (Weight Percent)

Sample	Supplier	Mn	Al	Mg	Si	Cb	Zr	Ca	Ag	Cr	Ni	V	Co	Cu	Sn	Mo	B	Li	Na	K	Fe
FCT-11 Fines	Continental Coatings	0.2-0.5	0.1	0.05	0.2-0.4	<0.1	0.02-0.05	<0.1	<0.005	0.1	<0.005	0.005	<0.01	0.005	0.02	<0.01	<0.01	0.1-1	0.01-0.1	0.5	
FCT-11H	Continental Coatings	0.2-0.5	0.1	0.05	0.1-0.2	<0.1	< 0.02	<0.1	<0.005	0.01	<0.005	0.005	<0.01	0.005	0.02	<0.01	<0.01	<0.01	0.01-0.1	<0.1	
FCT-11CP	Continental Coatings	0.02	0.01	0.02	0.02	<0.1	< 0.02	<0.1	<0.005	<0.01	0.005	<0.005	<0.01	<0.005	0.07	<0.01	<0.01	<0.01	< 0.01	<0.1	
FCT-11SP	Continental Coatings	0.2-0.5	0.2	0.05	0.2-0.4	<0.1	0.02-0.05	<0.1	<0.005	0.01	<0.005	0.005	0.01	<0.005	0.02	<0.01	<0.01	0.1-1	0.01	0.2	
Pseudobrookite	Astro Met	<0.01	0.02	0.01	0.02	<0.1	< 0.02	<0.1	<0.005	<0.01	<0.005	<0.005	<0.01	<0.005	0.05	<0.01	<0.01	<0.01	0.1	<0.1	
Ceria	Lindsay	<0.005	<0.005	<0.005	<0.005		< 0.02	<0.1	<0.01	<0.01	<0.005	<0.005	<0.01	<0.005	<0.01	<0.01	<0.01	<0.01	0.01	<0.1	
Iron Titanate on AISI-310 Stainless Steel	DuPont	0.2-0.5	0.2	0.05	0.2	<0.1	< 0.02	<0.1	<0.005	0.1	<0.005	<0.005	<0.01	<0.005	0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	
FCT-11H on Cb-1Zr	Continental Coatings	0.2-0.5	0.1-0.2	0.05	0.1	<0.1	< 0.02	<0.1	<0.005	<0.01	<0.005	<0.005	<0.01	<0.005	0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	
FCT-11H on W/on Cb-1Zr	Continental Coatings	0.2-0.5	0.1-0.2	0.05	0.3	<0.1	< 0.02	<0.1	<0.005	<0.01	<0.005	<0.005	<0.01	<0.005	0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	
Iron Titanate	DuPont	0.2-0.5	0.2	0.05	0.3	<0.1	< 0.02	<0.1	<0.005	0.1	<0.005	<0.005	<0.01	<0.005	0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	
Tungsten	Metco	-	-	Trace	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Trace
FCT-11H on AISI-310 Stainless Steel	Continental Coatings	0.2-0.5	0.2	0.05	0.1	<0.1	< 0.02	<0.1	<0.005	0.02	0.01	<0.005	<0.01	<0.005	0.01	<0.01	<0.01	<0.01	< 0.01	<0.01	

ELECTRON MICROPROBE ANALYSIS TECHNIQUES

In general, an electron probe microanalyzer contains an electron optical column which generates a very small-diameter beam (about one micron) of high energy electrons (about 30 kilovolts). The electron beam is focused on the surface of the specimen, which is viewed by an optical microscope. Exact registration of the electron beam on the point of interest is ensured by aligning the microscope reticle and electron beam on the spot to be analyzed. As a result of the electron bombardment, the specimen gives off characteristic X-rays corresponding to the elements present. The X-rays are analyzed by diffracting them with a crystal and measuring them with an appropriate detector. The output of the detector is channeled through electronic signal processing equipment and then to a strip chart recorder. In this manner, spectral scans are generated.

X-ray image distribution photomicrographs are qualitative or semiquantitative measurements which may be made over small areas of the specimen by scanning the area with the electron beam. Since the output of the spectrometer, tuned for a specific spectral line, is an indication of the relative concentration of the corresponding element, displays of the location and concentration of that element may be obtained. This is accomplished by displaying the raster scan of the specimen on an oscilloscope so that the X and Y coordinates of the specimen correspond to the same axes of the oscilloscope. Then by having the X-ray intensity modulate the oscilloscope, a picture of the elemental distribution may be shown. Permanent photographic records may then be made from the oscilloscope.

Similarly, specimen current images may be obtained and photographed from the oscilloscope. Since only a portion of the incident electrons, which make up the analyzing electron beam, penetrate into the sample to induce X-ray emission, the remaining portions are backscattered and are normally referred to as backscattered electrons. This backscattered fraction or backscattered current has a positive correlation with the atomic number of the element being analyzed, that is, the greater the atomic number of the material, the greater the backscatter fraction. That portion of electrons that does penetrate into the specimen gives rise to a current flow in the sample, this current being referred to as the sample current. This current varies as the inverse of the backscatter fraction. Therefore, there is a different measureable current for each atomic number in the periodic table. If now the sample is rastered, as in X-ray image scanning, a picture of atomic number variations across the specimen may be obtained. This presentation is useful because the sample current mode is sensitive to chemistry changes on the surface of the sample and a sample current image appears quite similar to a light optical photomicrograph.

If now the X-ray spectrometer and associated electronics are aligned to a particular radiation, concentrations of a specific element at specific points in the sample may be determined. This is accomplished by comparing the relative intensities generated by the sample and a standard (or pure element) for a predetermined period of time. This ratio, however, must be corrected for dead-time, background, absorption, and sometimes fluorescence of the emitted X-rays. This is termed point-count analysis.

Finally, by aligning the two analyzing spectrometers to particular characteristic X-ray wavelengths and then slowly translating the sample under the electron beam, the elemental distributions of two elements may be obtained simultaneously. In a similar manner, an X-line line scan is generated by electronically sweeping the analyzing beam across the X axis of the specimen and having the resultant X-ray intensity variations modulate the Y axis of the oscilloscope. Scans showing relative concentrations as a function of distance are thereby obtained. These scans may also be photographed.

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