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THERMAL CONTROL COATING DEVELOPMENT MATERIALS REPORT

OCTOBER, 1969

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ENGINEERING REPORT
ER-7369

THERMAL CONTROL COATING DEVELOPMENT
MATERIALS REPORT

BY

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Prepared Under Contract No. NAS-9-8247

By

TRW INC.

Cleveland, Ohio

For

MANNED SPACECRAFT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Materials Application
Materials Technology
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FOREWORD

The attached report on the selection and application of thermal control coatings is the result of work done by Materials Technology, TRW Equipment Group, during the period from July 1968 through June 1969 on the HEPS (Hypergolic Electrical Power System) program under NASA Contract NAS-9-8247.

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SUMMARY

Contract No. NAS-9-8247 requires the submission of a materials report every six months. This report summarizes all thermal control coating studies conducted on the program during the last reporting period.

Thermal control coating requirements for the high temperature ($\sim$ 1300°F) components of the HEPS were studied. Two coatings were selected for development of coating procedures on the materials of construction, copper and Hastelloy X. Metallographic examination was conducted and microprobe studies were made of both coatings on several substrates.

Fe_2TiO_5 was selected as the coating to be applied to HEPS components. A specification detailing the procedure to be followed in coating parts was written.

Fe_2TiO_5 and $CaTiO_3$ have been applied previously to 310 stainless steel and columbium-1% zironium alloy but not to copper and Hastelloy X as required by the HEPS program. Consequently, work was done to test suitability of the Fe_2TiO_5 and $CaTiO_3$ for these materials and to develop an application procedure.

DC92-007 was selected as the coating to be applied to low temperature (200-400°F) components. Tests were run to add to known emissivity and absorptivity data.

INTRODUCTION

The need to maintain equipment temperatures in a lunar environment was immediately recognized as a major task in the HEPS program. A number of adequately sized radiating surfaces, which provide a sound means of energy dissipation, were incorporated in the system design. The temperatures of these radiating surfaces will be determined by their net energy gain or loss rate and by their absorptance and emittance characteristics. Thermal control coatings are needed to provide these characteristics and maintain appropriate temperatures.

Table 1 lists the various radiating surfaces, their materials of construction, operational ambient temperature ranges and thermal gradients, and the selected thermal control coatings. The indicated thermal environments of the radiating surfaces suggested a desirability for two thermal control coatings systems; one for the high temperature requirement ($>$ 950°F) and another for the lower temperature ($<$ 400°F) components. Other factors which were considered in the coating selection were total hemispherical emittance stability, solar absorptivity stability, adherence and substrate compatibility in a lunar environment. In addition, the coating application process and the necessary handling methods for coated components during system assembly were also reviewed.

High Temperature Thermal Control Coating

A thorough literature survey, plus a visitation with personnel of the Space Power Systems Division at the NASA Lewis Research Center, yielded only two high temperature ($>$ 950°F) high emissivity coatings which appeared to be well

TABLE 1

SELECTED THERMAL CHARACTERISTICS AND THERMAL CONTROL COATINGS FOR RADIATING SURFACES

COMPONENT	MATERIALS OF CONTRUCTION	OPERATIONAL AMBIENT TEMP.°F MIN.	MAX.	MAXIMUM OPERATIONAL THERMAL GRADIENT °F.	THERMAL CONTROL COATING
Scroll & Fin Assembly	Hastelloy X & OFHC Copper	950	1350	< 50	Iron Titanate (Fe_2TiO_5)
Combustion Chamber	Hastelloy X & OFHC Copper	700	1000	700-1000 Actual Range	Iron Titanate (Fe_2TiO_5)
Rectifier Filter Panel (Cold Plate)	6061 Aluminum	200(E)	325(E)	< 50(E)	DC 92-007
Oil Radiator Panel	6061 Aluminum	350(E)	400(E)	350(E)-400(E) Anticipated Range	DC 92-007
Speed Control	6061 Aluminum	180(E)	210(E)	< 20(E)	DC 92-007
Voltage Regulator	6061 Aluminum	210(E)	240(E)	< 30(E)	DC 92-007

(E) Estimated

established for space use [1]. These coatings [iron titanate (Fe_2TiO_5) and calcium titanate ($CaTiO_3$)] which were evaluated on substrates of 310 stainless steel and columbium -1% zirconium, exhibited emittance stability, adherence and substrate compatibility. The iron titanate (Fe_2TiO_5) coating exhibited exceptional stability after long-term exposure at 1800°F under vacuum while the calcium titanate experienced a chemical breakdown after short exposure at 1650°F while under vacuum[1]. The emissivity of calcium titanate and iron titanate are reported in Table 2.

