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FOREWORD

This report describes the research activity carried out in fulfillment of Contract NAS3-4174 during the period from November 15, 1965, through May 14, 1966. Contributors to this report included C. Williams and R. Persons. The work was conducted under the direction of the Space Power Systems Division, Lewis Research Center, National Aeronautics and Space Administration, with R. L. Davies and J. A. Milko as Project Managers. Previous reports covering work under this contract are CR-54268 (PWA-2518), CR-54444 (PWA-2608), and CR-54891(PWA-2750).

ABSTRACT

The testing of coatings applied to AISI-310 stainless steel and columbium-1 percent zirconium was continued during the report period. In addition, the study of the adherence, compatibility, and emittance of coatings applied to beryllium was completed.

Analysis of a columbium-1 percent zirconium tube coated with iron titanate and tested at 1700°F for 10,000 hours was completed. Earlier work has shown that this coating-substrate combination had adequate adherence and emittance characteristics for space radiator use at 1700°F. Emittance values in the range of 0.88 to 0.84 were obtained during the course of the test. Analysis conducted during this report period disclosed the occurrence of limited diffusion of coating constituents into the substrate, diffusion of oxygen into the substrate across both the coated and uncoated substrate surfaces, and a small amount of zirconium diffusion from the substrate into the coating. The substrate was found to be partially recrystallized after the test, but it was also found to be somewhat harder than would be expected for stress-relieved and partially recrystallized columbium-1 percent zirconium. This hardness increase is attributed to the diffusion of oxygen and coating constituents into the substrate. It is felt that a significant portion of this hardening is attributable to specimen preparation and test conditions and is not related to coating-substrate interactions.

Testing of an aluminum-oxide-aluminum-titanate-coated columbium-1 percent zirconium tube was completed, and the specimen was analyzed. During 10,000 hours of testing at 1700°F, the emittance of the tested specimens dropped from 0.87 to 0.80. It was evident that the coating deteriorated during the test, and, therefore, it appears that this coating-substrate combination is not suitable for space radiator use.

Testing of AISI-310 stainless-steel tubes coated with iron titanate and calcium titanate was continued at 1350°F. Total test times accumulated at the end of the report period were 13,920 hours for the iron-titanate-coated specimen and 14,920 hours for the calcium-titanate-coated specimen. Both specimens have an emittance of about 0.88 at present.

Beryllium plates coated with calcium titanate, iron titanate, or zirconium titanate were aged for 100, 500, and 1000 hours at 800°F and either 1200°F or 1400°F. Initially, aging was attempted at 1400°F, but excessive beryllium vaporization occurred, and the higher aging temperature was lowered to 1200°F. All coatings demonstrated adequate adherence and compatibility with beryllium for 1000 hours at 1200°F, although the bond strength of the zirconium-titanate coating was somewhat weaker than that of the other coatings. Aging produced no changes in the coatings or substrates other than permanently increasing the emittance of calcium titanate to 0.92. Iron titanate and zirconium titanate both demonstrated stable emittance values of 0.91 at 900°F.

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I. INTRODUCTION

A program is being conducted to determine the suitability of selected high-emittance materials for use as coatings on nuclear space powerplant radiators. The program is divided into three phases.

In one phase, which was completed during the report period, selected coating materials were applied to beryllium and evaluated for emittance stability, adherence, and chemical and metallurgical changes when exposed to elevated temperatures for extended periods.

In the second phase, selected coatings are being evaluated for emittance stability, adherence, and compatibility when applied to AISI-310 stainless steel or columbium -1 percent zirconium. The tests were scheduled to run 10, 000 hours at 1350°F or 1700°F, but the contract was amended at the end of the report period to provide for running two of the tests for 20, 000 hours.

In the third phase, which was started at the end of the report period, two 5000-hour thermal cycling endurance tests will be conducted on iron-titanate coatings applied to columbium - 1 percent zirconium substrates.

II. BACKGROUND

During the first eighteen months of the program, seven materials were screened for long-term emittance testing, and three were selected and tested for extended periods. The coating-substrate combinations selected were: iron titanate on AISI-310 stainless steel, iron titanate on columbium-1 percent zirconium, calcium titanate on AISI-310 stainless steel, and aluminum-oxide-aluminum-titanate on columbium-1 percent zirconium. Testing of the iron-titanate-coated columbium-1 percent zirconium was terminated after 10,000 hours, and analysis was started.

Phase II of the program, consisting of coated-beryllium compatibility studies, was started. The studies consisted of adherence and emittance evaluations of beryllium plates coated with selected materials. Two materials had been selected at the end of the first eighteen months, namely, calcium titanate and iron titanate. A third material remained to be selected.

III. BERYLLIUM STUDIES

A. Introduction

The study to determine the compatibility, adherence, and emittance stability of selected high emittance coatings applied to beryllium for space radiator applications was completed during the report period. A number of beryllium samples were plasma-arc sprayed with iron titanate, calcium titanate, and zirconium titanate. The first two of these materials had demonstrated high emittance and good bond strength for periods of at least 10,000 hours on other metal substrates. Zirconium-titanate-coated stainless steel specimens had demonstrated an emittance of about 0.88 for 290 hours at temperatures of 800°F to 1200°F. Two other candidate coatings, anodized beryllium and aluminum-oxide-aluminum-titanate, were investigated. Neither of these coatings proved satisfactory, but the results obtained are reported at the end of this section.

The coated beryllium specimens were aged for periods of 100, 500, and 1000 hours at temperatures of 800°F, 1200°F, and 1400°F. Initially, aging was to be conducted at 800°F and 1400°F, but early testing at 1400°F in vacuums of 1×10^{-7} mm Hg or better resulted in vaporization of the beryllium. This beryllium vaporization during the course of the test had no apparent effect on the stability or adherence of the coating. Consequently, the maximum temperature for later tests was lowered to 1200°F by directive of NASA. The specimens were aged in groups of three to determine the reproducibility of the data.

To determine the effect of aging on the emittance properties of the specimens, emittance tests were conducted on the aging test specimens by transient techniques and on strip specimens by steady-state techniques.

One specimen from each group was examined for metallurgical properties after aging. The coatings were analyzed by X-ray diffraction and spectrographic analysis, and the substrates were examined for microhardness and microstructure. In addition, electron-beam microprobe analyses were performed on one specimen from each group that was aged at 1200°F for 1000 hours. The analyses were performed by the Advanced Metals Research Corporation, Burlington, Massachusetts and by the United Aircraft Research Laboratory using a Norelco analyzer.

Although microhardness measurements were made for specimens from each group, it was not possible to provide a meaningful correlation between hardness and depth below the surface. The reason for this is the anisotropic properties of the beryllium crystal.[1] Diamond pyramid hardness values varied by as much as 262 kg/mm^2 in adjacent areas (with a representative value of 190 kg/mm^2), presumably because the measurements were made on different crystals. With this large a difference being produced by crystal orientation, any small changes in over-all hardness with depth were completely undetectable, since the effects of impurities or aging and those of orientation were inseparable. Consequently, it was deemed inappropriate to tabulate the hardness values obtained together with the depths at which the measurements were made. Such a tabulation might, in some cases, appear to indicate a trend, which, in fact, has no justifiable basis.

Some difficulty was encountered at welded thermocouple junctions on beryllium specimens tested for prolonged periods at temperatures above 1100°F. Welding caused embrittlement of the beryllium which resulted in substrate failure around the thermocouple during testing. Attempts to improve the welding technique by using an inert atmosphere and various energy levels during welding failed to produce satisfactory results. Consequently, an alternate attachment scheme was developed which used a small platinum plug to maintain contact between the beryllium and the thermocouple leads. The junctions were made by drilling a 0.0135-inch diameter hole through the specimen, passing 0.003-inch diameter platinum-platinum 10 percent rhodium wires through the hole, and then securing the wires by forcing a tapered platinum plug into the hole. All material protruding from the rear of the specimen was removed. A typical installation is shown in Figure 1. The thermocouples installed in this manner performed well, with no thermocouple failures occurring during the tests. The accuracy of the thermocouples was checked by comparing temperature indications from adjacent platinum-platinum 10 percent rhodium and Chromel Alumel thermocouples. In all cases, the two sets of data agreed within ±1.5 percent.

B. Beryllium Analysis

The beryllium plates used for the aging specimens were procured from the Beryllium Corporation in the form of 3-inch by 3-inch by 0.10-inch plates. The material was designated as high purity IS-2 ingot sheet. Spectrographic analysis of the material, as received, revealed the presence of the following impurities: 0.06% Si, 0.05% Fe, 0.02% Ni, 0.01% Ti, 0.01% Mn, and traces of Cr, Cu, Mg, Pb, Au, and Sn. Chemical analysis showed 0.8% BeO to be present.

The plates were received in two shipments, each from different heats, and the microstructures of the material differed significantly between shipments. As shown in Figure 2, the material received in the first shipment was characterized by elongated grains, whereas the material received in the second shipment consisted of equi-axed, recrystallized grains. The white streak at the coating-substrate interface is produced by coating removal during specimen preparation. Cross-hatch lines in the substrate material are indicative of twinning caused by cold working.

C. Emittance Test Procedure

1. Introduction

Initially, it had been intended to conduct emittance testing on strip specimens at steady-state conditions, and some measurements were successfully made with this procedure. However, difficulties were encountered in preparing suitable strips from beryllium. The problem resulted primarily from the necessity of grit blasting brittle beryllium strips which were only 0.010 inch thick. Several strips were broken during attempts to obtain adequate surface roughness, and coating strips with less roughness resulted in coating separation. The use of thicker strips would result in excessive thermal conduction during emittance testing which would cause inaccurate results. Consequently, a previously developed thermal decay technique was used.

2. Theory of Thermal Decay Emittance Testing

The thermal decay method of emittance measurement depends on the equality of the net energy radiated by the specimen and the heat lost from the specimen indicated by the rate of temperature change.

The method is valid providing the convective and conductive energy losses are negligible. For these conditions, the heat balance is given by the following equations.

$$MC \frac{dT}{dt} = - \epsilon_1 A_T \sigma (T^4 - T_s^4) \qquad (1)$$

or

$$\epsilon_1 = - \frac{MC}{A_T \sigma (T^4 - T_s^4)} \left(\frac{dT}{dt} \right) \qquad (2)$$

where

M = Mass of specimen
A_T = Total radiating area
C = Specific heat
ϵ_1 = Total hemispherical emittance
σ = Stefan-Boltzmann constant
T_s = Heat sink temperature
T = Specimen temperature

The emittance calculated by equation 2 is the effective specimen emittance, which is affected by the emittance of each of the radiating surfaces. For specimens which are coated on only one side, such as those tested in the program, equation 2 may be rewritten to account for the emittance of the uncoated sides:

$$\epsilon_1 = -\frac{MC}{A_1 \sigma (T^4 - T_s^4)} \left(\frac{dT}{dt}\right) - \frac{A_2 \epsilon_2}{A_1} \qquad (3)$$

where

A_1 = Area of the coated portion of the specimen
ϵ_2 = Emittance of uncoated portion of the specimen
A_2 = Area of uncoated portion of the specimen

3. Thermal Decay Apparatus

The thermal decay apparatus consists of a vacuum chamber, an evacuation system, an instrumentation flange, specimen heaters, and temperature measurement instrumentation. The apparatus is shown in Figure 3.

The specimen is housed in an 8-inch diameter, 16-inch long cylindrical chamber with convoluted walls. The interior of the chamber is painted with Krylon flat black paint. The combination of high emittance paint and irregular walls results in a heat sink with an emittance closely approaching unity.

The test chamber is mounted on a multiport vacuum base plate with provisions for feedthroughs for high voltage leads, thermocouple leads, and coolant flow. The base plate was manufactured by Varian Associates. The chamber is enclosed by a Pyrex bell jar, and the system is evacuated to 1×10^{-5} mm Hg or less by a Veeco VS-400 pumping station. Specimen temperatures are recorded by a Bristol Dynamaster strip chart recorder, and sink temperatures are measured with a Leeds and Northrup 8686 potentiometer. The specimens were heated by a Sel Model 135 electron-beam power supply which generated an electron beam between thoriated tungsten filaments and the uncoated surface of the specimen.

4. Specimen Preparation

The specimen weight and dimensions were measured following polishing and prior to instrumentation. A two-mil by thirty-mil 304 stainless-steel ribbon was then attached at each of two adjacent corners of the specimen by capacitative discharge welding, and two Chromel-Alumel thermocouples were attached to the coated side of the specimen by welding. One thermocouple was attached at the center and the second was attached approximately one inch away from the center to determine if serious temperature gradients occurred during testing. Three thoriated tungsten filaments were placed parallel to and approximately 0.1 inch away from the polished surface of the specimen. A schematic drawing of the specimen installation is shown in Figure 4.

5. Test Procedure

For emittance measurement, the specimen was initially heated to about 1100°F by an electron beam. The electron beam was generated by heating the filaments to approximately 3000°F and applying a negative potential of 5000 volts to the filaments relative to the specimen. The resulting beam current of approximately 100 milliamps heated the specimen to the required temperature in approximately 10 minutes. When the starting temperature was reached, the electron beam was shut off, the sink temperature was measured, and the strip chart recorder started. Testing was concluded when the specimen reached 400°F. Throughout the test, the sink temperature was maintained at a constant level by coolant which circulated continuously through the chamber.

Heating the thoriated filaments to 3000°F in vacuum resulted in some vaporization of the thorium, which later condensed on the uncoated surface of the specimen. The effective emittance of a polished beryllium surface with an amount of thorium condensate equal to that deposited during typical specimen heating was determined. The emittance was found to vary from 0.16 at 500°F to 0.22 at 1000°F. Corresponding values for clean beryllium are 0.15 and 0.18. The values obtained for thorium-plated beryllium were used for the emittance of the "uncoated" surfaces in equation 3.

D. Test Results

1. Calcium - Titanate Coating

a. Aging Tests - Calcium-titanate-coated beryllium plates have been aged at 800°F, 1400°F, and 1200°F for periods of 100, 500, and 1000 hours. The results of aging at 800°F for 100 and 500 hours were reported in the previous semiannual report, NASA CR-54891, Section IV.[2] During this report period, calcium-titanate-coated specimens were aged at 800°F for 1000 hours, at 1400°F for 100 hours, and at 1200°F for 500 and 1000 hours, all at a vacuum of 1×10^{-7} mm Hg or better.

After being aged at 800°F for 1000 hours, the specimens exhibited no changes in appearance other than a slight darkening of the coating (see Figure 5). As shown, no cracking, spalling, or indication of bond disruption occurred.

Three calcium-titanate-coated plates were aged at 1400°F for 100 hours in a vacuum of 1×10^{-8} mm Hg. As shown in Figure 6, the coating was considerably darker after aging than before, although the texture was unchanged, and no cracking or spalling of the coating was observed. Spectrographic analysis of the coating detected the presence of beryllium, and X-ray diffraction analysis detected the probable presence of BeO. Since the aging conditions were known to be marginal with respect to the vapor pressure of beryllium, and since it appeared that vaporization had, in fact, occurred, it was decided that the maximum aging temperature should be lowered to 1200°F.

Subsequently, two additional groups of specimens were aged at 1200°F, one for 500 hours and the other for 1000 hours. As shown in Figure 6, the specimens were darker after aging than before, with the color change being greater for the specimens aged for the longer period. However, the color change for these specimens was always less than that for the specimens aged at 1400°F. No spalling, cracking, or change in texture occurred.

One specimen from each group was examined for metallurgical, chemical, and mechanical properties. All of the specimens were weighed before and after aging, and the results are shown in Table 1. As shown, the weight change of

TABLE 1

Weights of Calcium-Titanate - Coated Beryllium Specimens Before and After Aging

Specimen	History	Weight (gm) Before Test	Weight (gm) After Test	Percent Change in Weight
7	1000 Hours at 800°F	29.825	29.816	0.03
8	1000 Hours at 800°F	29.896	29.886	0.03
9	1000 Hours at 800°F	29.828	29.819	0.03
				0.03 av
10	100 Hours at 1400°F	30.386	30.361	0.08
11	100 Hours at 1400°F	30.498	30.476	0.07
12	100 Hours at 1400°F	30.366	30.340	0.09
				0.08 av
13	500 Hours at 1200°F	30.428	30.420	0.03
14	500 Hours at 1200°F	30.410	30.399	0.04
15	500 Hours at 1200°F	29.884	29.859	0.08
				0.05 av
16	1000 Hours at 1200°F	30.638	30.628	0.03
17	1000 Hours at 1200°F	30.549	30.542	0.02
18	1000 Hours at 1200°F	30.540	30.532	0.03
				0.03 av

all specimens except for those aged at 1400°F was very small, generally about 10 milligrams. Because the weight changes were almost insignificant, no attempt was made to determine causes for the variations observed. The specimens aged at 1400°F lost approximately 0.025 gram. A considerable portion of this loss is attributed to the beryllium lost through vaporization.

The results of the spectrographic analyses are presented in Table 2. With the exception of the specimens aged at 1400°F, no significant changes occurred in the impurities present.

TABLE 2

Spectrographic Analysis Results for Calcium-Titanate Coatings Applied to Beryllium

	Impurities (Weight Percent)								
History	Al	Be	Cr	Cu	Fe	Mg	Mn	Ni	Si
As Sprayed	Trace	0	0	0.01	Trace	Trace	Trace	Trace	0.02
1000 Hours at 800°F	Trace	0	0	Trace	Trace	0.01	Trace	0	0.01
100 Hours at 1400°F	Trace	Trace	0	Trace	Trace	Trace	Trace	0	Trace
500 Hours at 1200°F	Trace	0	0.02	0	Trace	Trace	Trace	0	Trace
1000 Hours at 1200°F	0.01	0	0	0	Trace	Trace	Trace	0	Trace

X-ray diffraction tests detected $CaTiO_3$ as the only phase present in all coatings except for those aged at 1400°F. Traces of BeO were detected in these coatings, as expected in view of the vaporization which occurred.

Photomicrographs were taken of one specimen from each test. The microstructure of all specimens remained unchanged as a result of aging, except for those aged at 1400°F. These specimens exhibited some annealing, as expected. Typical photomicrographs of a specimen aged for 1000 hours at 800°F and 1200°F are shown in Figure 7. The beryllium for these specimens was received in the first shipment and exhibits the elongated structure characteristic of that shipment.

An electron-beam microprobe analysis was performed on the cross-section of one of the specimens aged at 1200°F for 1000 hours and on a specimen which was not aged. The electron-beam traverse over the cross section was made at an angle of 45 degrees to the substrate-coating interface to a depth of 3 mils. The distributions of calcium and titanium were determined. As shown in Table 3, only a slight amount of diffusion of calcium and titanium into the beryllium was detected. The aged specimen showed a calcium gradient from 0.03 percent at the surface to less than 0.01 percent 0.5 mil below the surface. A titanium concentration of 0.01 percent extended to a depth of 0.4 mil. Oxygen concentrations were too low to measure in either of the specimens. Although the concentrations of calcium and titanium are higher for the aged specimen than for the unaged specimen, the total amounts are extremely small on an absolute scale and represent a level of diffustion which, in all probability, is not detrimental to the material properties.

On the basis of the chemical and metallurgical examinations conducted in conjunction with the aging of calcium-titanate-coated beryllium plates, it is concluded that calcium titanate and beryllium are compatible for periods up to 1000 hours at temperatures up to 1200°F in vacuum.

b. Emittance Tests - A beryllium strip coated with a 4-mil thick layer of calcium titanate was tested for emittance at 1200°F for 626 hours. Initially, the emittance was about 0.88, but after 100 hours, the emittance began to decrease, reaching a final value of 0.78. Examination of the specimen after testing revealed that coating separation had occurred, causing the emittance decrease.

Additional tests were conducted on unaged and aged coated plates in the thermal decay apparatus. The emittance of the unaged specimen ranged between 0.73 at 400°F and 0.68 at 1000°F as shown in Figure 8. Subsequently, the emittance of a specimen which had been aged at 1200°F for 1000 hours was measured, and the emittance was found to range between 0.89 at 400°F and 0.92 at 900°F (see Figure 8). The increase in emittance produced by aging was expected since previous short-term endurance tests of calcium-titanate-coated stainless steel had shown similar trends. The process is similar to a curing process, since the coating maintains the higher emittance level once it is attained.

To explore the curing phenomenon further, the unaged specimen was installed in the thermal decay test equipment and aged at a temperature of approximately 1000°F, with emittance measurements being made at intervals during the process. The emittance values obtained at 900°F are plotted in Figure 8. As shown, the emittance increased from the 0.68 value obtained previously to 0.95 after 135 minutes of aging. The fact that the final value was higher than that obtained from the specimen aged at 1200°F for 1000 hours is due to the deposition of additional amounts of thorium on the uncoated specimen surface from the thoriated-tungsten filament used in the thermal decay apparatus. This phenomenon was discussed on page 7 of this report. The deposition raised the emittance of the uncoated surface above the value assumed in the calculations. Consequently, the calculated value of the emittance for the coated surface is slightly higher than the true value.

TABLE 3

Concentrations of Calcium and Titanium Across Beryllium Plates Coated With Calcium-Titanate

As Sprayed			After Aging 1000 Hours at 1200°F		
Distance Below Surface (Mils)	Concentration (Weight Percent)		Distance Below Surface (Mils)	Concentration (Weight Percent)	
	Ca	Ti		Ca	Ti
0.0	0.02	0.01	0.0	0.03	0.01
0.07	0.01	0.01	0.07	0.02	0
0.14	0.01	0.01	0.14	0.02	0.01
0.21	0.01	0	0.21	0.01	0.01
0.28	0.01	0.01	0.28	0.01	0.01
0.35	0.01	0	0.35	0.01	0.01
0.42	0.01	0	0.42	0.01	0
0.50	0	0	0.49	0.01	0.01
0.57	0	0	0.57	0	0
0.64	0.01	0	0.64	0	0
0.71	0	0	0.71	0	0
0.78	0	0	0.78	0	0
0.85	0	0	0.85	0	0
0.92	0	0	0.99	0	0
1.0	0	0	1.1	0	0
1.1	0	0	1.3	0	0
1.3	0	0	1.4	0	0
1.4	0	0	1.6	0	0
1.6	0	0	1.7	0	0
1.7	0	0	1.8	0	0
2.0	0	0	2.0	0	0
2.4	0	0	2.3	0	0
2.8	0	0	2.7	0	0
3.1	0	0	3.0	0	0

Note: Minimum detectable concentrations of calcium and titanium are 0.01 weight percent. Concentrations below this level are reported as 0.

2. Iron Titanate Coating

a. Aging Tests - Iron-titanate-coated beryllium plates have been aged at 800°F and 1200°F for periods of 100, 500, and 1000 hours. The results of aging specimens for 100 hours at 800°F were reported in the previous semiannual report, NASA CR-54891, Section IV.[2] During the report period, specimens were aged at 800°F for 500 and 1000 hours and at 1200°F for 500 and 1000 hours.

The appearance of typical specimens aged at 800°F for 500 and 1000 hours is shown in Figure 9. As shown, the specimens were slightly darker after aging than before, but no cracking or spalling occurred.

An attempt was made to age three coated plates at 1400°F for 100 hours. (This test was attempted prior to the test at 1400°F on calcium-titanate-coated plates which resulted in lowering the maximum aging temperature to 1200°F). Because of faulty instrumentation, however, aging was actually conducted at about 1500°F, and extensive vaporization of the beryllium plate occurred.

Subsequently, iron-titanate-coated plates were satisfactorily aged at 1200°F for 500 and 1000 hours. As shown in Figure 10, no cracking or spalling occurred, and the coatings were only slightly darker after aging than before. In view of the results from these tests, it was not considered necessary to age iron-titanate-coated specimens at 1200°F for 100 hours.

One specimen from each group except from those aged at 1500°F was examined for metallurgical, chemical, and mechanical properties. Since coated beryllium is clearly unsuited for radiator use at 1500°F, no useful data could be obtained by analyzing specimens aged at that temperature.

The weights of the specimens before and after aging are shown in Table 4. All specimens lost between 0.002 and 0.007 gram, which represents an identifiable weight change, but an insignificant amount in relation to the total specimen weight.

The results of the spectrographic analyses are presented in Table 5. Aging revealed the presence of small amounts of chromium and zirconium which were not detected in the coating before aging. These elements may have been present in the sprayed coating as non-homogeneous impurities introduced during the spraying operation or during sample preparation prior to analysis. In any event, their concentrations are not sufficient to affect the coating properties detrimentally. X-ray diffraction analysis detected the presence of no phases other than Fe_2TiO_5 in any of the coatings.

TABLE 4

Weights of Iron Titanate-Coated Beryllium Specimens Before and After Aging

Specimen	History	Weight (gm)		Percent Change in Weight
		Before Test	After Test	
4	500 Hours at 800°F	30.367	30.360	0.02
5	500 Hours at 800°F	30.165	30.161	0.01
6	500 Hours at 800°F	30.117	30.111	0.02
				0.02 av
7	1000 Hours at 800°F	30.570	30.567	0.01
8	1000 Hours at 800°F	30.456	30.454	0.01
9	1000 Hours at 800°F	30.103	30.100	0.01
				0.01 av
10	500 Hours at 1200°F	30.391	30.388	0.01
11	500 Hours at 1200°F	29.979	29.977	0.01
12	500 Hours at 1200°F	29.188	29.181	0.02
				0.01 av
13	1000 Hours at 1200°F	29.927	29.925	0.01
14	1000 Hours at 1200°F	30.093	29.090	0.01
15	1000 Hours at 1200°F	29.594	29.590	0.01
				0.01 av

TABLE 5

Spectrographic Analysis Results for Iron-Titanate Coatings Applied to Beryllium

History	Impurities (Weight Percent)							
	Al	Cr	Cu	Mg	Mn	Ni	Si	Zr
As Sprayed	0.5	trace	0.01	0.2	0.5	trace	0.4	0
500 Hours at 800°F	0.8	0.3	0.01	0.2	0.5	0.1	0.3	0.1
1000 Hours at 800°F	0.7	0.15	0.01	0.15	0.4	0.1	0.2	0.1
500 Hours at 1200°F	1.0	0.5	0	0.2	0.2	0	0.5	0
1000 Hours at 1200°F	0.7	0.3	0	0.3	0.4	0	0.4	0

Examination of the microstructures of the specimens revealed no changes from those of unaged specimens. Typical photomicrographs of specimens aged for 1000 hours at 800°F and 1200°F are shown in Figure 11. The beryllium for the specimen tested at 800°F was received in the first shipment and that for the specimen tested at 1200°F was received in the second shipment.

One of the specimens aged for 1000 hours at 1200°F was analyzed by electron-beam microprobe analysis for the concentrations of iron and titanium. The results are presented in Table 6. As shown, the iron gradient extended from a concentration of 0.02 percent at the surface to less than 0.01 percent at a depth of 0.2 mil. The titanium concentrations were slightly higher. At the surface, the concentration was 0.05 percent, but the concentration was below the 0.01 percent minimum detection level of the apparatus at a depth of 0.28 mil. Point concentrations of iron and titanium were detected at several random locations within the substrate. These are believed to be precipitates present as impurities in the substrate before coating. They are clearly outside of the diffusion pattern observed and are not believed to be associated with the coating. It must be emphasized that the concentrations of iron and titanium are extremely small and confined to a very small depth beneath the surface. They do not indicate a significant amount of diffusion, nor is it felt that sufficient concentrations are present to detrimentally affect the substrate properties.

The aging tests and subsequent analyses indicate that iron titanate and beryllium are compatible for at least 1000 hours at temperatures up to 1200°F.

b. Emittance Tests - The emittance of iron-titanate-coated beryllium was measured through steady-state testing and through thermal-decay testing. Emittance values are presented in Figure 12.

A beryllium strip coated with iron titanate was tested for 670 hours during the previous report period[2] before the test was terminated by a thermocouple failure. During the current report period, the specimen was reinstrumented and tested for an additional 300 hours. Throughout the test, the emittance ranged from 0.88 to 0.92 for temperatures between 1100°F and 1200°F.

Two coated beryllium plates were tested by the thermal decay method. One plate was unaged and the other had been aged for 1000 hours at 1200°F. In both cases, the emittance was about 0.91 over the entire temperature range from 400°F to 1000°F, as shown in Figure 12.

The emittance tests demonstrated that iron titanate has stable emittance characteristics when applied to beryllium and exposed to temperatures up to 1200°F for 1000 hours.

TABLE 6

Concentrations of Iron and Titanium Across Beryllium Plate Coated with Iron-Titanate and Aged at 1200°F for 1000 Hours

Distance Below Surface (Mils)	Concentration (Weight Percent)	
	Fe	Ti
0.0	0.02	0.05
0.07	0.01	0.03
0.14	0.01	0.01
0.21	0	0.01
0.28	0	0
0.35	0	0
0.42	0.03	0.01
0.49	0.04	0.01
0.57	0	0.01
0.64	0.04	0.01
0.71	0	0.01
0.78	0	0
0.92	0	0
1.1	0	0
1.2	0	0
1.3	0	0
1.5	0	0
1.6	0	0
1.8	0	0
2.1	0	0
2.4	0	0
2.8	0	0.2
3.1	0	0

Note: Minimum detectable concentrations of iron and titanium are 0.01 weight percent. Concentrations below this level are reported as 0.

3. Zirconium Titanate Coating

a. Selection - Zirconium titanate ($Zr\ Ti\ O_4$) was selected as the third material to be coated on beryllium plates and aged. Previously, the material was tested at 1700°F as a coating on a columbium-1 percent zirconium tube as a candidate for long-term endurance testing. The coating did not exhibit adequate emittance stability at 1700°F for long-term testing, but the emittance at temperatures below 1700°F was about 0.88, so the material appeared to be promising for use at lower temperatures. Consequently, a short-term endurance test of a zirconium-titanate-coated columbium-1 percent zirconium tube was conducted at 1200°F for 290 hours. The emittance remained steady at about 0.88 throughout the test, and, therefore, zirconium titanate was considered to be suitable for additional testing on beryllium.

b. Specimen Preparation - Some difficulty was encountered in obtaining a satisfactory coating. Initially, several beryllium plates were grit blasted with 60-mesh silicon carbide and a line pressure of 80 psi to produce a surface roughness of about 75 microinches AA. The coatings applied to these surfaces, however, were not satisfactory because separation occurred at the edges of some of the plates. Consequently, the plates were cleaned by grit blasting with a line pressure of 100 psi, which resulted in a surface roughness of about 85 microinches AA. Coatings applied to these surfaces exhibited adequate bond strength.

Details of the zirconium titanate powder used were presented in NASA CR-54444.

c. Aging Tests - Zirconium-titanate coated beryllium plates were aged at 800°F for 100, 500, and 1000 hours and at 1200°F for the same periods. Three plates were aged in each test. After aging, the specimens aged for the longer periods were slightly darker than the unaged specimens, but the color change was small, as shown in Figures 13 and 14. In no case was there any cracking, spalling, or other indication of coating separation.

One specimen from each test group was subjected to metallurgical, chemical, and mechanical examination. Specimen weights before and after aging are shown in Table 7. Similar to the other specimens, the zirconium-titanate-coated plates generally lost small amounts of weight during aging. Weight losses ranged from 0 to 0.006 gram, which represents an insignificant weight change in relation to the total weight of the specimen.

TABLE 7

Weights of Zirconium-Titanate-Coated Beryllium Specimens Before and After Aging

Specimen	History	Weight (gm) Before Test	Weight (gm) After Test	Percent Change in Weight
1	100 Hours at 800°F	29.283	29.284	0.003
2	100 Hours at 800°F	29.590	29.589	0.003
3	100 Hours at 800°F	30.018	30.018	0
				0.002 av
4	500 Hours at 800°F	29.783	29.777	0.02
5	500 Hours at 800°F	30.041	30.035	0.02
6	500 Hours at 800°F	30.145	30.139	0.02
				0.02 av
7	1000 Hours at 800°F	30.863	30.860	0.01
8	1000 Hours at 800°F	29.740	29.737	0.01
9	1000 Hours at 800°F	29.275	29.272	0.01
				0.01 av
10	100 Hours at 1200°F	29.960	29.958	0.007
11	100 Hours at 1200°F	29.740	29.737	0.010
12	100 Hours at 1200°F	29.736	29.735	0.003
				0.007 av
13	500 Hours at 1200°F	29.746	29.742	0.01
14	500 Hours at 1200°F	29.839	29.835	0.01
15	500 Hours at 1200°F	29.835	29.832	0.01
				0.01 av
16	1000 Hours at 1200°F	29.551	29.551	0
17	1000 Hours at 1200°F	30.195	30.194	0.003
18	1000 Hours at 1200°F	29.635	29.634	0.003
				0.002 av

Spectrographic analysis detected the impurities listed in Table 8. As shown, the impurities in the aged coatings are about the same as those in the unaged coating. X-ray diffraction analysis detected $Zr\ Ti\ O_4$ as the only phase present in the coatings.

TABLE 8

Spectrographic Analysis Results for
Zirconium-Titanate Coatings
Applied to Beryllium

	Impurities (Weight Percent)						
History	Al	Cu	Fe	Hf	Mg	Mn	Si
Unsprayed Powder	0.3	0	trace	0.6	0.01	trace	0.3
As Sprayed	0.1	0	0.1	0	0.1	trace	0.05
100 Hours at 800°F	0.1	0	0.1	0	0.1	trace	0.05
500 Hours at 800°F	0.2	0.01	0.1	0	0.01	trace	0.15
1000 Hours at 800°F	0.1	trace	0.05	0	trace	trace	trace
100 Hours at 1200°F	0.05	0.01	0.02	0	trace	trace	trace
500 Hours at 1200°F	0.2	0.01	0.2	0	0.01	trace	0.15
1000 Hours at 1200°F	0.05	trace	trace	0	trace	trace	trace

Photomicrographs were taken of all specimens, and the results revealed no changes in microstructure caused by aging. Typical photomicrographs for a specimens aged at 800°F and 1200°F for 1000 hours are shown in Figure 15. The beryllium for these specimens was received in the second shipment.

An electron-beam microprobe analysis was performed by the United Aircraft Research Laboratory on a zirconium-titanate-coated beryllium plate which was aged for 1000 hours at 1200°F. The analysis determined the concentrations of zirconium and titanium in the beryllium. The results are presented in Table 9. A zirconium concentration of 1.01 percent was measured at the surface, but the concentration decreased to less than 0.02 percent at depths greater than 0.5 mil. The titanium concentration at the surface was found to be 1.69 percent, but the concentration dropped below 0.05 percent within the first 0.35 mil. The concentration of zirconium and titanium within 0.2 mil of the surface are substantially higher than the concentrations of the coating constituents on other specimens. However, the higher concentrations extend only to a depth which is about equal to the roughness height of the substrate. Consequently, it appears that minute particles of the first coating were imbedded into the substrate during the second grit blasting to remove the coating. Subsequent diffusion would produce the observed concentrations. In any event, the concentrations are extremely small and extend to very small depths, and, therefore, do not represent any substantial coating diffusion into the substrate.

TABLE 9

Concentrations of Zirconium and Titanium Across Beryllium Plate Coated With Zirconium-Titanate and Aged at 1200°F for 1000 Hours

Distance Below Surface (Mils)	Concentration (Weight Percent) Zr	Ti
0.0	1.01	1.69
0.07	0.59	0.83
0.14	0.29	0.39
0.21	0.10	0.16
0.28	0.06	0.06
0.35	0.03	0
0.40	0	0
0.50	0.04	0
0.80	0	0
1.20	0	0
1.60	0	0
1.90	0	0
2.30	0	0
2.40	0	0
2.60	0	0
6.1	0	0
13.2	0	0
20.3	0	0
38.0	0	0
56.0	0	0.07

Note: Minimum detectable concentrations of zirconium and titanium are 0.02 and 0.05 weight percent, respectively. Concentrations below these levels are reported as 0.

The aging tests and subsequent analyses indicate that zirconium titanate is compatible with beryllium for at least 1000 hours at 1200°F. However, it should be noted that the zirconium-titanate coatings were more difficult to apply than the other coatings tested. In addition, localized coating separation occurred when the plates were cut for metallographic examination after aging, so the bond strength appears to be weaker for this coating than for the other coatings.

d. Emittance Tests - Total hemispherical emittance measurements were made on zirconium-titanate-coated beryllium specimens by the thermal decay method. Both unaged specimens and specimens which had been aged at 1200°F for 1000 hours were tested. The emittance values obtained were similar for both specimens, varying from 0.84 to 0.91 over the temperature range of 400°F to 900°F. These values are shown in Figure 16.

4. Other Candidate Coatings

Two other coatings were considered for use in the beryllium compatibility studies, but both were found to be unsuitable.

The first of these was anodized beryllium. Anodic coatings of various thicknesses were prepared on several beryllium specimens by the Summit Finishing Company, Thomaston, Connecticut. The emittance of the specimens was measured in the thermal decay rig before and after aging at 900°F for about 3 hours in a vacuum of about 1×10^{-6} mm Hg. The specimens outgassed during aging, and the coating color changed from black to brown. In addition, the emittance decreased from about 0.88 to 0.80. On the basis of the instability of the coating and emittance, this coating was rejected as unsuitable for further study.

The second material considered was aluminum-oxide-aluminum-titanate. This material was coated on a columbium-1 percent zirconium tube and subjected to a short-term emittance test. The emittance obtained was only about 0.75 between 800°F and 1200°F, and, therefore, this material was also rejected.

IV. LONG-TERM EMITTANCE TESTING

A. Introduction

The long-term total hemispherical emittance testing of three coated specimens was continued during the report period. These tests were originally scheduled to be terminated after 5000 hours of continuous testing. However, in May 1965, the contract was extended, and the test period was increased to 10,000 hours. In May 1966, the test period for two specimens was again extended to a total of 20,000 hours.

During the report period, the columbium-1 percent zirconium tube coated with iron titanate (for which testing was terminated after 10,000 hours during the previous report period) was analyzed. The columbium-1 percent zirconium tube coated with aluminum-oxide-aluminum-titanate completed 10,000 hours of testing during the current report period; testing was terminated; and the specimen was analyzed. Testing of the remaining specimens, iron titanate and calcium titanate on AISI-310 stainless-steel tubes, is continuing. During the course of the long-term testing, the specimens were periodically cycled between the test temperature and room temperature. The time required to cool from the test temperature to 300°F was approximately 1 minute, and the time required for reheating to the test temperature was approximately 4 minutes.

B. Test Results

1. Iron-Titanate on Columbium-1 Percent Zirconium

The columbium-1 percent zirconium tube coated with a 4-mil thick layer of iron titanate completed 10,000 hours of testing in vacuum at 1700°F during the report period which ended November 14, 1965. The emittance data from this sample as well as much of the post-test evaluation were discussed in the previous semiannual progress report[2]. However, microprobe analysis and metallographic examination of the substrate cross-section were completed during the current reporting period and are reported below. For completeness, the test results reported previously are summarized.

During the 1700°F, 10,000-hour endurance test, the emittance of the specimen decreased slightly from 0.88 to 0.84. Most of the decrease occurred between 600 and 1800 hours, during which the emittance dropped from 0.88 to 0.85. A vacuum of 1×10^{-7} mm Hg or better was maintained throughout the test period. During testing, the specimen was thermally cycled from 1700°F to room temperature a total of 51 times. No evidence of any cracking or spalling of either the coating or substrate was seen either during or after the test. There was no apparent change in the appearance of the coating other than a slight change in color.

Neither spectrographic nor X-ray diffraction analysis revealed any significant change in coating composition or crystallographic structure after testing for 10, 000 hours.

Vacuum fusion analysis of the columbium-1 percent zirconium substrate prior to testing detected the presence of 0. 03 percent oxygen. After the endurance test, a second analysis was performed on the entire substrate cross-section, and 0. 33 percent oxygen was detected. In order to determine the distribution of the oxygen, two additional tests were made, one after mechanically removing approximately 3 mils from the outer surface, and the second after mechanically removing about 7 mils, thereby leaving only a 3-mil thickness. The analyses indicated that removing the outer 3 mils lowered the oxygen content to 0. 26 percent. The analysis of the 3-mil thickness beneath the inner surface indicated an oxygen content of 0. 32 percent. The analyses indicate that, first, the oxygen content increased significantly during the endurance test, and, second, that the regions within 3 to 4 mils of each surface contain a higher oxygen content than the center section.

Microhardness traverses were made on cross-section samples of a columbium-1 percent zirconium tube in the as-received condition and on the coated tube after endurance testing. The as-received tube had an average diamond pyramid hardness of 145 kg/mm^2, with essentially no difference in hardness between the surfaces and the center of the cross-section. The hardness level measured indicates that the material received on the order of 50 percent cold working following the last heat treatment. A total of six traverses were made across the endurance-tested sample, and, as shown in Table 10 and Figure 17, the hardness was considerably higher close to the surfaces than towards the center of the cross-section, with gradients extending inward about 3 or 4 mils from both surfaces. The hardness at the center of the cross-section is essentially the same as that of the untested tube. The gradients beneath the outer surface were relatively smooth and reproducible, whereas the data for the gradient beneath the inner surface was somewhat erratic. This behavior indicates that diffusion occurred during endurance testing and, possibly, that the diffusion across the outer surface was more uniform than that across the inner surface.

Samples of the columbium-1 percent zirconium material were examined metallographically both before and after endurance testing. The appearance of the substrate after coating and before endurance testing is shown in Figure 18. The microstructure is typical of that for cold-worked columbium-1 percent zirconium. After testing, the microstructure indicates that extensive, but still incomplete, recrystallization occurred (Figure 19). In addition, individual grains are visible on the substrate surface of the coating-substrate interface (see Figure 20). These grains are different in appearance from the remainder of the substrate and may be indicative of the formation of a new phase through interaction of the coating and substrate during testing. (The white regions on both sides of the section are nickel plating applied before polishing to prevent rounding of the specimen edges).

TABLE 10

Microhardness Traverse Results for Endurance-Tested Columbium - 1 Percent Zirconium Tube Coated With Iron-Titanate

Traverse 1

Depth (Mils)	Diamond Pryamid Hardness (kg/mm^2)
0.5	191
1.5	196
2.5	170
4.0	141
5.0	144
6.5	168
8.0	196

Traverse 2

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
0.75	201
1.5	182
2.5	156
4.0	139
5.25	138
6.5	174
7.75	180

Traverse 3

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
0.75	201
2.0	188
3.5	151
5.5	137
7.5	159
9.5	164

Traverse 4

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
2.0	182
3.0	153
4.0	142
6.0	138
7.5	159
8.5	168

Traverse 5

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
1.0	194
2.25	169
3.5	142
5.0	132
6.5	160

Traverse 6

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
0.75	191
2.5	164
4.0	142
5.5	139
7.5	161

Electron-beam microprobe analyses were conducted by the Advanced Metals Research Corporation, Burlington Massachusetts, on both untested and endurance-tested iron-titanate-coated columbium-1 percent zirconium specimens. The substrate was analyzed for iron and titanium concentrations across the entire cross-section. An attempt to determine oxygen concentrations was also made, but the oxygen level was too low for meaningful data to be obtained. The data for the coated, untested substrate indicated only slight concentrations of iron and titanium. The concentrations at the surface were 0.10 weight percent for both iron and titanium, with the concentrations dropping below the detectability limits at depths of 0.8 mil and 0.7 mil, respectively. This diffusion probably occurred during plasma arc spraying. The data for the endurance-tested tube (Table 11 and Figure 21) indicates that diffusion of both iron and titanium occurred during testing. The iron content was 0.97 weight percent at the surface and decreased to an undetectable level at a depth of 4 mils. The titanium concentration at the surface was 0.43 weight percent and decreased to an undetectable level within about 1.5 mils.