It was desired that a high emissivity coating be applied to the HEPS scroll and fin assembly which experienced a 1350°F maximum use temperature and to the combustion chamber which experiences a 1000°F maximum use temperature. Both Fe_2TiO_5 and $CaTiO_3$ coatings appeared thermally acceptable. Although the basic materials of construction (Hastelloy X and OFHC Copper) were well established by years of engineering development, the substrates/coatings compatibility was in doubt. To resolve this problem, a test utilizing six substrates consisting of three base materials, Hastelloy X, OFHC copper and type 310 stainless steel (as test standard), with base metal and nickel plated surfaces was initiated (see Figure 1). Both the iron titanate and the calcium titanate were applied by plasma torch to the six substrates by the Development Chemistry Section of Pratt & Whitney Aircraft Division of United Aircraft Corporation, East Hartford, Connecticut under the supervision of Dr. Robert E. Cleary. These coated specimens (12 groups) were visually examined upon receival. A few specimens, apparently "set-up" pieces or "damaged in handling," were eliminated from the evaluation. A number of the specimens from each group were exposed to a temperature of 1400°F for 1 hour in a vacuum. These thermally exposed coated specimens are shown in Figures 2 through 7. Visual examination revealed both of the applied coatings to be adherent to all of the substrates. All of the nickel plated OFHC copper specimens exhibited blistering. Further examination revealed separation at the nickel plate/base metal interface. Both of the coatings appeared to be adherent to even the blistered portions of these nickel plated OFHC copper specimens. An evaluation, which included many methods of removing varying amounts of surface metal from the OFHC copper and different nickel plating procedures, clearly indicated that the blistering could be attributed to foreign material contained in the outer 0.004 inch surface "skin" of the OFHC copper. Adverse effects of surface contaminants in OFHC copper on electrodeposited nickel has also been reported by L. Missel[2].

"As coated" and "as coated and thermally exposed" specimens from each of the 12 groups were mounted in epoxy and carefully prepared for electron beam microprobe analysis by polishing with fine diamond abrasive. This analytical method, described in Appendix A, is capable of indicating the chemical composition gradient or profile of the critical elements in the applied coating and its substrate. A comparison of the chemical composition gradient of an "as coated specimen" with that of an "as coated and thermally exposed specimen" will indicate the relative stability of any coating-substrate system.

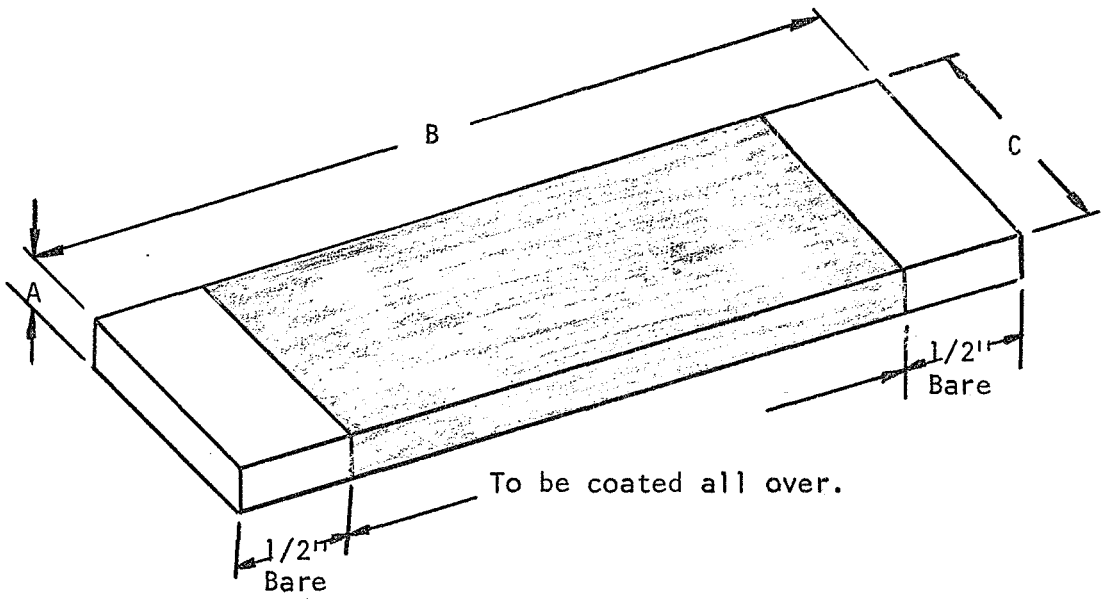
NOTE:
Numbers in parentheses refer to references listed at end of document.

TABLE 2

EMISSIVITY OF CALCIUM TITANATE AND IRON TITANATE[1]

THERMAL CONTROL COATING	TOTAL HEMISPHERICAL EMITTANCE (E_{tn})	TEST TEMP. °F	TEST DURATION (Hours)	THERMALLY CYCLED	TEST VACUUM (Torr)	SUBSTRATE	REMARKS
Calcium Titanate ($CaTiO_3$)	0.88-0.91	1350	20,000	112 times to RT	1×10^{-7}	Type 310 SS	Slight darkening of coating, no apparent texture change and no indication of cracking or spalling.
Iron Titanate (Fe_2TiO_5)	0.87-0.89	1350	20,000	114 times to RT	2×10^{-8}	Type 310 SS	Slight change in coating color, texture and integrity of coating unchanged.
Iron Titanate (Fe_2TiO_5)	0.88	1500/1800	5,000	3,125 times (1500-1800°F)	1×10^{-7}	Columbium -1% Zirconium	Slight Hairline crack appeared after 3500 hours of test. There was no texture or color change and no indication of separation or spalling.