In addition to the analysis of the substrate, an attempt was made to conduct a microprobe analysis of the coating for the presence of columbium and zirconium. It was not possible to obtain a complete gradient analysis because of the relatively porous nature of the coating. However, point analysis techniques detected the presence of zirconium in isolated regions of the coating. These regions were randomly distributed both radially and circumferentially, and, although not visible optically, the concentrations did fluoresce when excited by the electron beam. No columbium was detected at any point in the coating.

Several observations can be made concerning the data. First, the as-tested microstructure indicates that recrystallization has occurred in some areas of the specimen. From this it can be assumed that recovery is virtually complete in those areas which are not completely recrystallized. In view of the recrystallization that was observed and the long exposure to elevated temperature, it would be expected that the substrate microhardness would be in the range of 90 to 110 kg/mm^2, which is the normal range for cold-worked and annealed columbium-1 percent zirconium.[4] However, the observed hardness values were at least 40 to 50 kg/mm^2 higher than this, even in the recrystallized regions. This indicates that changes occurred during endurance testing in addition to recovery and recrystallization which produced a net increase in material hardness. Two phenomena might account for the increased substrate hardness: metallurgical changes to the precipitates and phases present, and diffusion of material into the substrate. In order to evaluate possible metallurgical changes occurring during testing, it would be necessary to conduct detailed X-ray diffraction and electron microscope analyses. Since this work was not within the scope of the present program, no statement concerning the possibility of such changes can

TABLE 11

Concentrations of Iron and Titanium Across Columbium -1 Percent Zirconium Tube Coated With Iron-Titanate and Endurance Tested at 1700°F for 10,000 Hours

Distance from Outer Surface (Mils)	Concentration (Weight Percent)	
	Fe	Ti
0	0.97	0.43
0.06	0.91	0.36
0.13	0.90	0.29
0.19	0.92	0.20
0.26	0.94	0.20
0.32	0.88	0.16
0.39	0.90	0.12
0.51	0.88	0.09
0.64	0.80	0.06
0.77	0.75	0.04
0.90	0.68	0.03
1.03	0.67	0.02
1.16	0.64	0.01
1.28	0.62	0.01
1.41	0.57	0.02
1.53	0.56	0.01
1.66	0.54	0
1.78	0.52	0
1.91	0.48	0
2.04	0.46	0
2.16	0.43	0
2.54	0.36	0
2.85	0.25	0
3.16	0.14	0
3.47	0.03	0
3.77	0.03	0
4.08	0	0

No iron or titanium was detected at any depths beyond 4.08 mils.

Note: Minimum detectable concentration for iron and titanium is 0.01 percent. Concentrations below this level are reported as 0.

be made. However, diffusion effects can be evaluated on the basis of the microprobe and vacuum fusion oxygen analyses. These analyses indicate that both iron and titanium diffused from the coating into the substrate and that the substrate oxygen content increased during testing.

Investigations of the effects of iron and titanium on columbium alloys indicate that both of these constituents increase the alloy hardness through solid solution strengthening effects. Specifically, 1 weight percent of iron has been found[5] to increase the diamond pyramid hardness by 50 kg/mm^2 over the base hardness, and 1 weight percent of titanium increases the hardness by 40 kg/mm^2. On the basis of the known concentrations of iron and titanium in the substrate, the corresponding increases in hardness were calculated for each mil of depth into the substrate for which detectable concentrations of these elements were found. Subtracting the values calculated from the average measured substrate hardness results in the lower curve shown in Figure 22. As shown, virtually all of the hardness gradient detected at the outer surface of the substrate can be accounted for by the solid solution hardening effects of the iron and titanium in this region.

The hardness gradient found on the inner surface as well as the general elevation of hardness across the entire cross-section above that anticipated remains to be explained. The possible hardening effects of the increased oxygen content were considered. Investigators have reported[5] that an increase of 0.1 weight percent of oxygen in columbium produces an increase in hardness of 85 kg/mm^2. This hardness is caused by a solid solution strengthening effect. In the case of oxygen diffusion into columbium-1 percent zirconium, it would be expected that, because of the high activity of zirconium, the initial quantities of oxygen entering the alloy would preferentially combine with the zirconium and precipitate as zirconium-oxide particles. This precipitate would have little, if any, effect on the room temperature hardness of the alloy.[5] This mechanism for the effective removal of both zirconium and oxygen from the alloy would continue until all of the available zirconium had been used up.

Once that point is reached, however, any additional oxygen entering the alloy would dissolve in the columbium matrix and produce a solution hardening effect. This mechanism can be applied to the substrate under investigation, which has been found to contain 0.72 percent zirconium. On a stoichiometric basis, this quantity of zirconium would react with 0.25 percent oxygen. Hence, the first 0.25 percent oxygen diffusing into the substrate, while physically present, would not be available for solution hardening of the columbium. The quantity of oxygen required to produce the observed general hardness level increase of 40 to 50 kg/mm^2 can be calculated and is found to be 0.05 weight percent. Adding this to the oxygen calculated to combine with zirconium (0.25 percent) yields a value of 0.30 percent as the calculated oxygen content for the entire substrate cross-section. This value compares well with the over-all specimen oxygen content of 0.33 percent determined by vacuum fusion analysis.

Oxygen diffusion also appears to be responsible for the hardness gradient observed beneath the inner surface. The total solid-solution oxygen required to produce the peak hardness shown at the inner surface would be approximately 0.09 percent. Adding this to the 0.25 percent oxygen which combines with zirconium yields 0.34 percent oxygen at the inner surface. This value is consistent with the results of the partial section vacuum fusion analysis which indicated an oxygen gradient in this area.

It should be emphasized at this point that the mechanism postulated above to explain the microstructural hardness and compositional results obtained on the tested substrate has not been verified. Considerably more refined and detailed testing and analysis would be necessary. As stated previously, it is entirely possible that changes in the composition and structure of the metallurgical phases present in the substrate, which it has not been possible to examine, play a part in producing the observed results. It is felt, however, that the postulated mechanism does explain all of the observed phenomena in general terms and that it provides a starting point for future investigations.

There are several possible sources of the oxygen which diffused into the substrate. The existence of an oxygen gradient extending inward from both substrate surfaces indicates that oxygen diffusion occurred across both surfaces. The obvious source of oxygen for the outer surface is the iron-titanate coating. The fact that diffusion across the coating-substrate interface occurs has already been demonstrated by the presence of iron and titanium in the substrate. For the inner surface, there are two possible sources of oxygen. First, it is possible that a thin oxide layer was formed on the inner surface during plasma-arc spraying of the coating, as postulated earlier.[2] During the endurance test, the oxygen in the oxide layer might be expected to diffuse into the substrate. The second source is the residual gases in the test chamber. It has been found that columbium absorbs significant quantities of oxygen from the residual gases in a vacuum. For example, H. Inouye[6] found an increase in oxygen content of approximately 125 ppm in columbium specimens exposed to a vacuum of 1×10^{-7} mm Hg for 1000 hours at 1700°F. It would be expected that exposure to these conditions for the longer periods for this program would result in even higher oxygen levels. From this it would appear that the hardness gradient observed on the inner surface is attributable to oxygen contamination resulting from the specimen coating techniques used as well as the specific test environment and is not the result of a coating-substrate interaction.

In summary, post-test analysis of the iron-titanate-coated columbium-1 percent zirconium tube revealed that iron and oxygen, and to a lesser extent, titanium, diffused into the substrate during the 10,000-hour exposure to vacuum and a temperature of 1700°F. Microhardness gradients extending inward from both substrate surfaces were found, as was a general increase in over-all hardness compared to that expected on the basis of the microstructure. A tentative explanation for the observed hardness changes has been postulated on the basis of the diffusion detected. However, in spite of the various phenomena which occurred during the test, neither a serious loss in the emittance of the coating nor any degradation of the coating integrity or adherence was observed.

2. Aluminum-Oxide-Aluminum-Titanate on Colubmium-1 Percent Zirconium

With the addition of 4700 hours of testing during the current report period, the columbium-1 percent zirconium tube coated with a 4-mil thick layer of aluminum-oxide-aluminum-titanate completed 10,000 hours of testing in vacuum at 1700°F. During the test, the specimen was subjected to a total of 63 thermal cycles between 1700°F and room temperature, with 26 of these cycles occurring during this report period. Thermal cycling produced no visible adverse effects on the specimen. The appearance of the specimen at 1700°F shortly before the end of the test is shown in Figure 23.

Initially, the specimen had an emittance of 0.87, but the emittance dropped steadily throughout the test, reaching a value of 0.80 at the completion of the test. A vacuum of 1×10^{-7} mm Hg or better was maintained throughout the test. The emittance values and the vacuum maintained are shown in Figure 24.

The appearance of the coating after testing is shown in Figure 25, together with a coated, untested specimen. It is evident that substantial changes occurred during testing. No spalling or cracking of the coating occurred, but the color changed from a uniform light gray to a much whiter color mottled with gray patches. This change was first observed after approximately 9000 hours of testing.

After testing, the specimen was sectioned for metallographic examination. The specimen cross-section is shown in Figure 26. The substrate microstructure prior to testing was the same as that for the iron-titanate-coated tube shown in Figure 18. Comparison of these figures indicates that the entire substrate recrystallized during testing. Photomicrographs of the coating-substrate interface are shown in Figure 27 and 28. The specimen shown in Figure 28 was etched to show the formation of a second phase at the coating-substrate interface. The layer is less than 0.1 mil thick and is virtually continuous around the interface circumference.

A total of four microhardness traverses were made on the substrate cross-section, and the results are presented in Table 12 and Figure 29. The results indicate a slight increase in hardness in the interior of the substrate, but the variation is within the accuracy limits of the test technique and probably does not represent a true increase. The over-all hardness is equal to that expected for fully recrystallized columbium-1 percent zirconium. The hardness of the phase at the coating-substrate interface could not be measured because of its thinness.

TABLE 12

Microhardness Traverse Results for Endurance-Tested Columbium-1 Percent Zirconium Tube Coated With Aluminum-Oxide-Aluminum-Titanate

Traverse 1

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
0.5	85
2.5	92
4.25	94
6.5	93
8.25	97

Traverse 2

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
1.0	86
3.5	91
5.5	99
7.25	104
9.25	85

Traverse 3

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
2	97
4	96
6	105
8	96

Traverse 4

Depth (Mils)	Diamond Pyramid Hardness (kg/mm^2)
2	96
4	101
6	113
8	96

Electron-beam microprobe analyses were conducted for aluminum and titanium concentrations in the tested substrate. The results are presented in Table 13 and Figure 30. As shown, high, steep gradients were detected for aluminum and titanium at the coating-substrate interface, indicating that the interface phase shown in Figure 28 is a quarternary alloy of aluminum, titanium, zirconium, and columbium. The results also show a very shallow aluminum gradient extending through virtually the entire section.

A vacuum fusion analysis for oxygen content was conducted on the full section of the substrate after the coating was removed mechanically and by acid etching. An oxygen content of 0.145 percent was found. The fact that this specimen had so high an oxygen level but still had a hardness equal to that associated with columbium-1 percent zirconium alloys with lower oxygen concentration provides substantiation for the assumption made for the iron-titanate-coated specimen that oxygen is ineffective as a solid solution hardening agent until it has reacted with all of the available zirconium.

A spectrographic analysis was made on the coating material both before and after testing. The results, shown in Table 14, indicate that small amounts of columbium and zirconium diffused into the coating during the test.

Detailed visual examination of the coating showed that the portions of the coating which appeared white consisted of three layers: a white layer on the outer surface, a light gray layer very similar in color to the as-sprayed coating, and, at the substrate surface, a thin, dense, very dark gray layer. In those portions of the coating which showed the darker, mottled appearance, the white layer was either very thin or non-existent.

In order to understand the reactions which had occurred, X-ray diffraction analyses were conducted on the various portions of the coating. The results are presented in Table 15.

As shown, only a questionable indication of the presence of aluminum titanate was found after testing. This indicates a virtually complete breakdown of the titanate compound. Some columbium diffusion evidently occurred during testing. The gray areas would appear to contain significant quantities of columbium both as a columbium-aluminum intermetallic compound and possible as columbium oxide.

TABLE 13

Concentrations of Aluminum and Titanium Across Columbium-1 Percent Zirconium Tube Coated With Aluminum-Oxide-Aluminum Titanate and Endurance Tested at 1700°F for 10,000 Hours

Distance from Outer Surface (Mils)	Concentration (Weight Percent)	
	Al	Ti
0	6.5	1.2
0.08	3.5	0.7
0.15	0.5	0.3
0.25	0.4	0.2
0.34	0.3	0.1
0.41	0.15	0.05
0.05	0.11	0.01
0.60	0.09	0.02
0.69	0.08	0.02
0.75	0.09	0.03
0.85	0.08	0.01
0.01	0.08	0.03
1.16	0.09	0
1.58	0.07	0
2.02	0.07	0
2.40	0.08	0
2.84	0.06	0
3.25	0.08	0
3.66	0.08	0
4.07	0.09	0
4.48	0.06	0
4.90	0.06	0
5.31	0.07	0
5.72	0.06	0
6.10	0.06	0
6.54	0.06	0
6.92	0.06	0
7.33	0.05	0
7.74	0.05	0
8.15	0.06	0
8.55	0.06	0
8.94	0	0
9.20	0.05	0
9.35	0	0
9.45	0.05	0
9.51	0.05	0
9.61	0	0
9.67	0	0
9.77	0.05	0
9.83	0	0
9.92	0.05	0
10.0	0.05	0

Note: Minimum detectable concentrations for aluminum and titanium are 0.03 and 0.01 percent, respectively. Concentrations below these levels are reported as 0.

TABLE 14

Spectrographic Analysis Results for Aluminum-Oxide-Aluminum Titanate Coating Applied to Columbium-1 Percent Zirconium

	Concentration (Weight Percent)						
	Cb	Cu	Fe	Mg	Mn	Si	Zr
As Received (Powder)	0	<0.01	0.5	0.6	trace	0.1	0
As Sprayed	0	<0.01	0.05	0.4	trace	0.1	0
After Endurance Test	0.04	<0.01	<0.01	0.01	0	<0.01	<0.02

TABLE 15

X-Ray Diffraction Analysis Results for Aluminum-Oxide-Aluminum Titanate Coating Applied to Columbium-1 Percent Zirconium Tube and Endurance Tested at 1700°F for 10,000 Hours

Powder-As Received	Al_2O_3, TiO_2, Al_2TiO_5, possibly TiO
Coating-As Tested	
Full Cross-Section	Al_2O_3, TiO_2, Ti_2O_3, Cb Al_3, CbO_2
White Area	Al_2O_3, TiO_2, possibly Al_2TiO_5
Gray Area	Al_2O_3, Cb Al_3, probably TiO and CbO_2

The white areas, however, were found to be free of these compounds and consisted almost completely of aluminum and titanium oxides. From these results, it is concluded that the reactions in the coating were initiated at the coating-substrate interface and moved slowly outward. This behavior appears to explain why no change in the coating was observed until after some 9,000 hours of testing.

Endurance testing and analysis of an aluminum-oxide-aluminum-titanate coated columbium-1 percent zirconium tube indicated that the coating remains well bonded to the substrate for 10,000 hours at a temperature of 1700°F, but that the coating is not sufficiently stable to maintain its chemical composition and emittance properties in the test environment. This would indicate that aluminum-oxide-aluminum-titanate is not a suitable coating material for space radiator applications at 1700°F.

3. Calcium Titanate on AISI-310 Stainless Steel

Testing of the AISI-310 stainless-steel tube coated with a 4-mil thick layer of calcium titanate was continued through the report period. An additional 4320 hours were accrued during the report period for a total accumulated time of 14,920 hours. Throughout the report period, the emittance has remained steady at 0.88. The emittance and vacuum maintained during the test are shown in Figure 31.

The specimen was thermally cycled 26 times between 1350°F and ambient with no adverse effects on coating adherence or emittance being observed. The speciment has now been cycled 77 times.

4. Iron Titanate on AISI-310 Stainless Steel

The AISI-310 stainless steel tube coated with a 4-mil thick layer of iron titanate was tested for an additional 4320 hours during the report period, resulting in a total accumulated time of 13,920 hours of testing in vacuum at 1350°F. The emittance has been very stable, showing only a slight decrease from 0.89 to 0.88 since the start of the test. Emittance and vacuum levels recorded throughout the test are shown in Figure 32.

The specimen has been thermally cycled a total of 77 times between 1350°F and ambient temperature, with 26 of the cycles being performed during the report period. No adverse effects on emittance or adherence have been observed.

V. CONCLUSIONS

Aging tests performed on coated beryllium plates demonstrated that beryllium is not suitable for space radiator use at a temperature of 1400°F because of excessive beryllium vaporization. Coatings of calcium-titanate, iron-titanate, and zirconium titanate were shown to be compatible with beryllium for at least 1000 hours at temperatures up to 1200°F, although the zirconium-titanate appeared to form a weaker bond with the beryllium than did the other coating materials. Analysis of the beryllium after aging revealed no changes other than insignificant, but detectable, diffusion of the coating constituents across the coating-substrate boundary, and an almost negligible decrease in weight. The coatings were generally unchanged by aging except for a slight darkening in color. An exception was the calcium titanate coating for which aging permanently increased the emittance from about 0.68 to 0.92. The emittance of both the iron-titanate coating and the zirconium titanate was about 0.91 at 900°F.

Analysis of an iron-titanate-coated columbium-1 percent zirconium tube endurance tested for 10,000 hours at 1700°F indicates that this coating substrate combination has adequate bond strength and emittance characteristics for space radiator use at 1700°F. Emittance values between 0.88 and 0.84 were achieved over a period of 10,000 hours. After 10,000 hours of testing at 1700°F, the substrate exhibited extensive but incomplete recrystallization and limited diffusion of iron and titanium across the coating-substrate interface. The oxygen content increased significantly, diffusing across both the inner and outer surfaces. The combined effects of diffusion of oxygen and coating constituents raised the substrate hardness somewhat above what would be expected for annealed columbium-1 percent zirconium. In addition, a very small amount of zirconium diffused into the coating. Aside from hardening the substrate, diffusion did not appear to affect either the coating or substrate detrimentally.

Analysis of a columbium-1 percent zirconium specimen coated with aluminum-oxide-aluminum titanate and tested for 10,000 hours at 1700°F indicated that this combination is not suitable for space radiator use at 1700°F. Adequate bond strenth was demonstrated, but the coating is not sufficiently stable to maintain its chemical composition and emittance properties in the test environment. During 10,000 hours of testing at 1700°F in vacuum, the emittance decreased steadily from 0.87 to 0.80.

Continued testing of AISI-310 stainless steel tubes coated with calcium-titanate and iron-titanate indicates that both of these coating-substrate combinations are suitable for space-radiator use at 1350°F. The calcium-titanate-coated tube has been tested for 14,920 hours, and the iron-titanate-coated tube has been tested for 13,920 hours. Both have exhibited nearly constant emittance values of about 0.88.

VI. FUTURE WORK

The two remaining long-term total hemispherical emittance tests being conducted on iron-titanate and calcium-titanate coatings on AISI-310 stainless steel will be continued up to at least 20, 000 hours at 1350°F.

In addition, two 5000-hour thermal cycling endurance tests will be started on iron-titanate coatings applied to columbium-1 percent zirconium substrates. The specimens will be cycled between two temperatures, with a one-hour heating cycle and a 36-minute cooling cycle. The first specimen will be cycled between 1500°F and 1800°F, and the second will be cycled between 1500°F and 1900°F. Both tests will be conducted at pressures of 1x 10^{-7}mm Hg or lower.

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3. W. Luoma and R. C. Emanuelson, Semi-Annual Progress Report on Determination of the Emissivity of Materials, PWA-2608, NASA CR-54444, Pratt & Whitney Aircraft, East Hartford, Connecticut, June 30, 1965.

4. J. R. Stewart, W. Lieberman, and G. H. Rowe, "Recovery and Recrystallization of Cb-1% Zr Alloy," Columbium Metallurgy (Volume 10), Metallurgical Society Conferences, 1960

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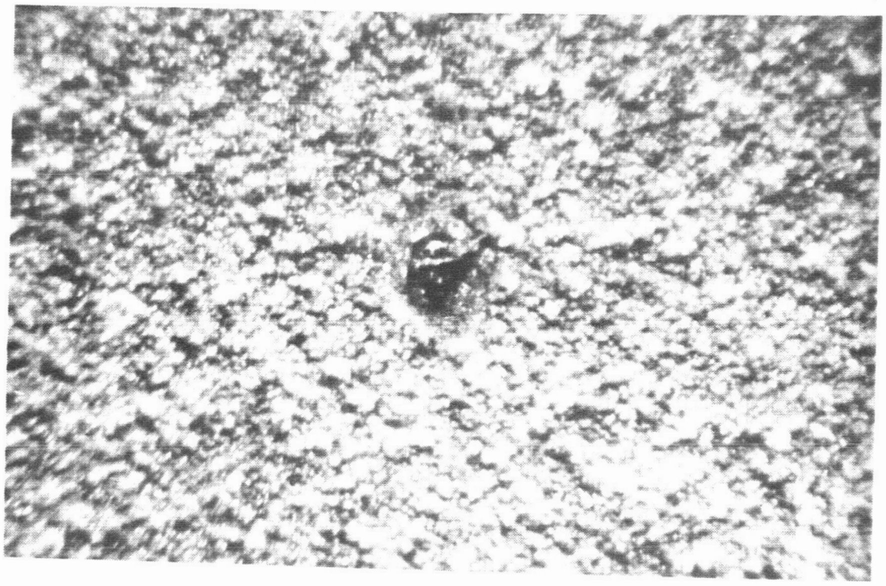
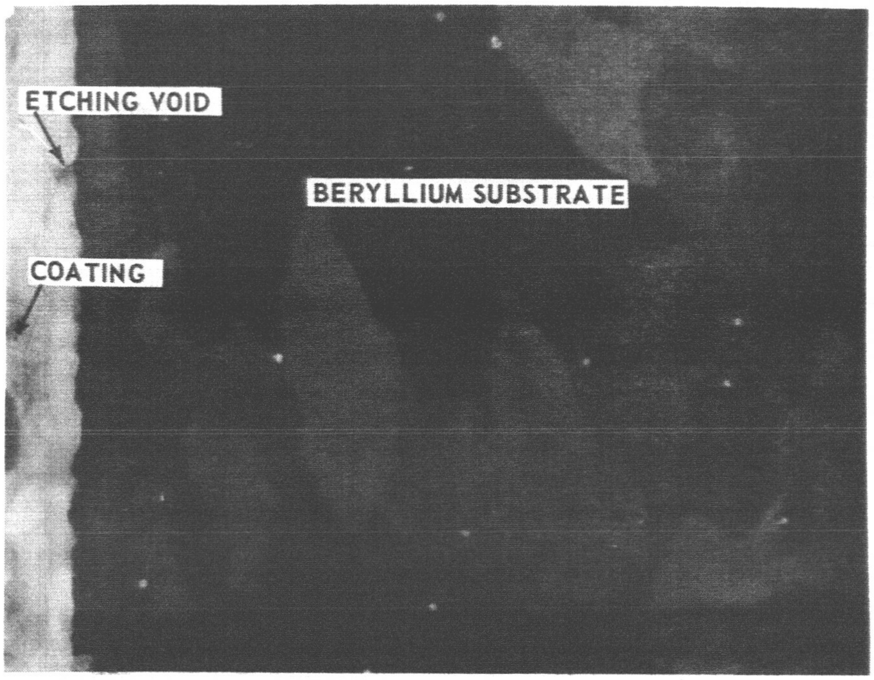
6. H. Inouye, Contamination of Refractory Metals by Residual Gases in Vacuums Below 10^{-6} Torr, ORNL-3674, N64-28983, Oak Ridge National Laboratory, September, 1964.



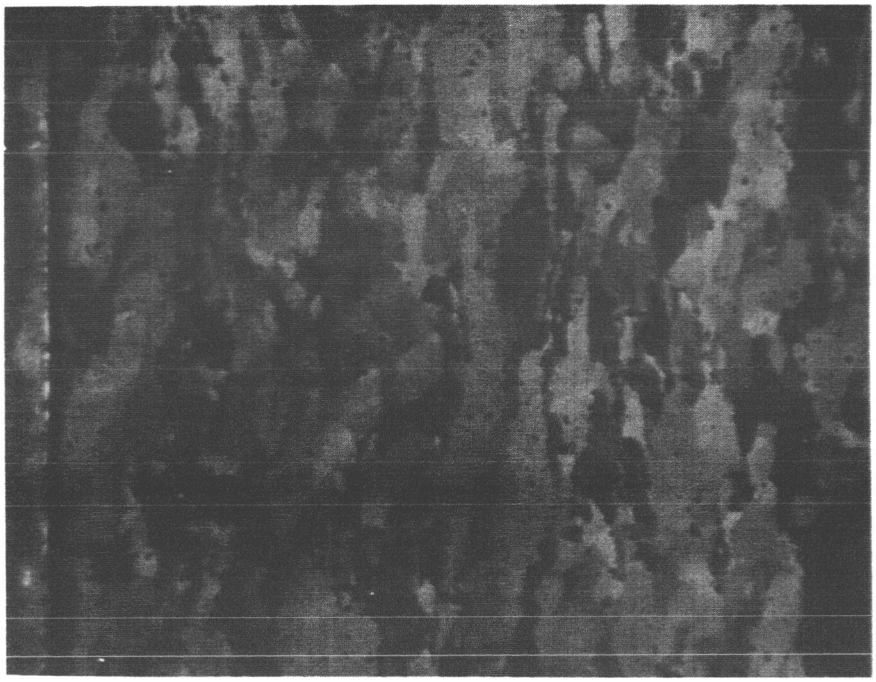
Back Mag: 20X

Front Mag: 20X

Figure 1 Typical Thermocouple Installation on Beryllium Plate



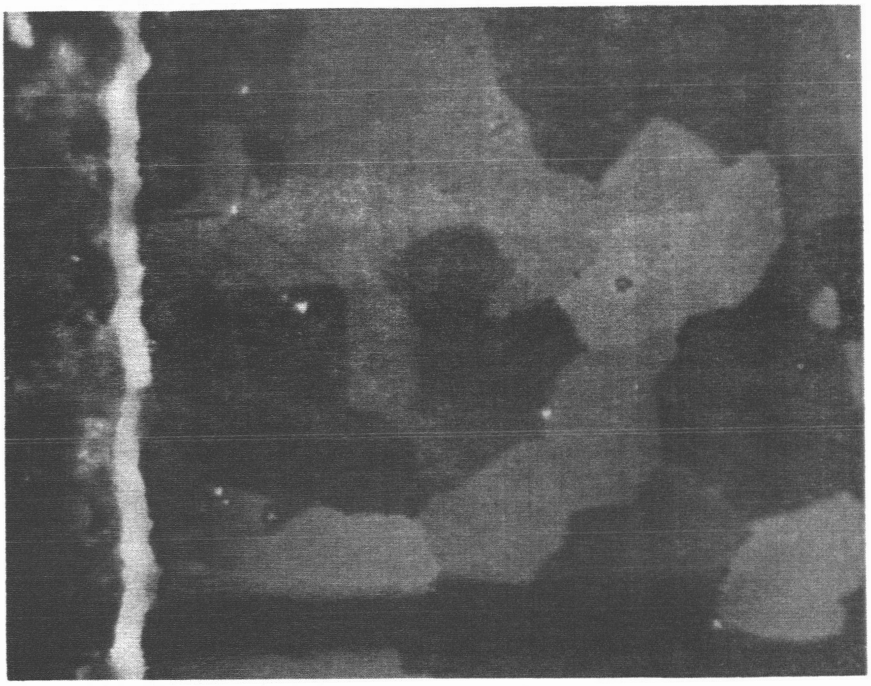
First Shipment 200X



First Shipment 50X

Etchant: 49% NH_2 SO_3 H, 16% $H_2C_2O_4$, 1

Figure 2 Typical Cross Sectional Phot
From First and Second Shipm



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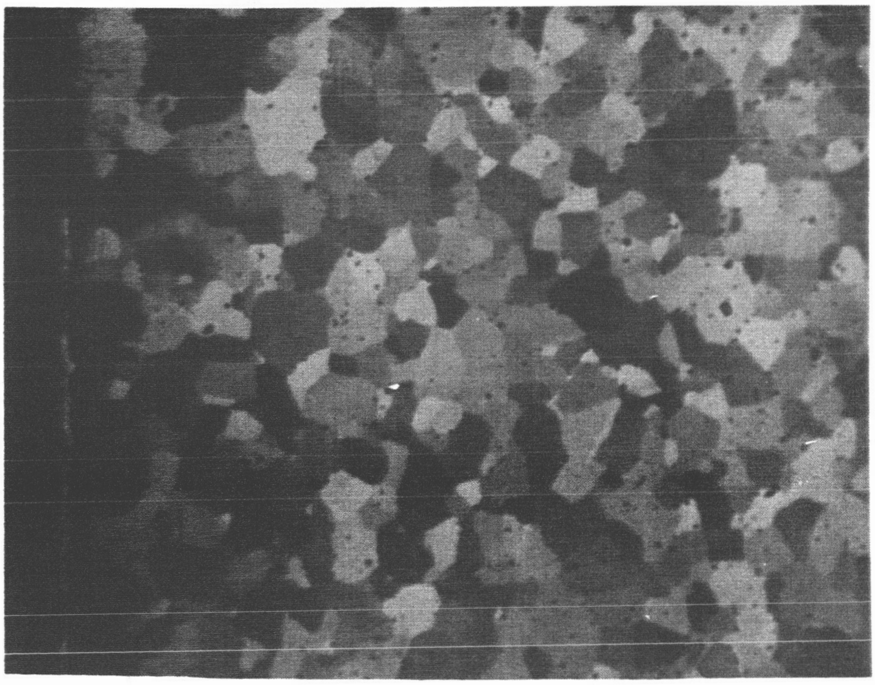

Second Shipment 50X

HF, 34%H_2O

micrographs of Beryllium Plates
ents

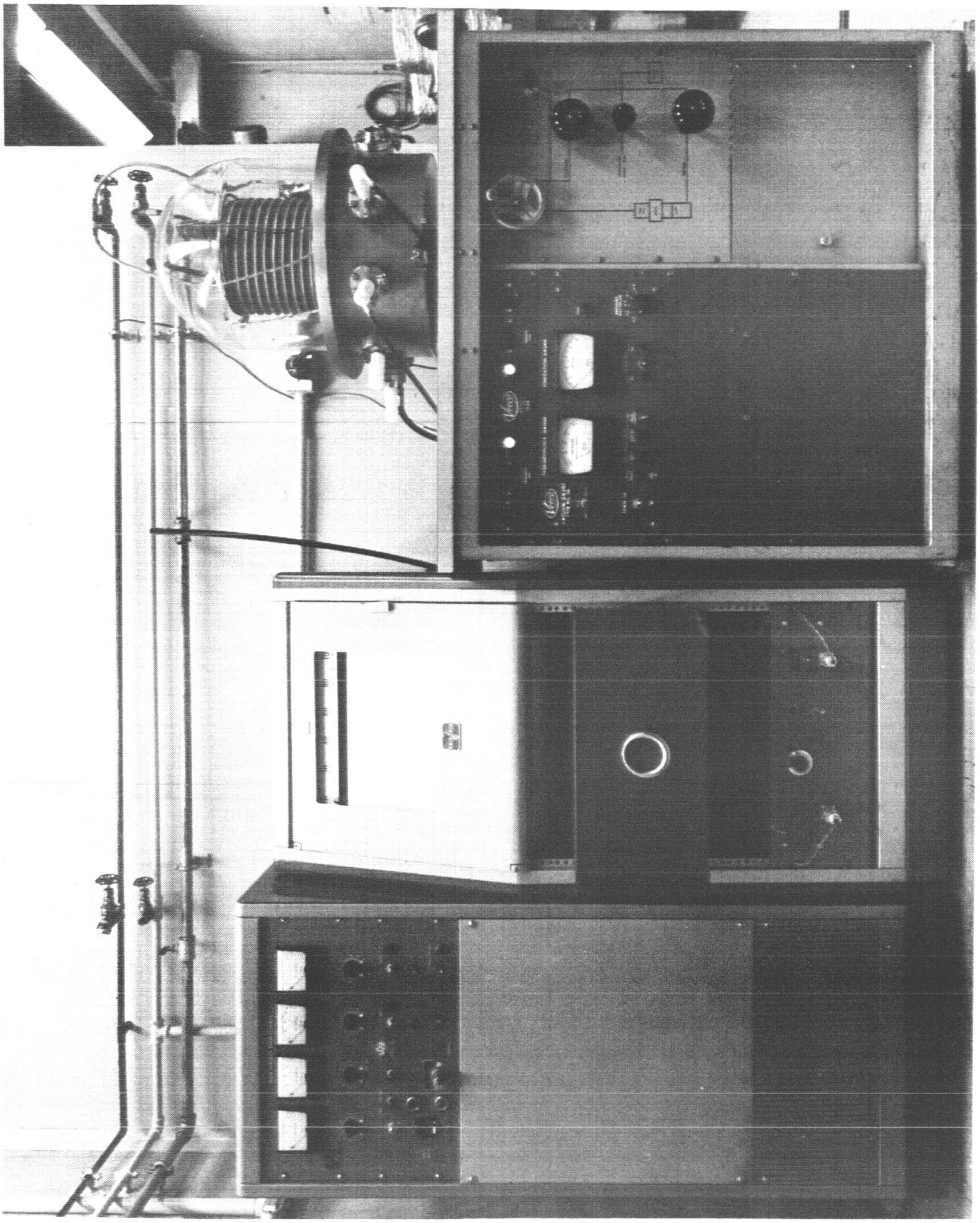

Figure 3 Thermal Decay Apparatus for Emittance Measurement X-21989

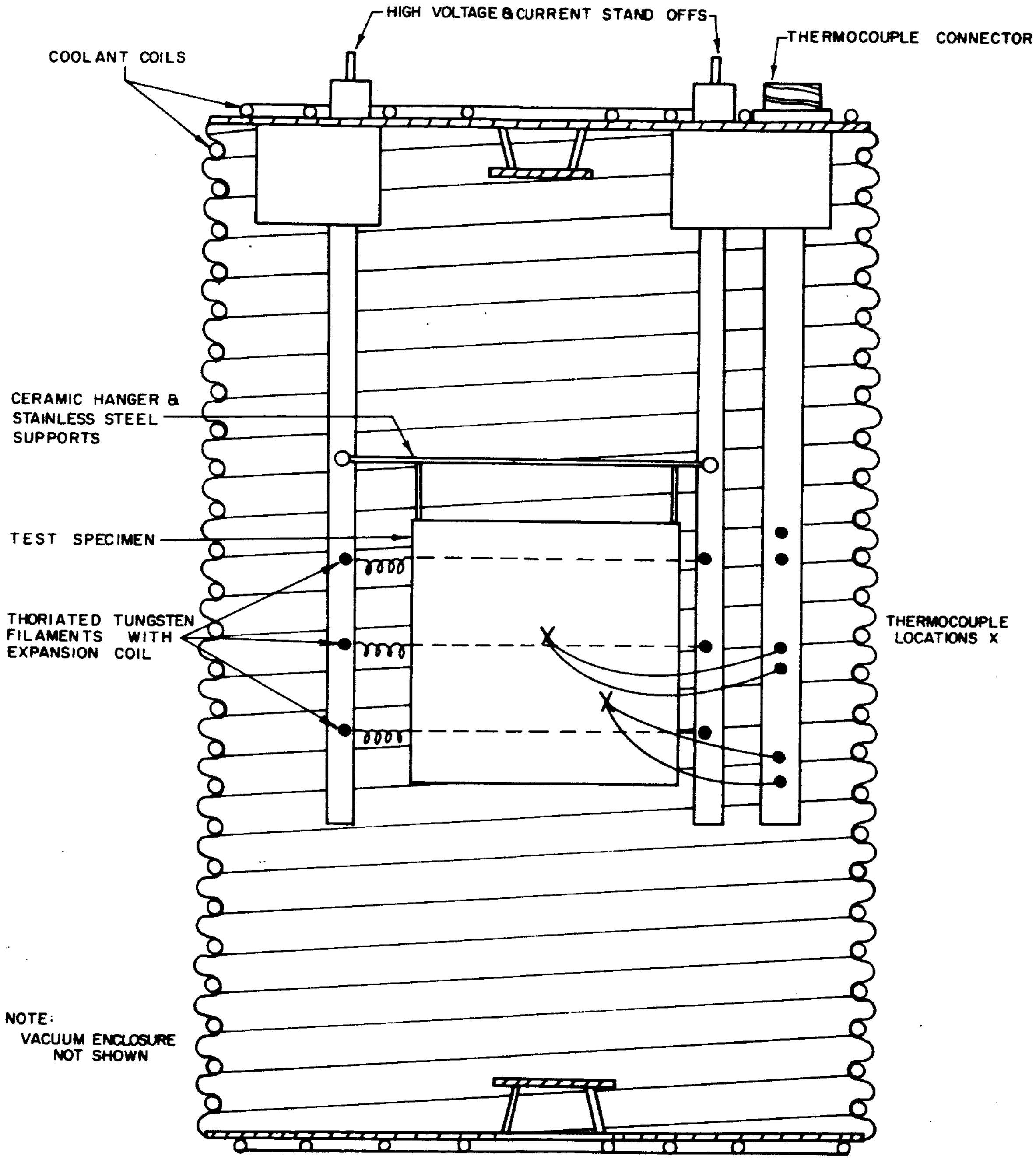

Figure 4 Schematic Drawing of Specimen Installation in Thermal Decay Emittance Test Apparatus

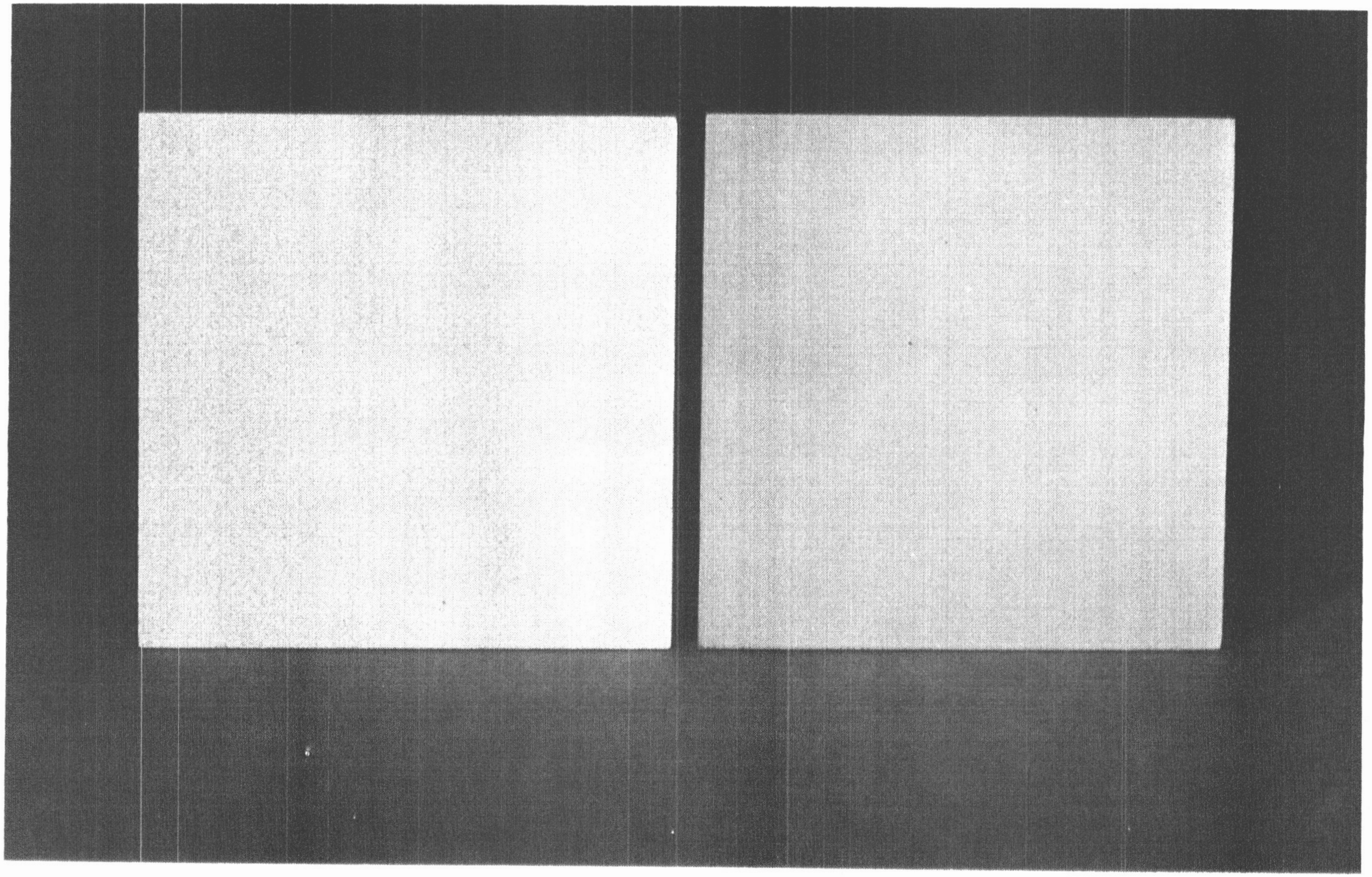

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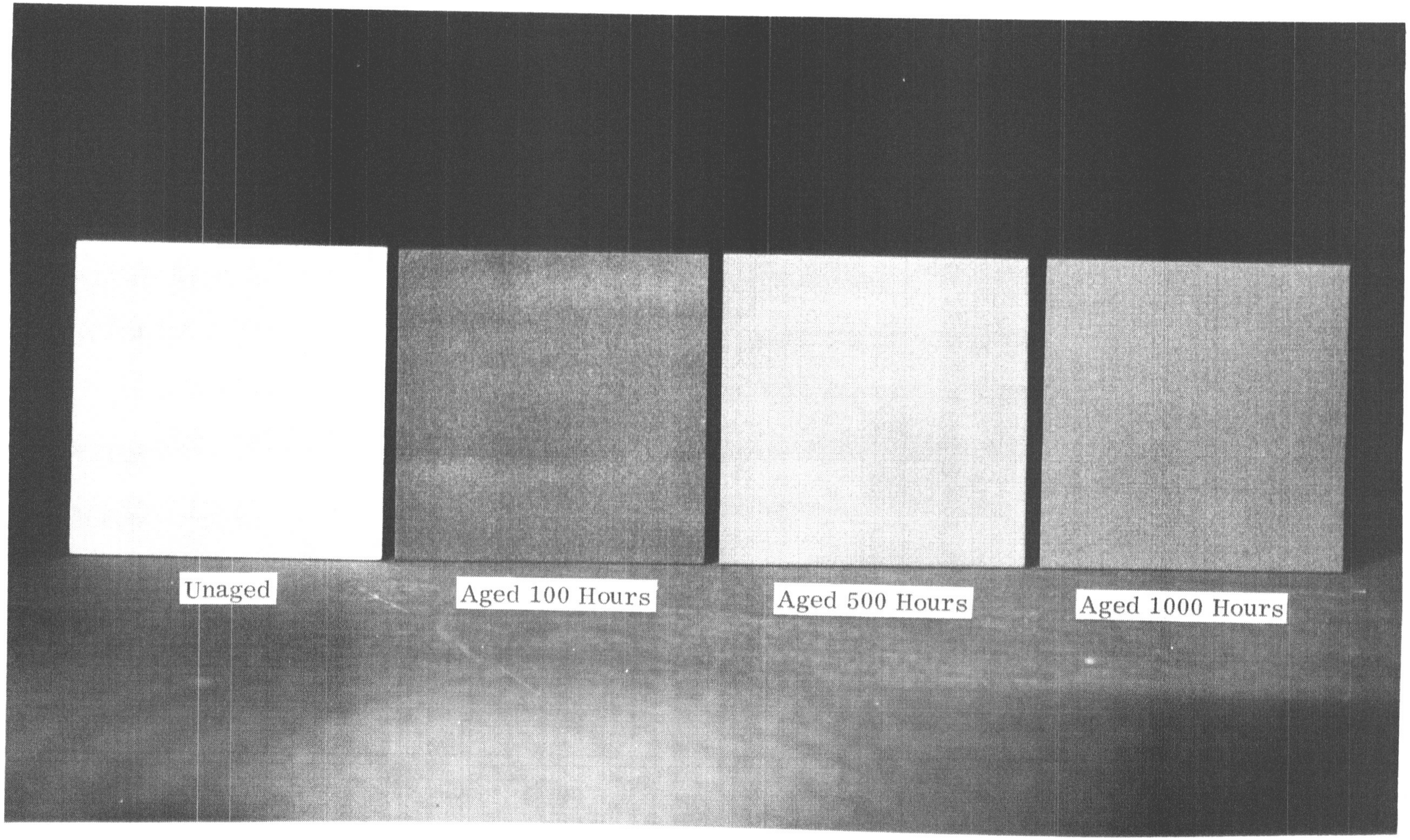
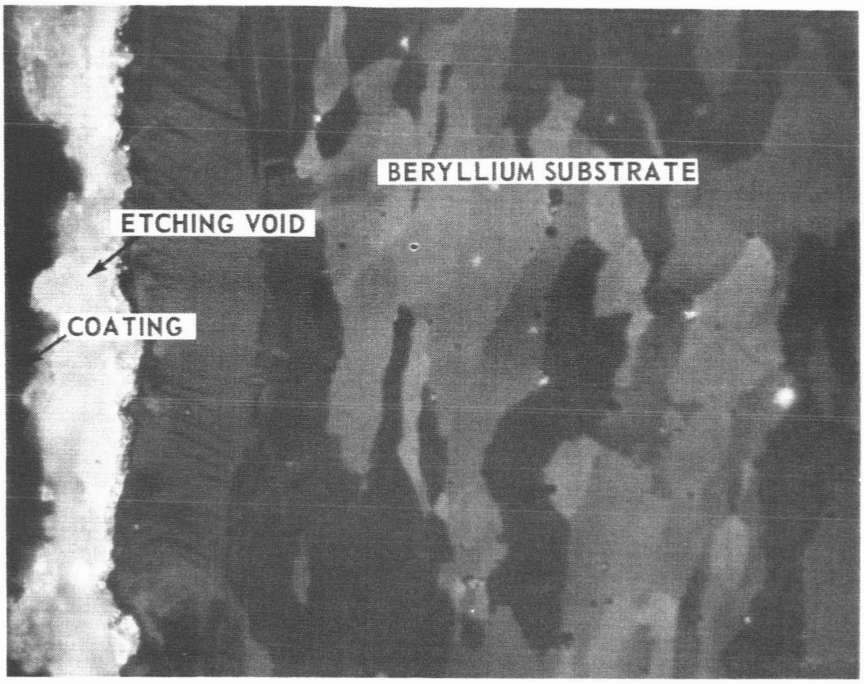
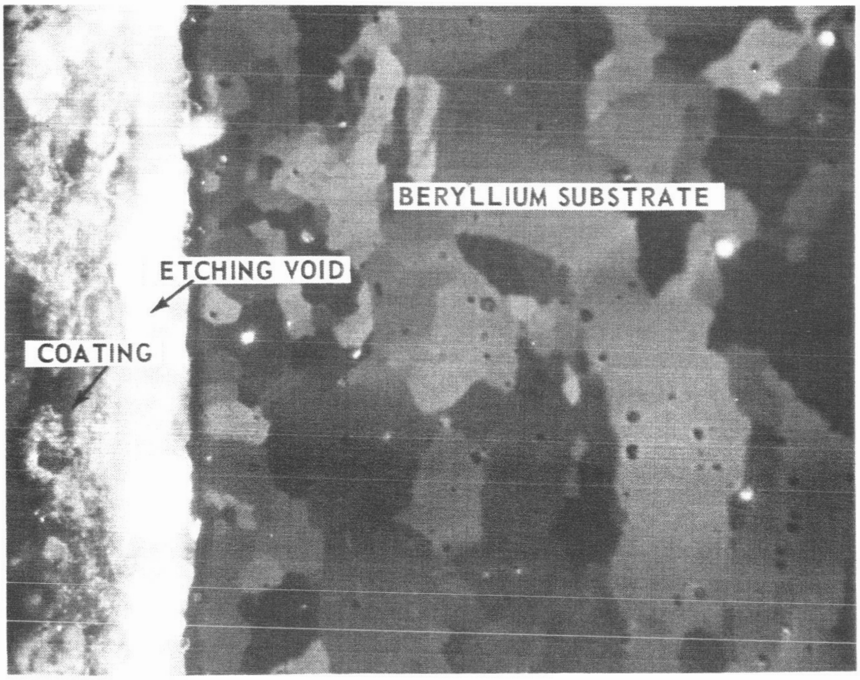
Figure 5 Appearance of Calcium-Titanate-Coated Beryllium Plate Before (Left) and After (Right) Being Aged at 800°F for 1000 Hours XP-66871



Mag: 0.6X

Figure 6 Appearance of Calcium-Titanate Coated Beryllium Plates Before Aging and After Aging at 1400°F for 100 Hours, at 1200°F for 500 Hours, and at 1200°F for 1000 Hours XP-66878





Etchant: 49% NH_2 SO_3H, 16% $H_2C_2O_4$, 1% HF, 34% H_2O Mag: 200x

Figure 7 Typical Cross Sectional Photomicrographs of Calcium-Titanate-Coated Beryllium Plates Aged for 1000 Hours at 800°F (Top) and 1200°F (Bottom)

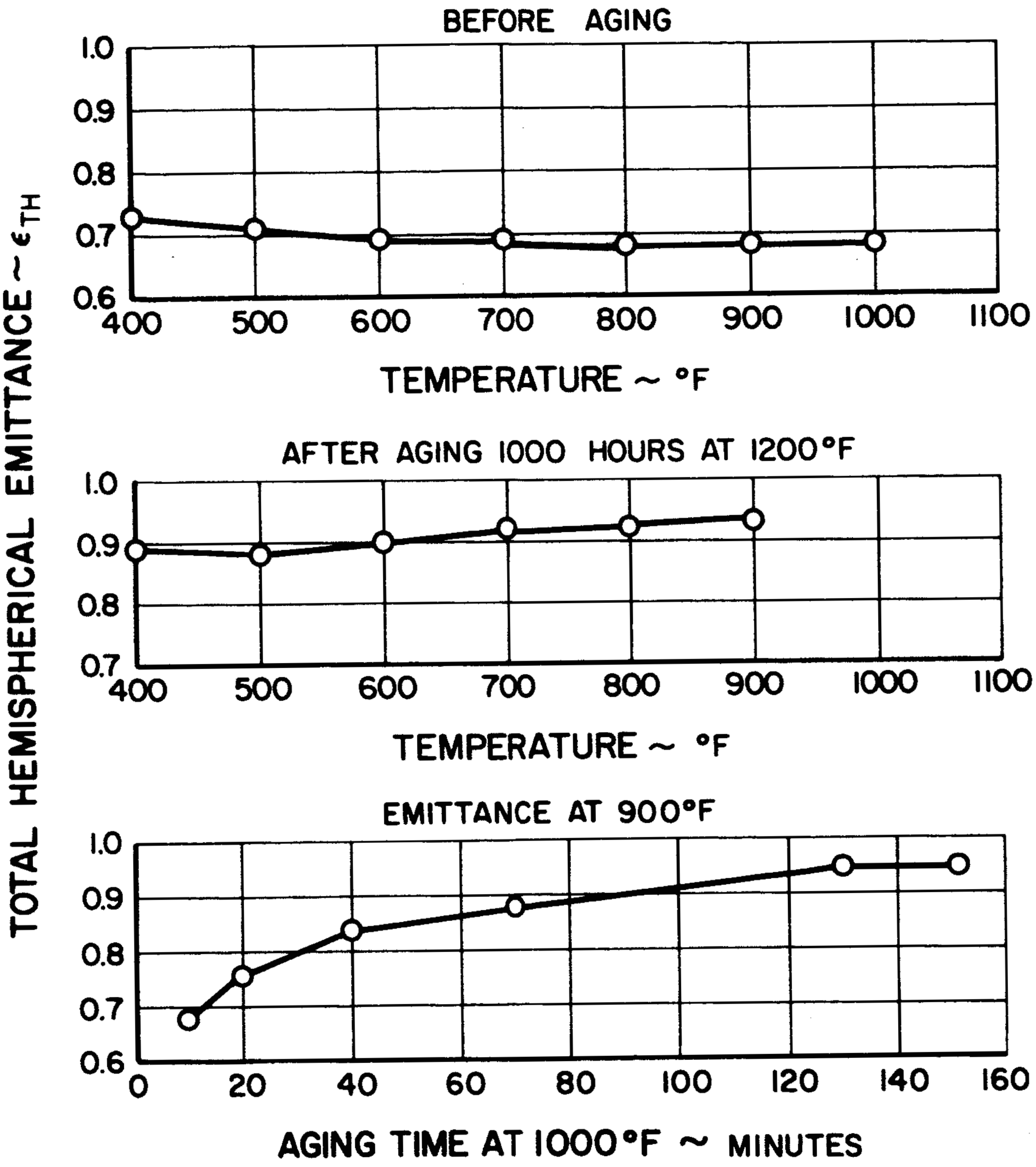
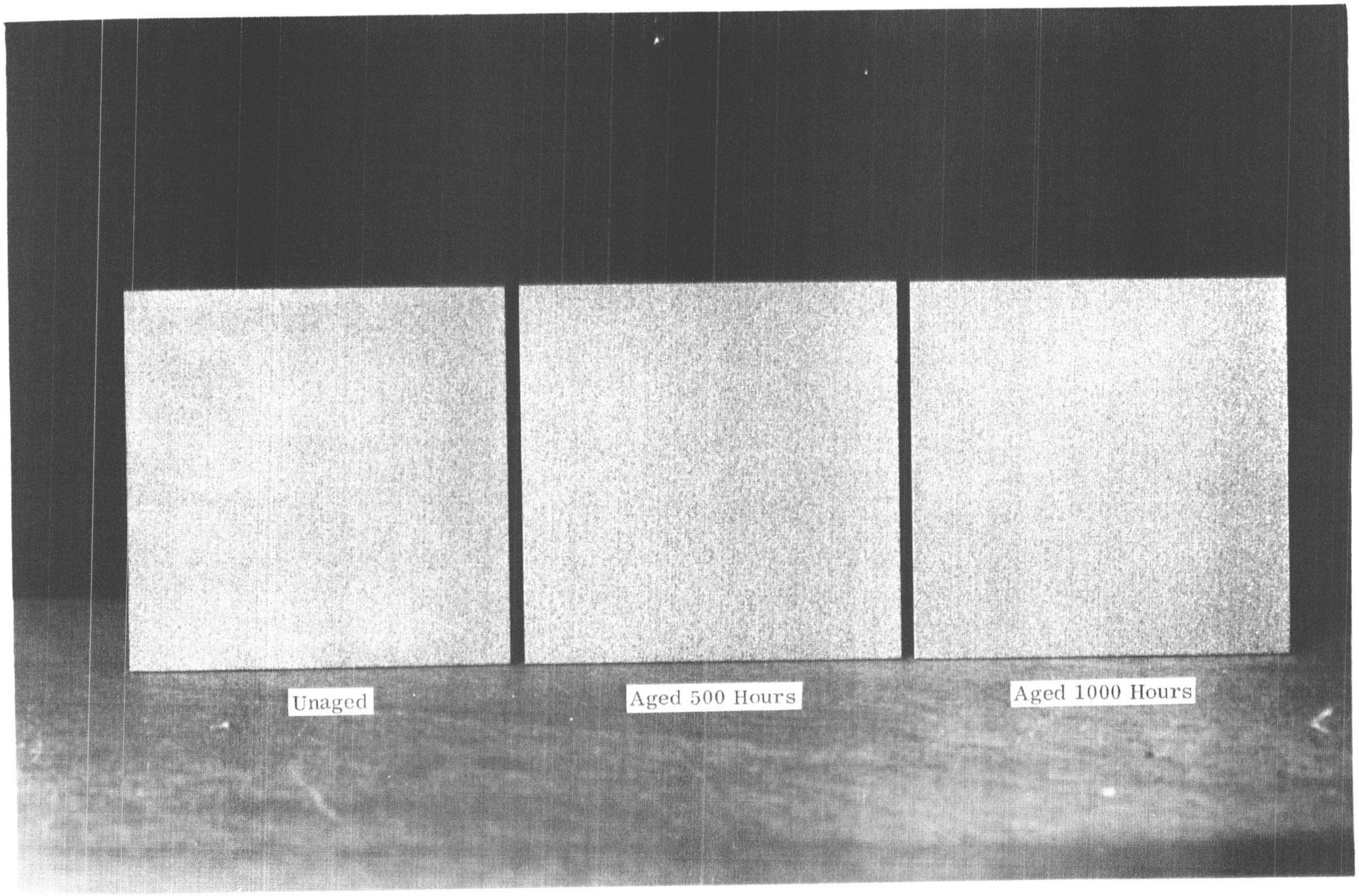
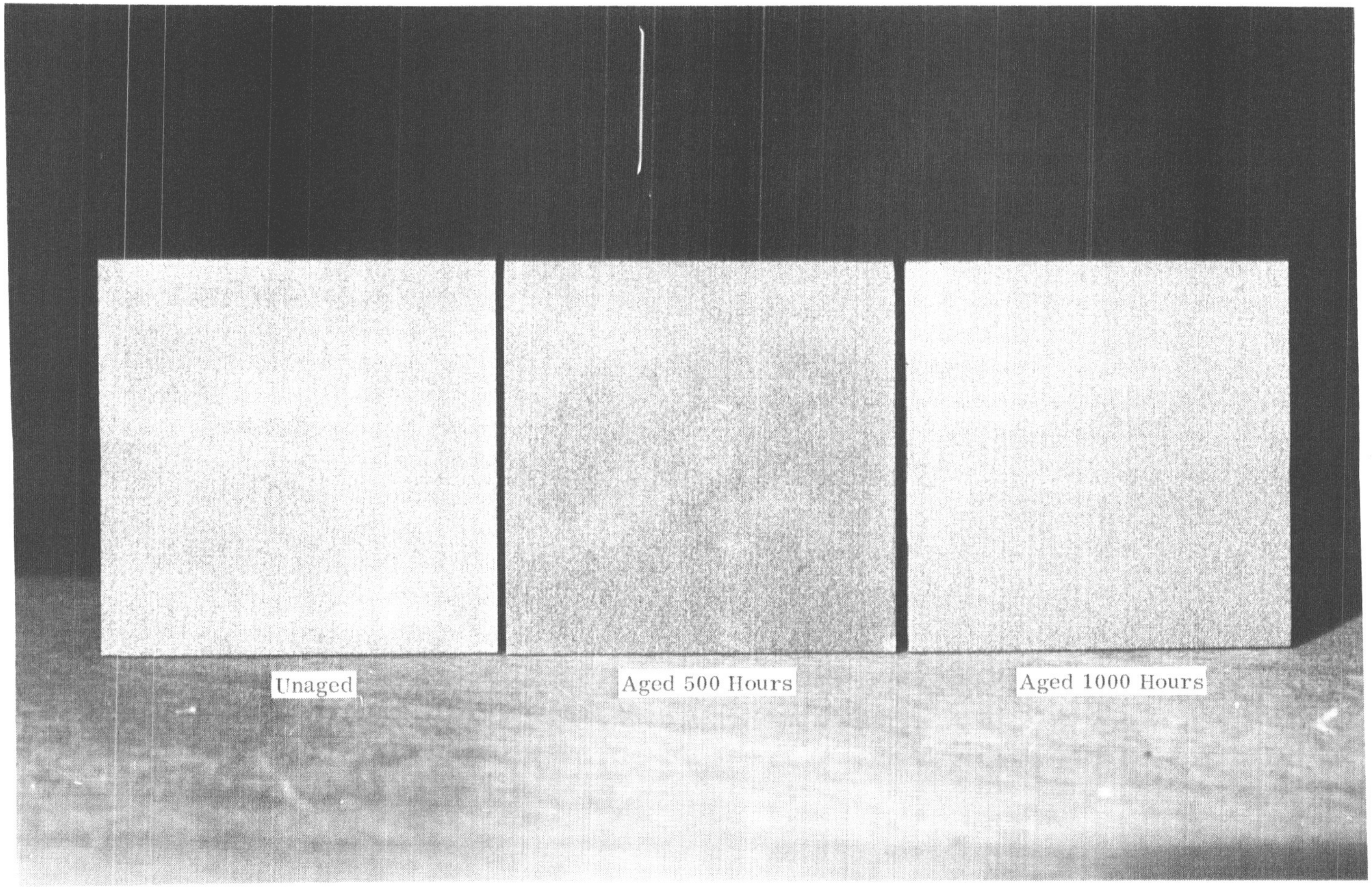


Figure 8 Total Hemispherical Emittance Measurement Results for Calcium-Titanate-Coated Beryllium Plates Using Thermal Decay Method



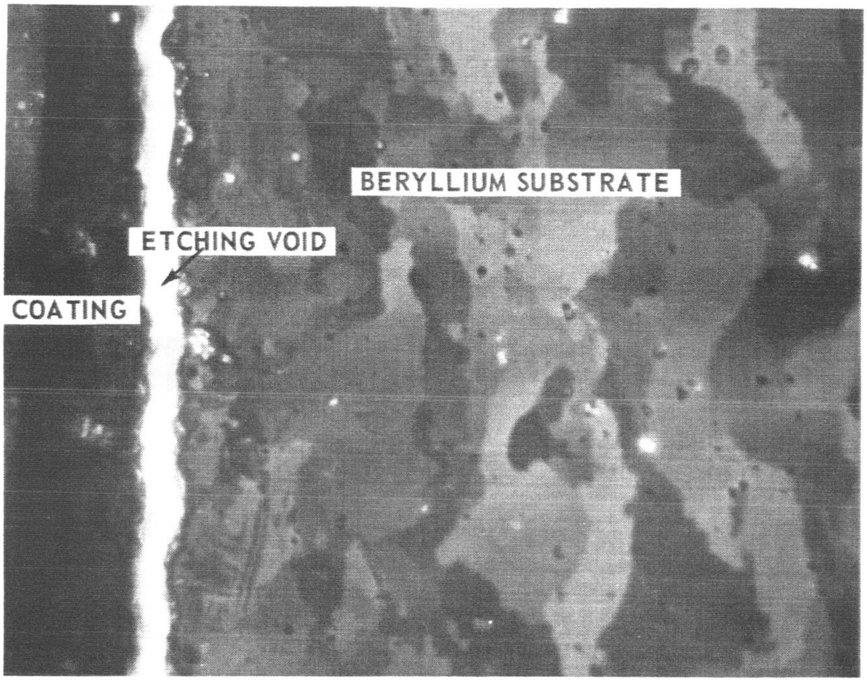
Mag: 0.7X

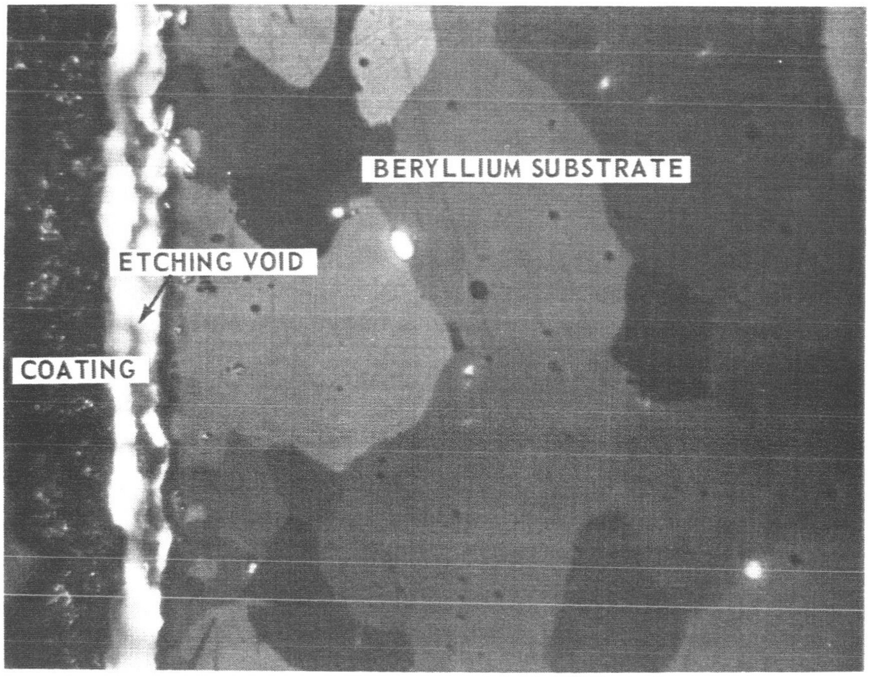
Figure 9 Appearance of Iron-Titanate-Coated Beryllium Plates Before Aging and After Aging at 800°F for 500 and 1000 Hours XP-66874



Mag: 0.7X

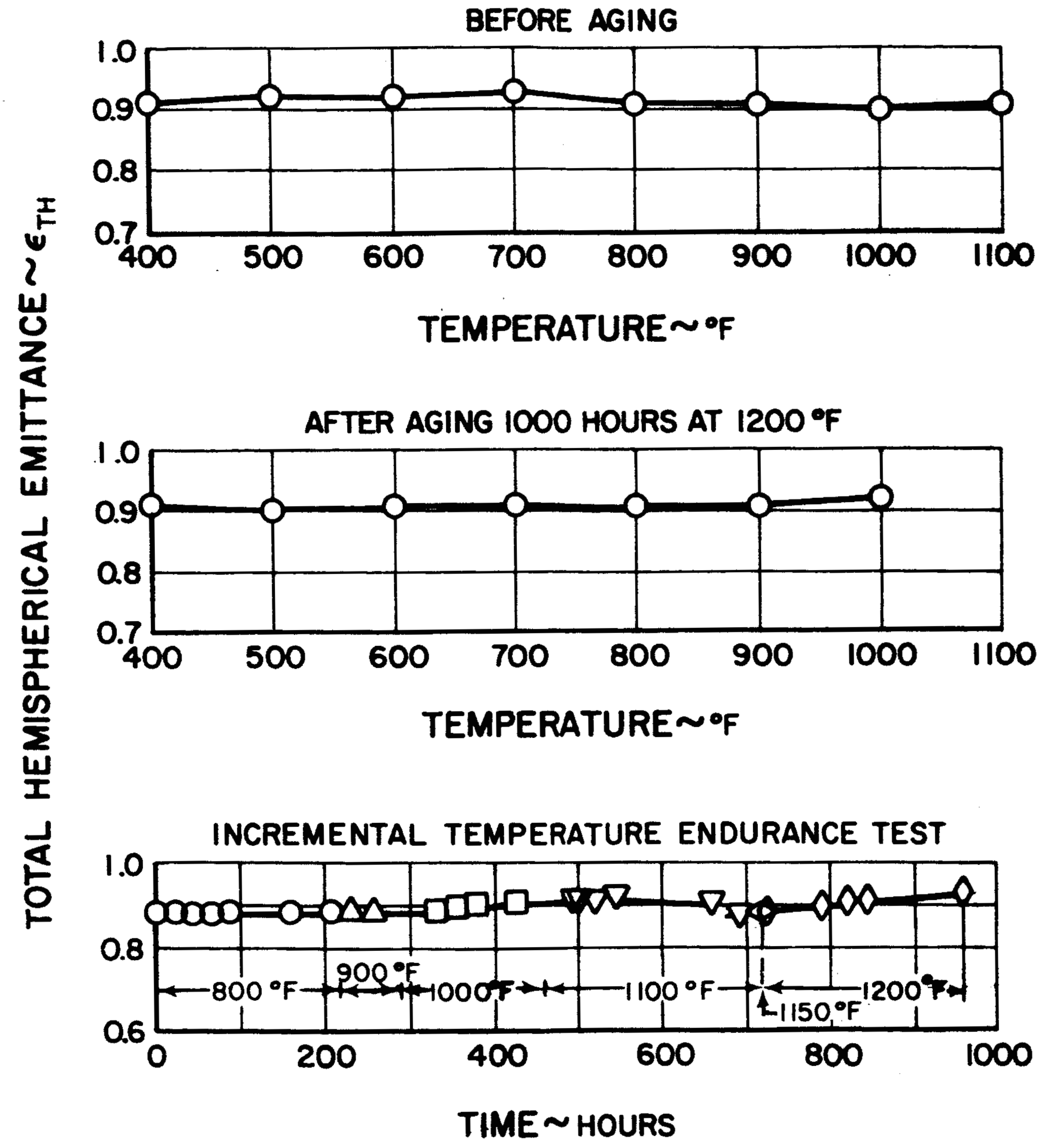
Figure 10 Appearance of Iron-Titanate-Coated Beryllium Plates Before Aging and After Aging at 1200°F for 500 and 1000 Hours XP-66875





Etchant: 49% $NH_2\ SO_3\ H$, 16% $H_2C_2O_4$, 1% HF, 34% H_2O Mag: 200x

Figure 11 Typical Cross Sectional Photomicrographs of Iron-Titanate-Coated Beryllium Plates Aged for 1000 Hours at 800°F (Top) and 1200°F (Bottom)

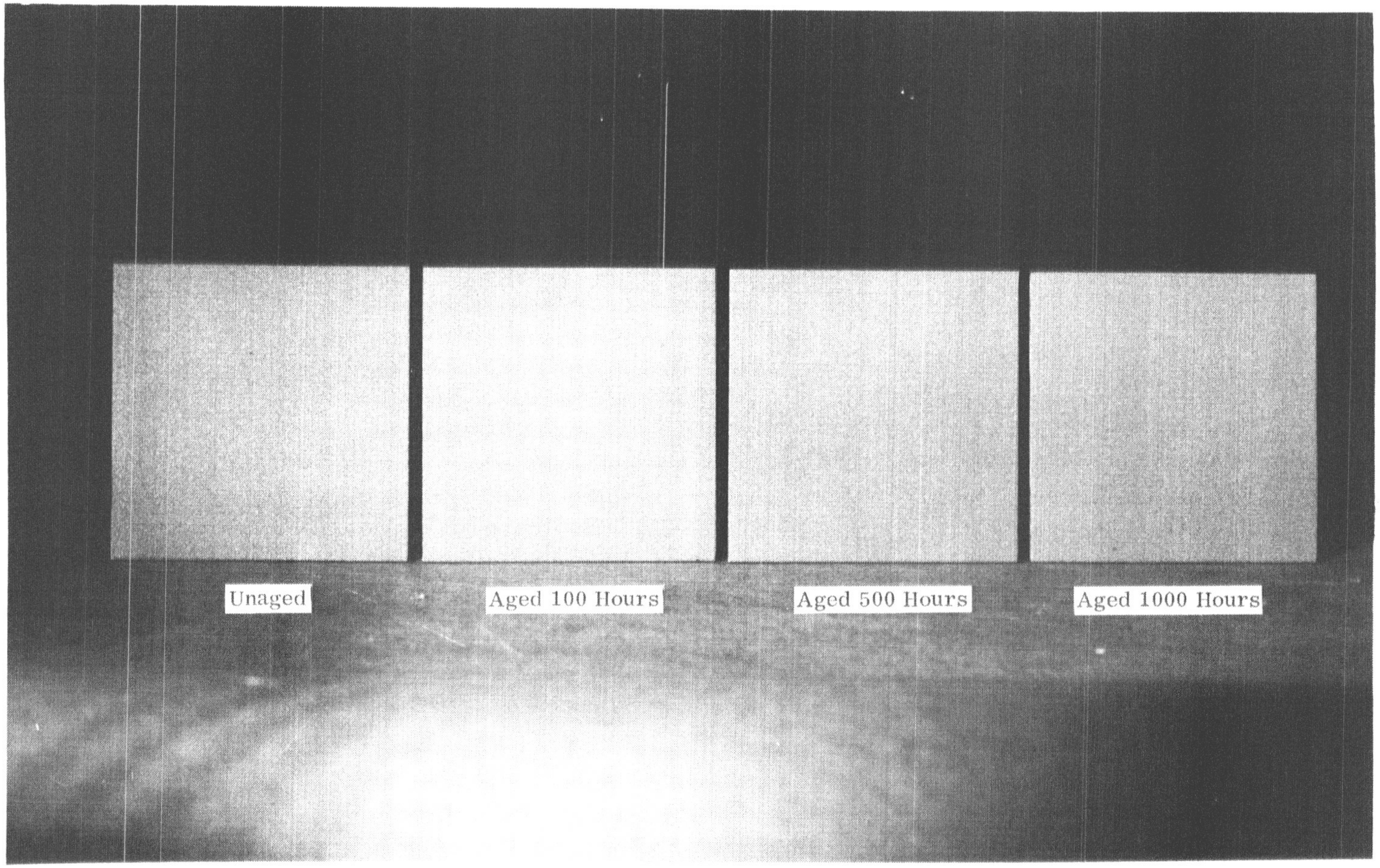


BEFORE AGING

AFTER AGING 1000 HOURS AT 1200 °F

INCREMENTAL TEMPERATURE ENDURANCE TEST

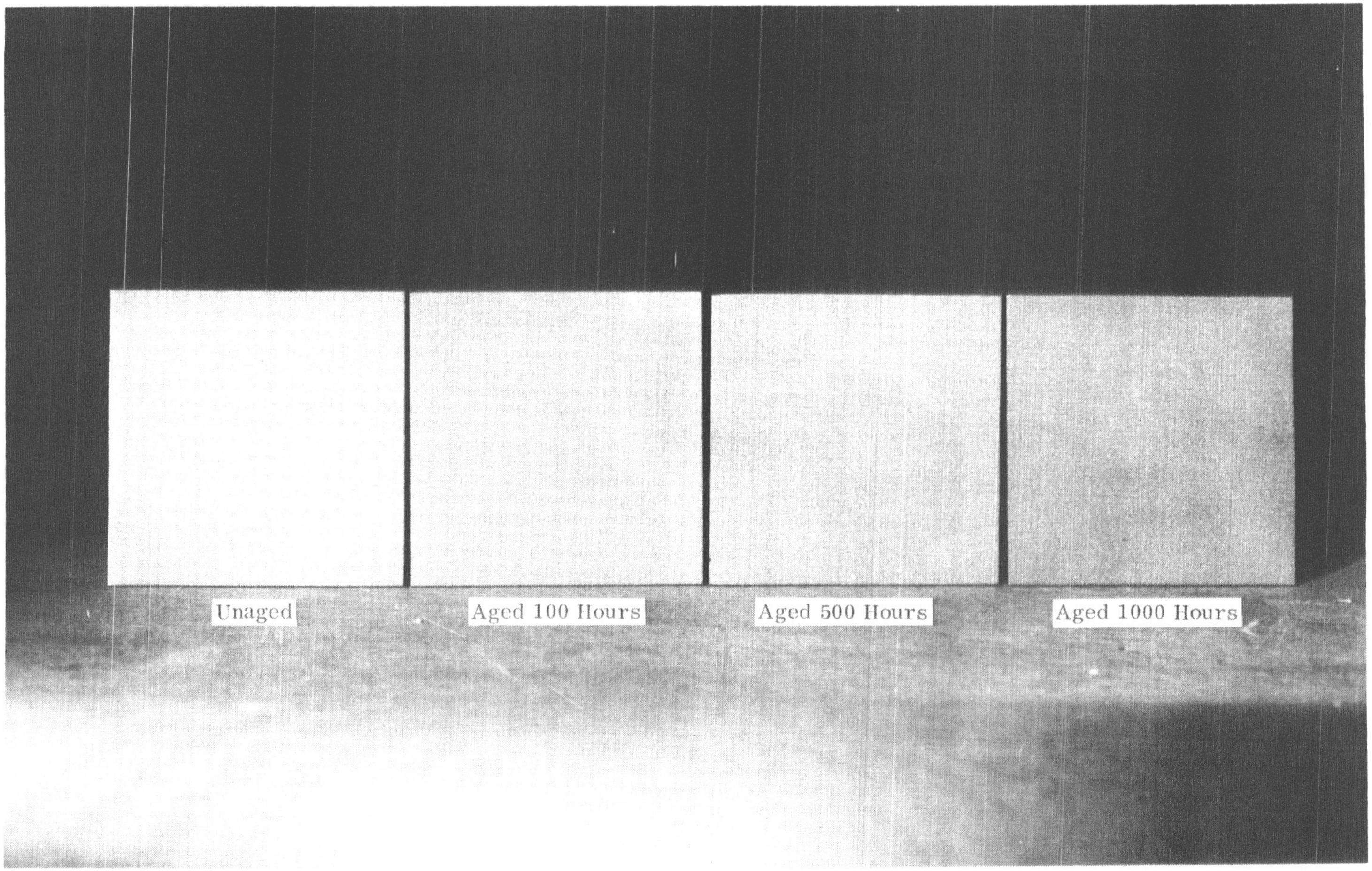
Figure 12 Total Hemispherical Emittance Measurement Results for Iron-Titanate-Coated Beryllium



Mag: 0.6X

Figure 13 Appearance of Zirconium-Titanate-Coated Beryllium Plates Before Aging and After Aging at 800°F for 100, 500, and 1000 Hours

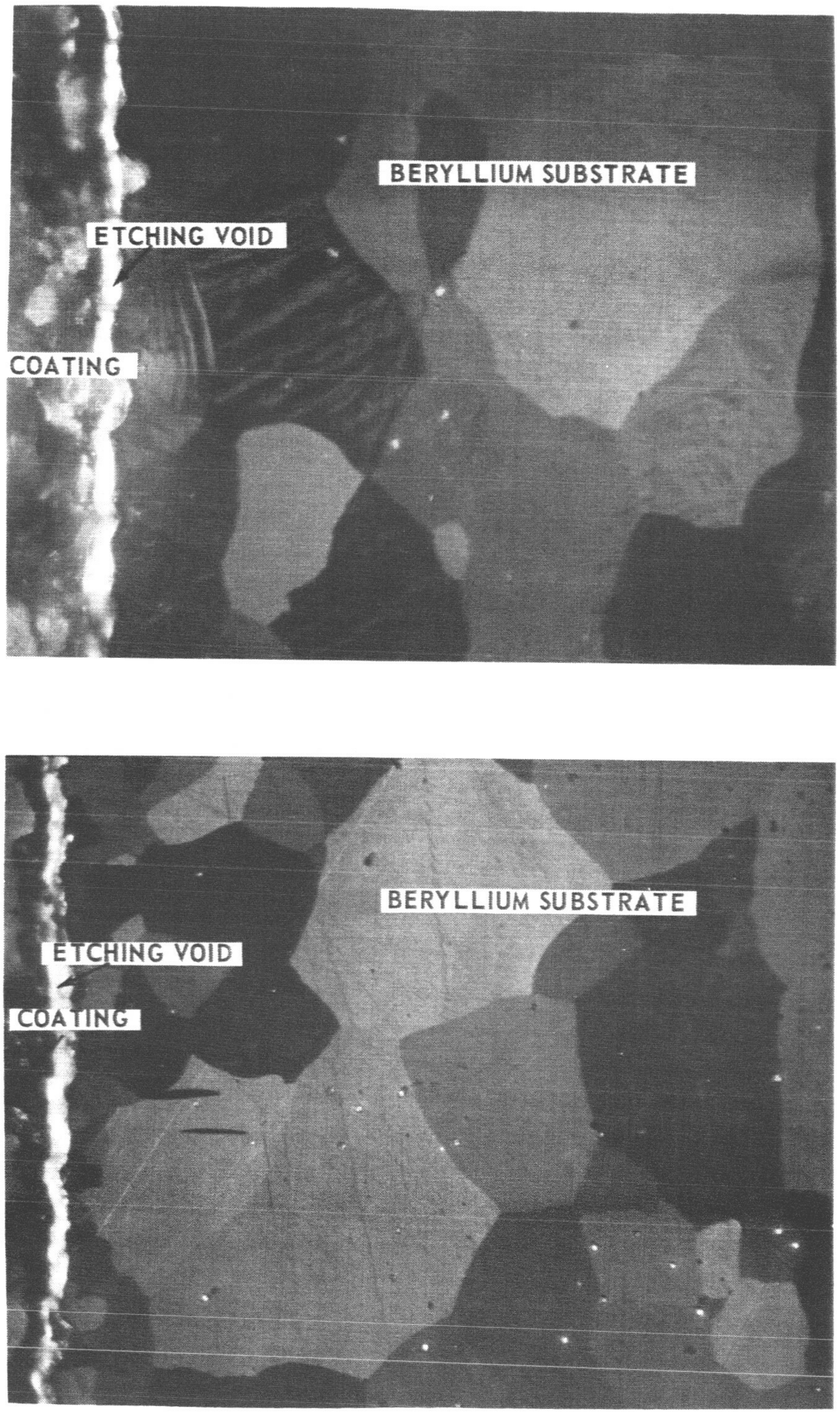
XP-66876



Mag: 0.6X

Figure 14 Appearance of Zirconium-Titanate-Coated Beryllium Plates Before Aging and After Aging at 1200°F for 100, 500, and 1000 Hours

XP-66877



Etchant: 49% NH_2 SO_3H_1 16%$H_2C_2O_4$, 1% HF, 34% H_2O Mag: 200x

Figure 15 Typical Cross Sectional Photomicrographs of Zirconium-Titanate-Coated Beryllium Plates Aged for 1000 Hours at 800°F (Top) and 1200°F (Bottom)

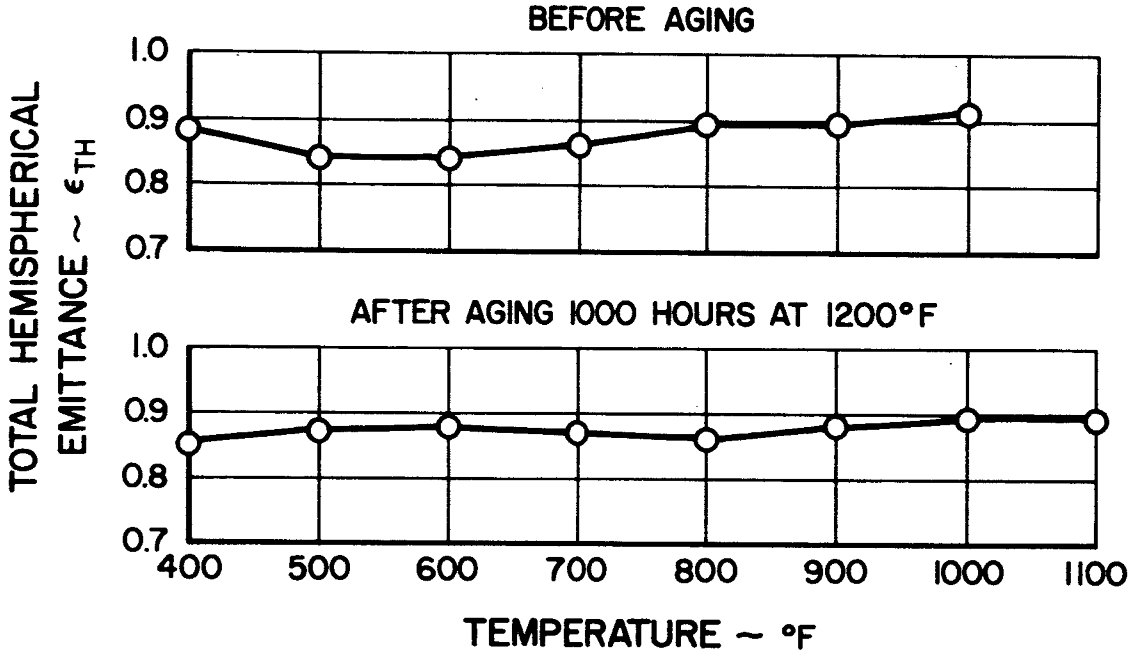


Figure 16 Total Hemispherical Emittance Measurement Results for Zirconium-Titanate-Coated Beryllium Plates

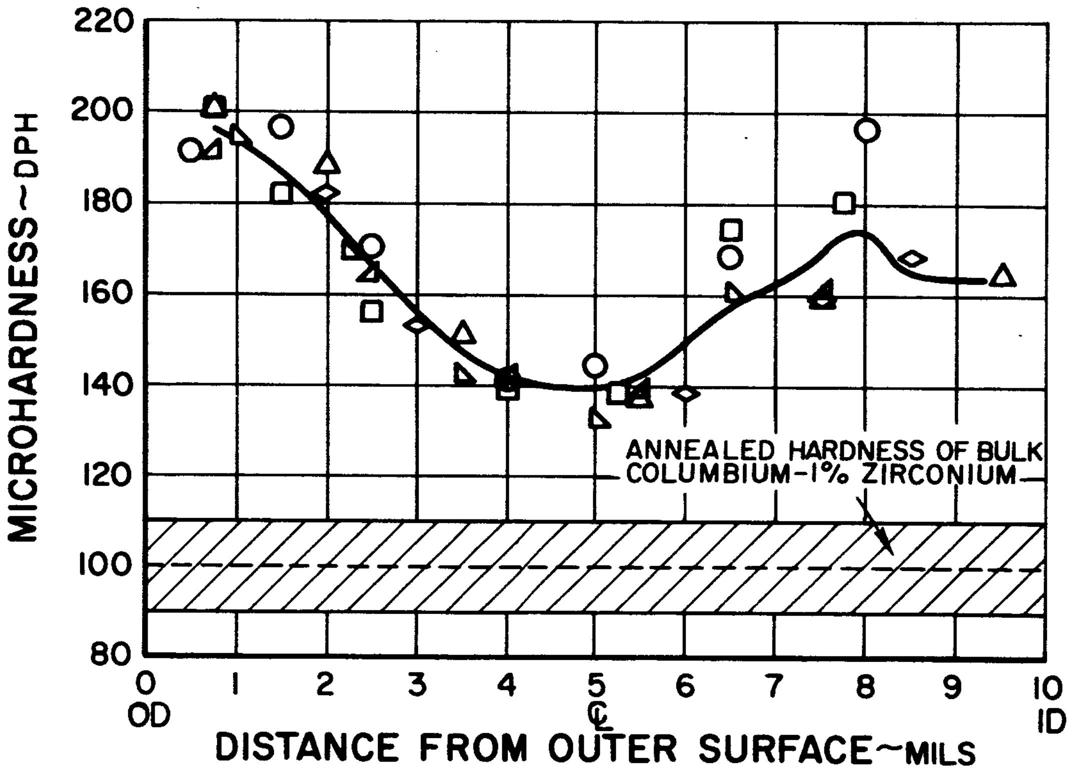
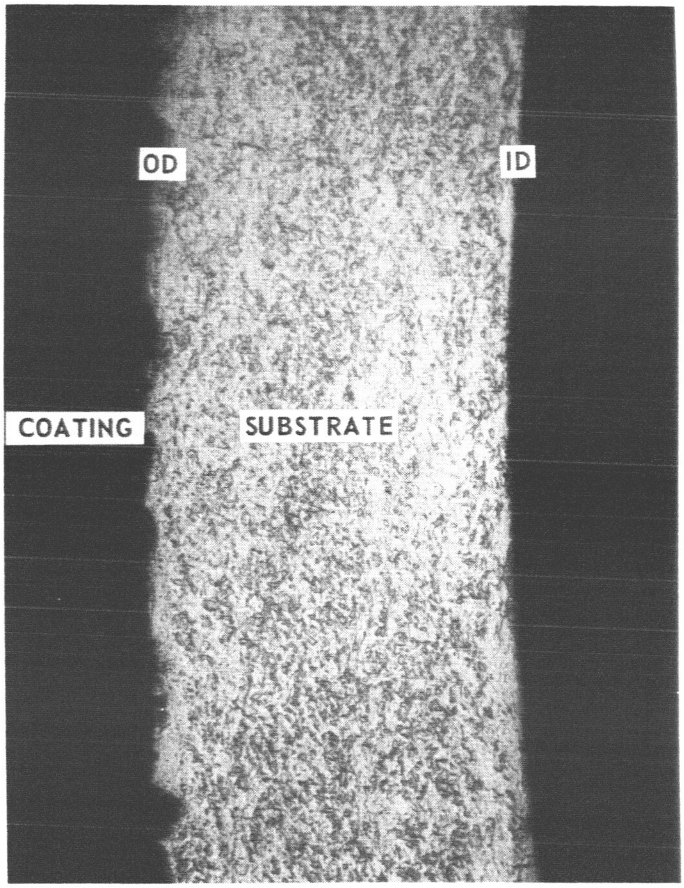
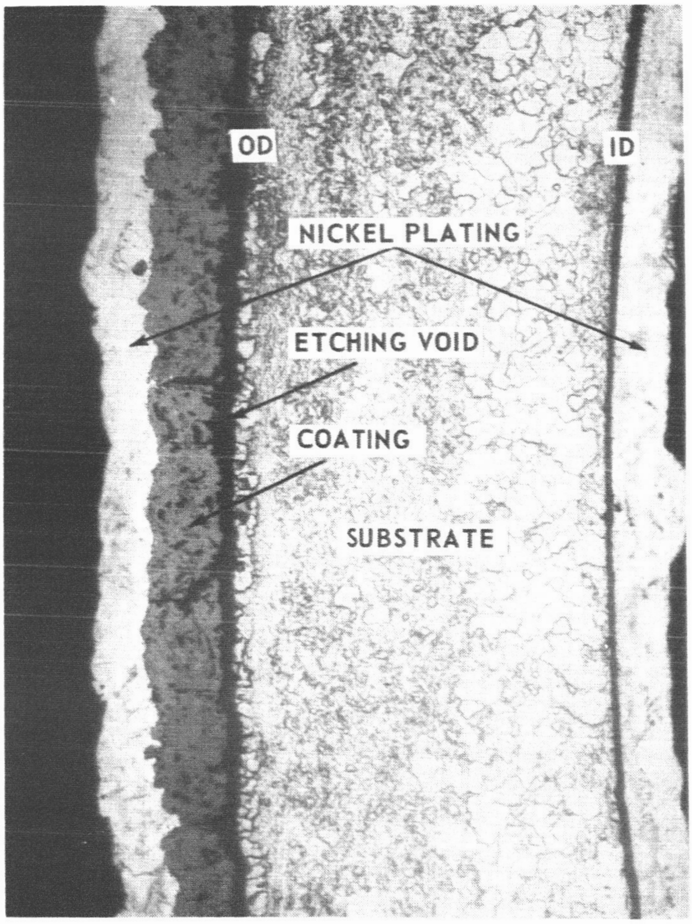


Figure 17 Microhardness Traverse Results for Endurance-Tested Columbium-1 Percent Zirconium Tube Coated With Iron-Titanate



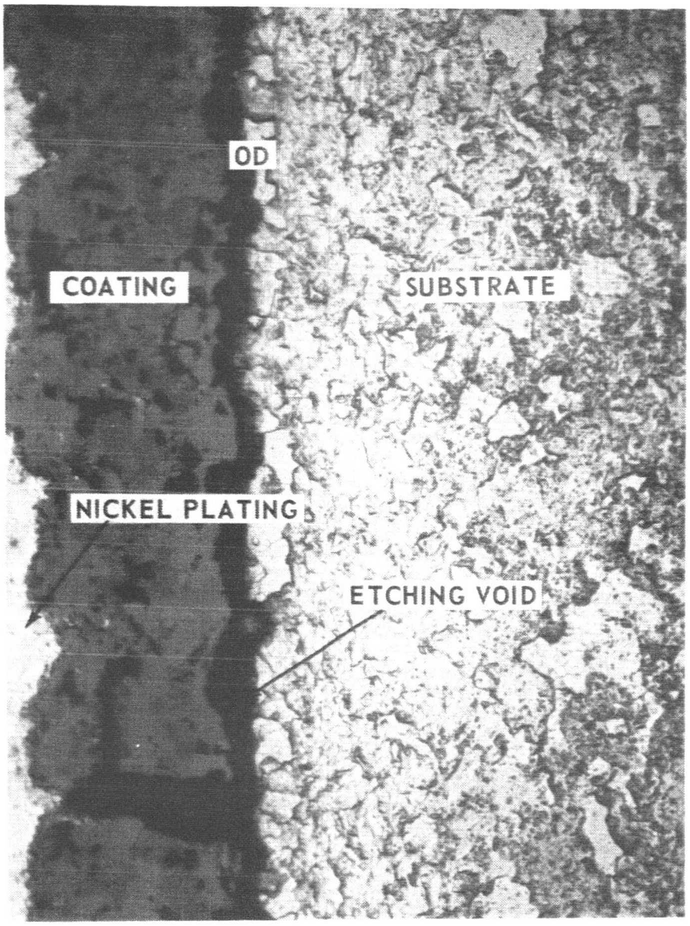
Etchant: 10% HF, 30% HNO, 60%H_2O Mag: 200x

Figure 18 Cross Sectional Photomicrograph of Columbium-1 Percent Zirconium Tube After Being Coated With Iron Titanate



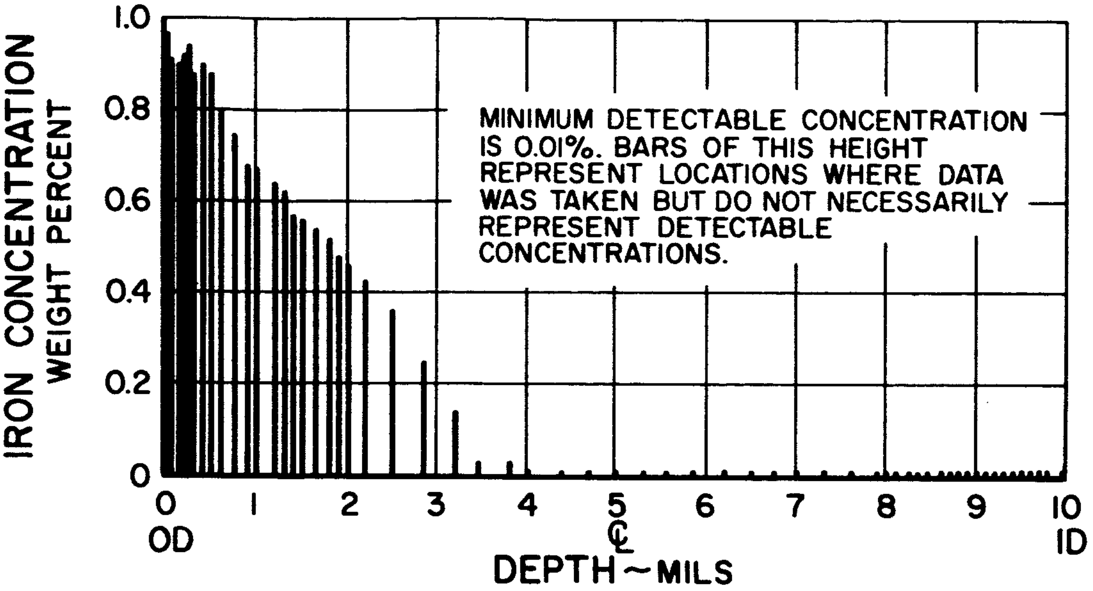
Etchant: 10% HF, 30% HNO_3, 60% H_2O Mag: 200x

Figure 19 Cross Sectional Photomicrograph of Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing at 1700°F for 10,000 Hours



Etchant: 10% HF, 30% HNO_5, 60% H_2O Mag: 500x

Figure 20 Cross Sectional Photomicrograph of Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing at 1700°F for 10,000 Hours



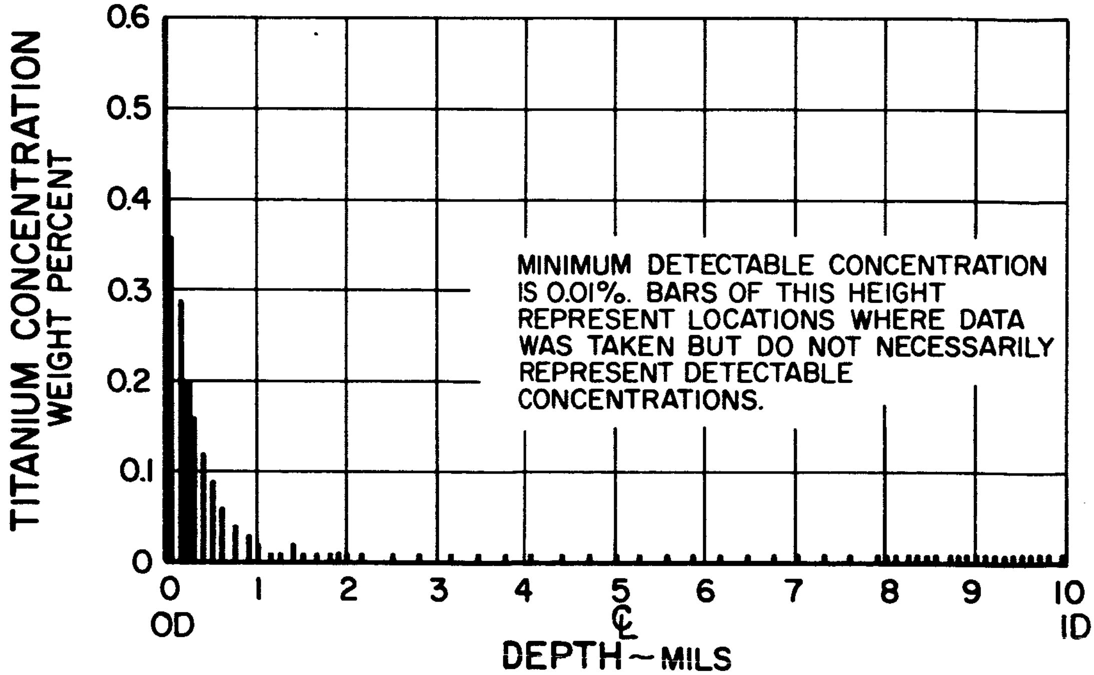


Figure 21 Concentrations of Iron and Titanium Across Columbium-1 Percent Zirconium Tube Coated With Iron-Titanate and Endurance Tested at 1700°F for 10,000 Hours

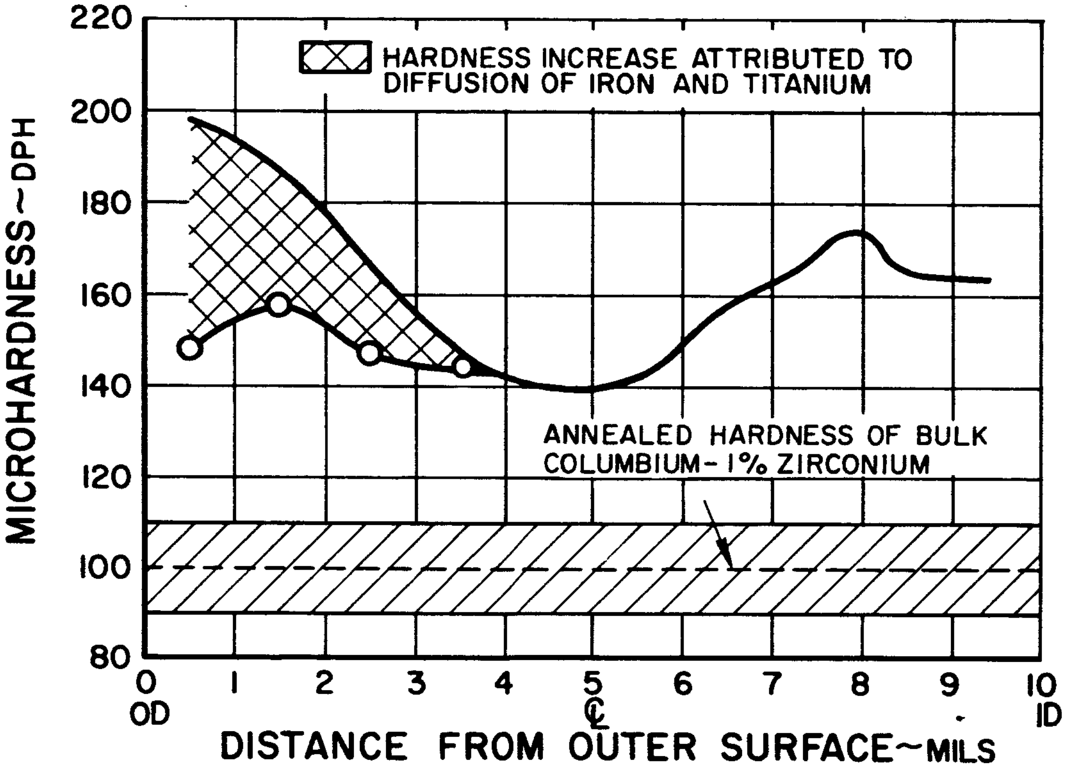
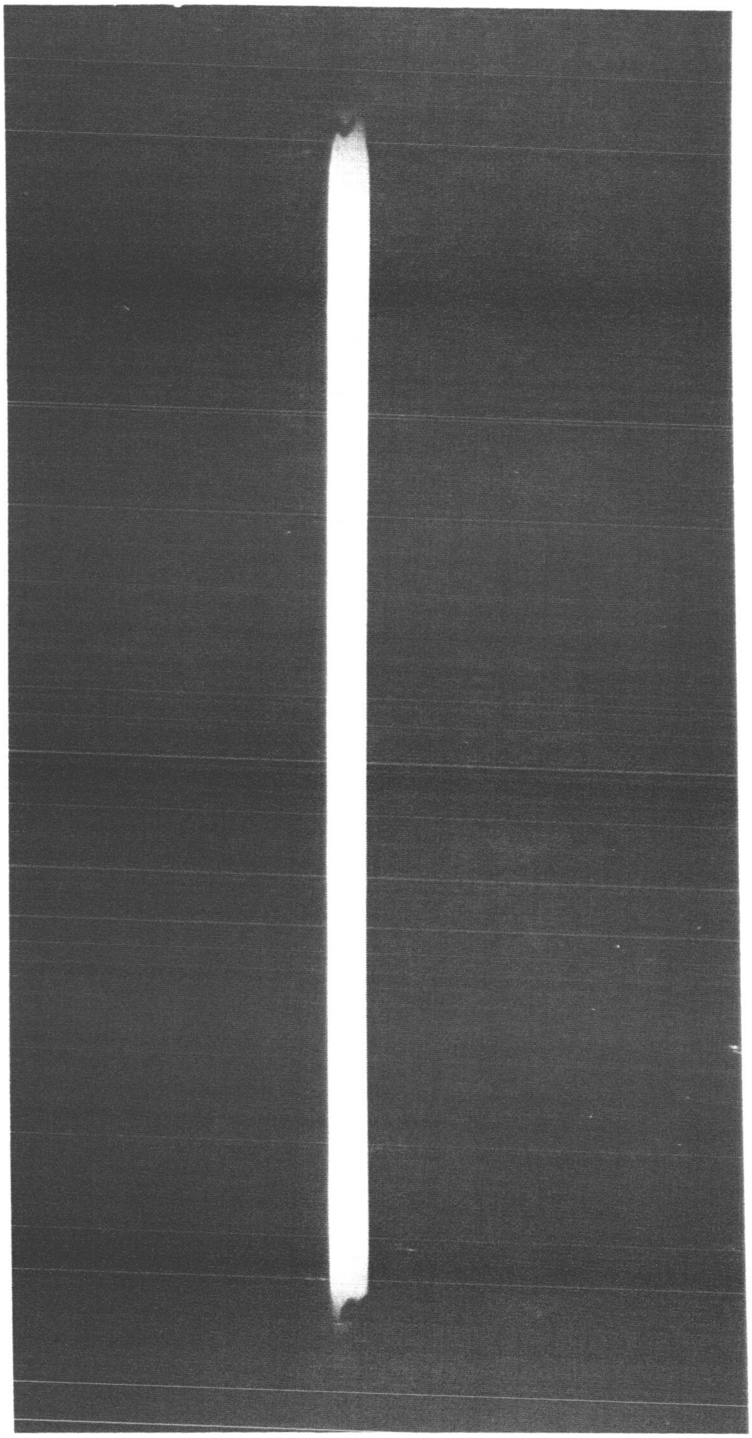


Figure 22 Effect of Iron and Titanium Diffusion on Hardness of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Endurance Tested at 1700°F for 10,000 Hours



Mag: 0.9X

Figure 23 Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube at 1700°F in Vacuum Prior to Completion of 10,000 Hours of Testing X-21860

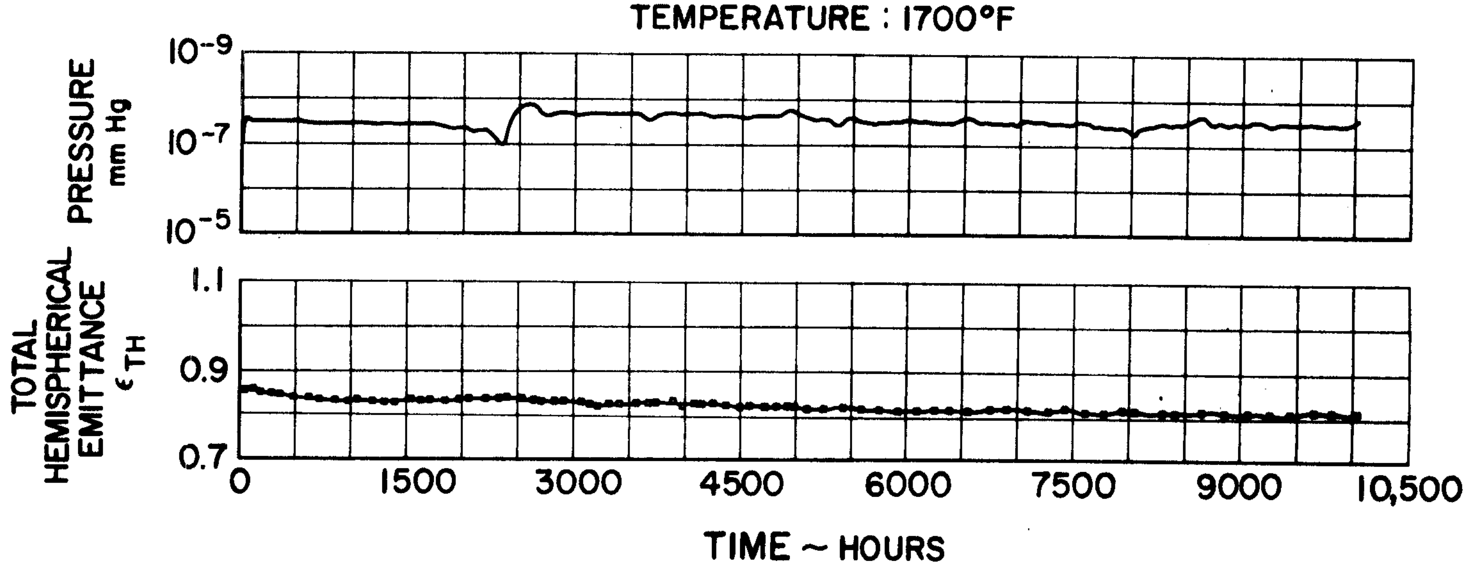
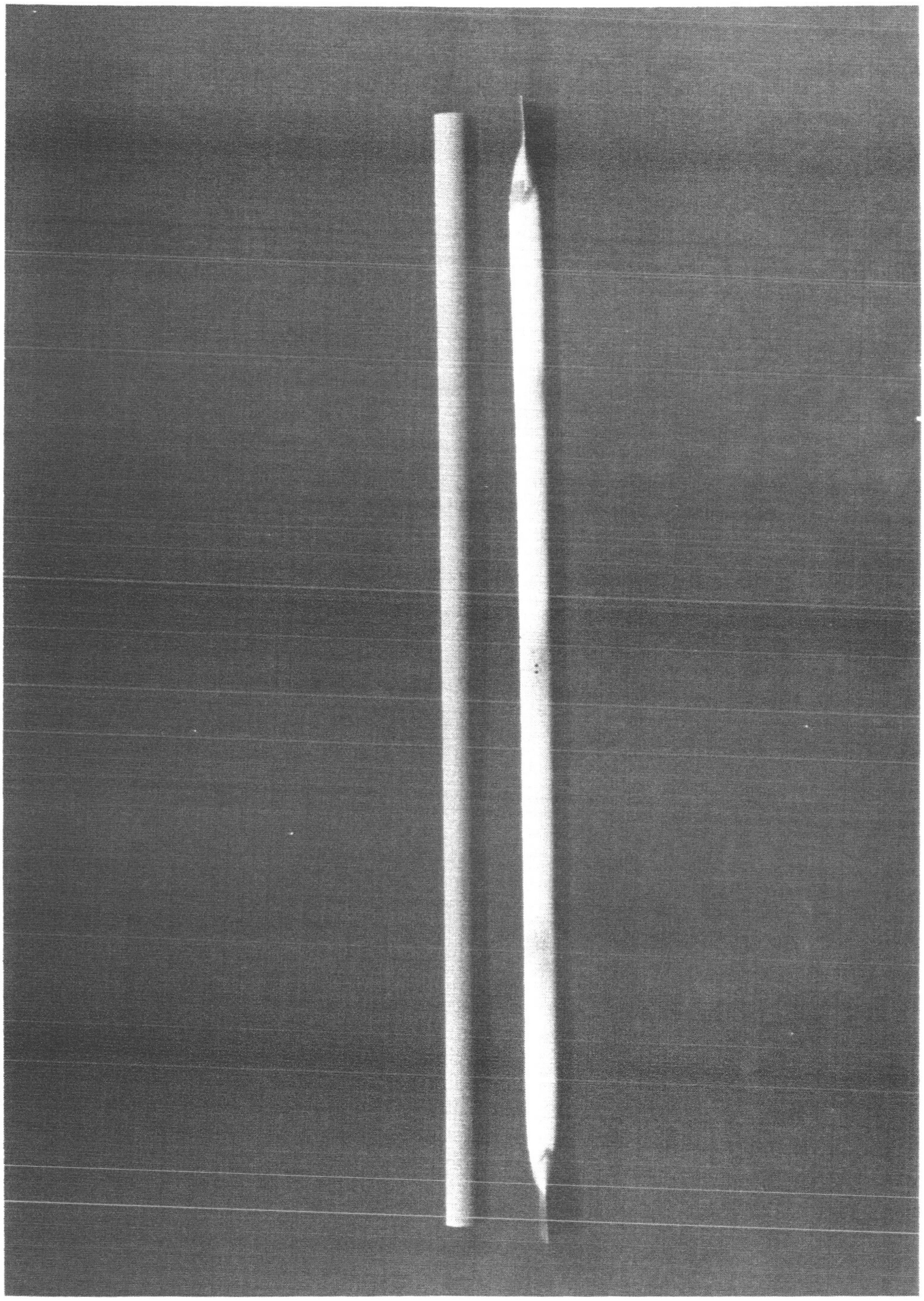


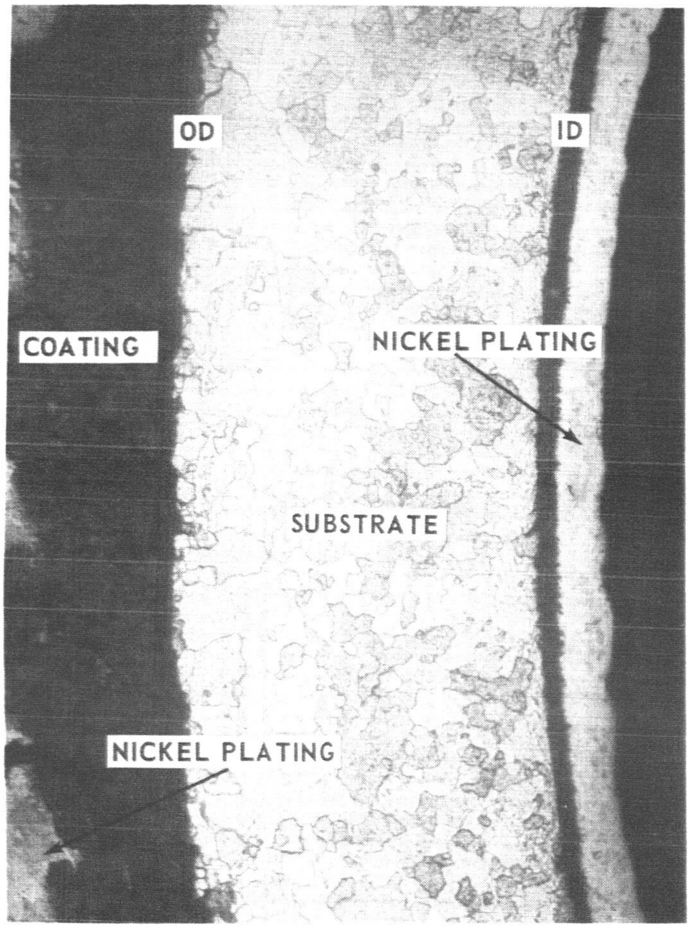
Figure 24 Pressure and Total Hemispherical Emittance for Long-Term Endurance Test of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium



Mag: 0.7X

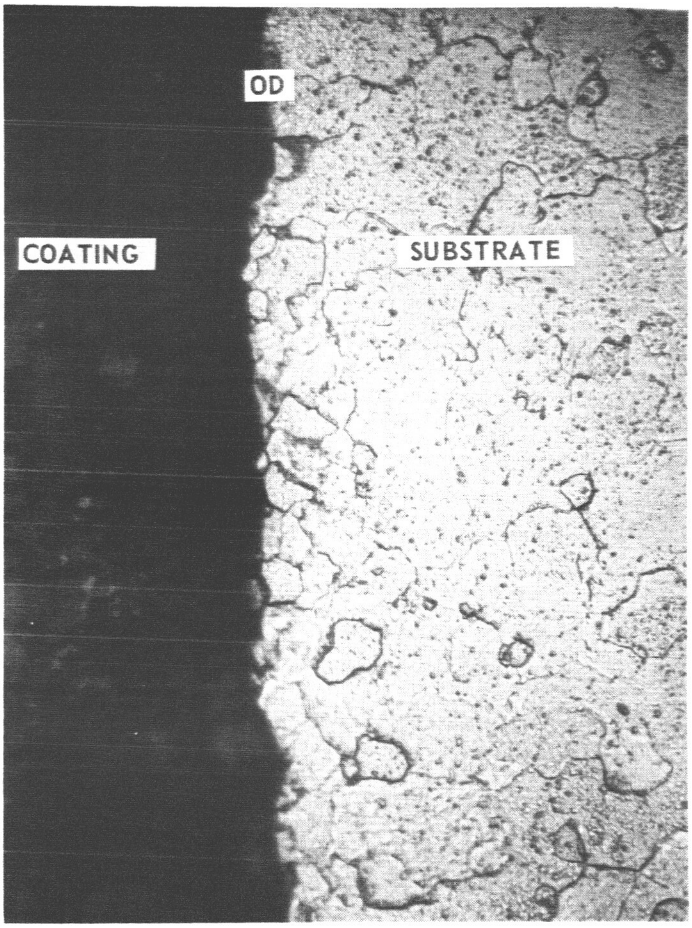
Figure 25 Appearance of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube Before (Left) and After (Right) Testing

XP-65742



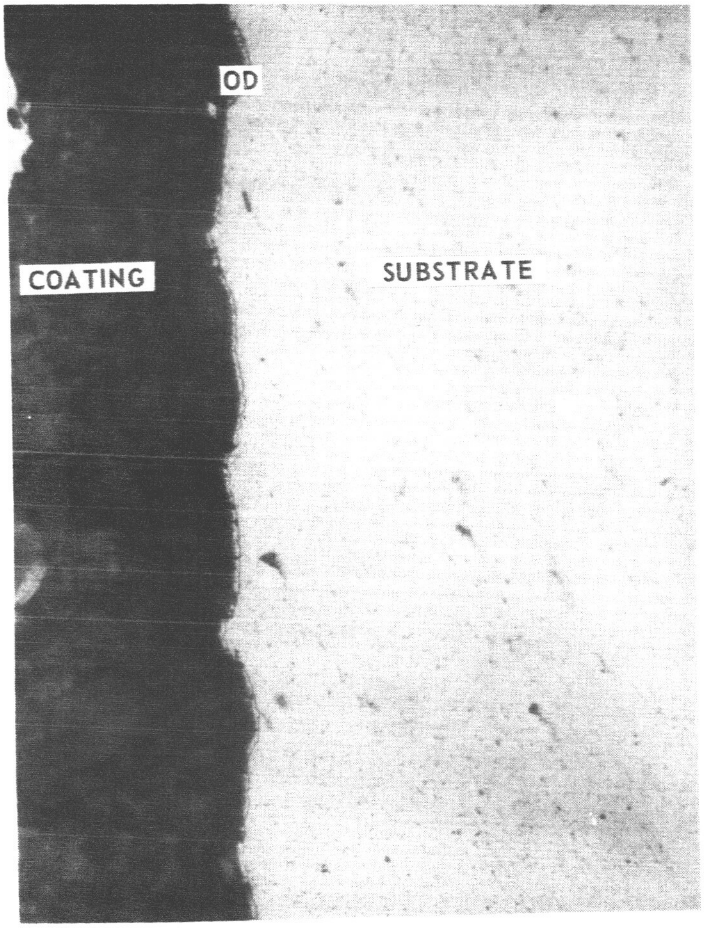
Etchant: 10% HF, 30% HNO_3, 60% H_2O Mag: 200x

Figure 26 Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing at 1700°F for 10, 000 Hours



Etchant: 10% HF, 30% HNO_3, 60% H_2O Mag: 500x

Figure 27 Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing at 1700°F for 10, 000 Hours



Etchant: 10% HF, 90% H_2O

Mag: 500x

Figure 28 Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing Etched to Show Second Phase at Coating-Substrate Interface

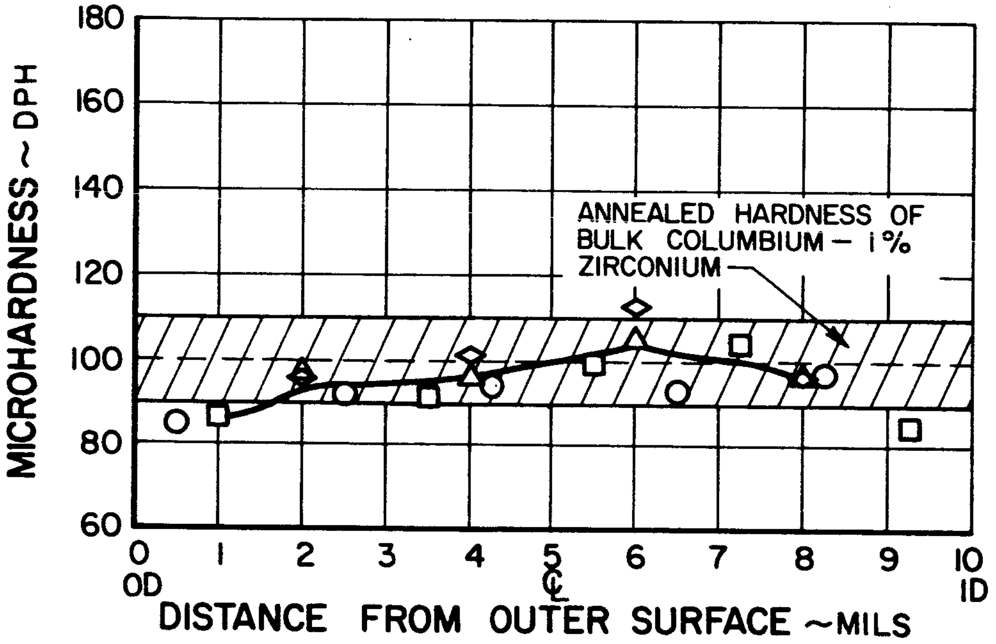


Figure 29 Microhardness Traverse Results for Endurance-Tested Columbium-1 Percent Zirconium Tube Coated With Aluminum-Oxide-Aluminum-Titanate

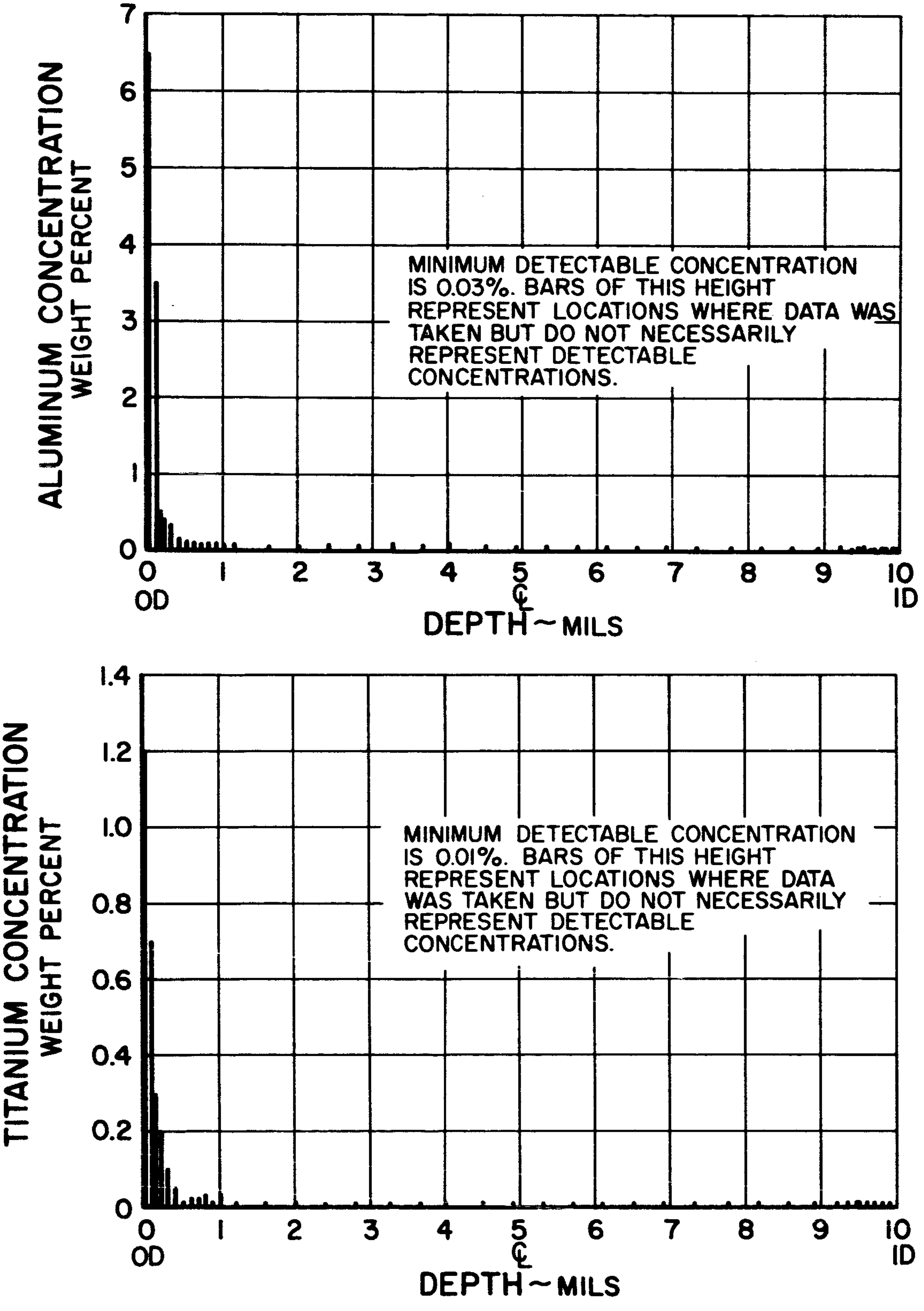


Figure 30 Concentrations of Aluminum and Titanium Across Columbium-1 Percent Zirconium Tube Coated With Aluminum-Oxide-Aluminum-Titanate and Endurance Tested at 1700°F for 10, 000 Hours

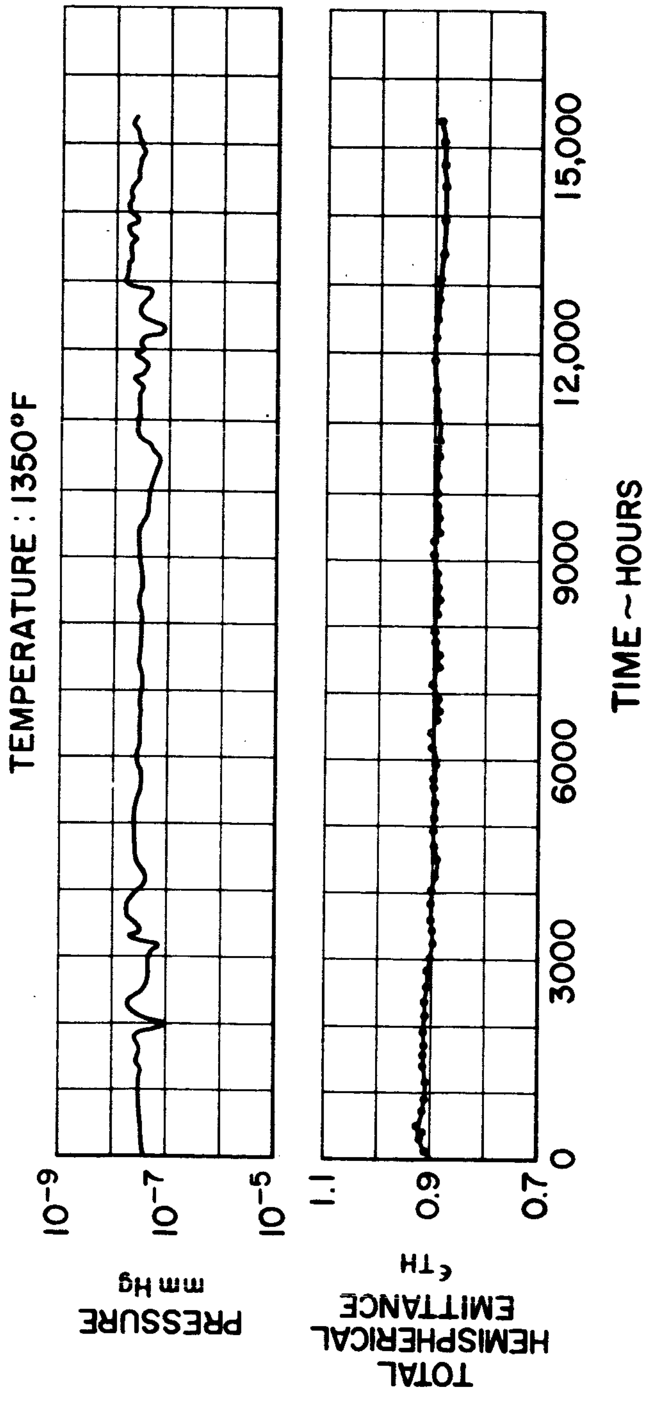


Figure 31 Pressure and Total Hemispherical Emittance for Long-Term Endurance Test of Calcium-Titanate-Coated AISI-310 Stainless Steel

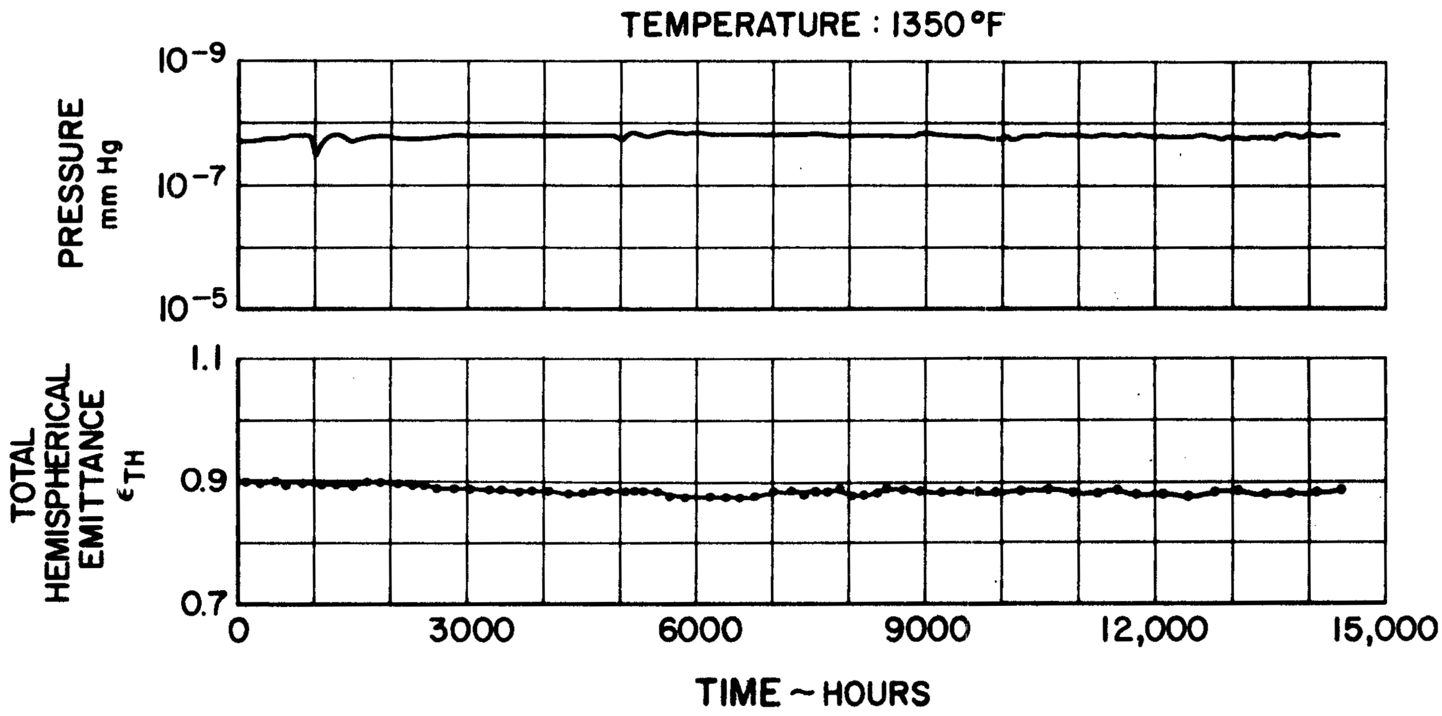


Figure 32 Pressure and Total Hemispherical Emittance for Long-Term Endurance Test of Iron-Titanate-Coated AISI-310 Stainless Steel