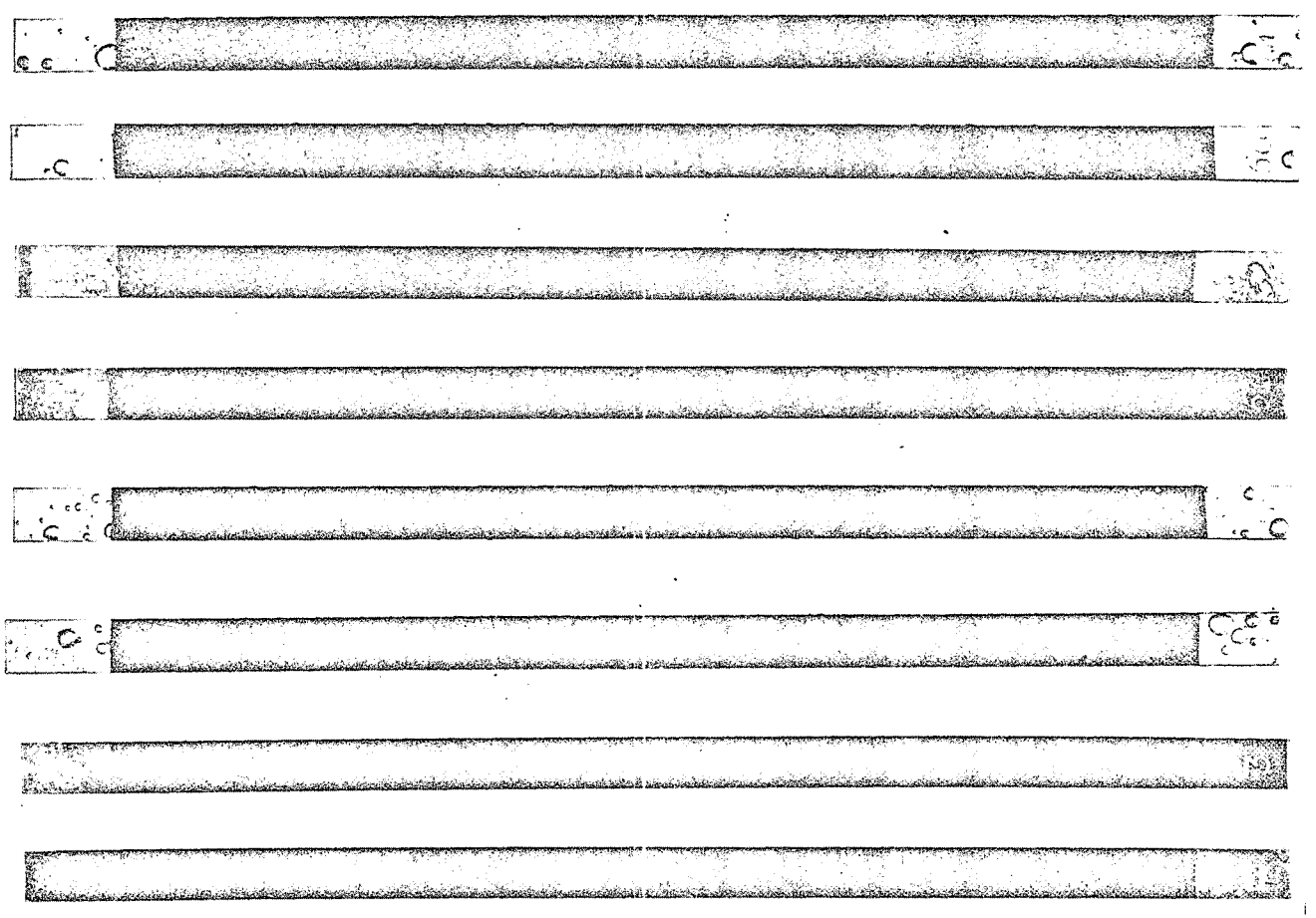
FIGURE 1 SPECIMENS FOR HIGH "E" COATING APPLICATION



LOT	BASE METAL	SURFACE COATING	A*	B*	C*	REMARKS
A	OFHC Copper	None	.020	6.0	.250±.010	Materials of Construction
B	OFHC Copper	Electrolytic Nickel Plate**	"	"	"	
C	Type 310 SS	None	.062	6.0	.4 - .5	Test Standard
D	Type 310 SS	Electrolytic Nickel Plate**	"	"	"	
E	Hastelloy X	None	.093	6.0	.4 - .5	Material of Construction
F	Hastelloy X	Electrolytic Nickel Plate**	"	"	"	

*Dimensions in inches.

**Plating Thickness Range .001"-.002"

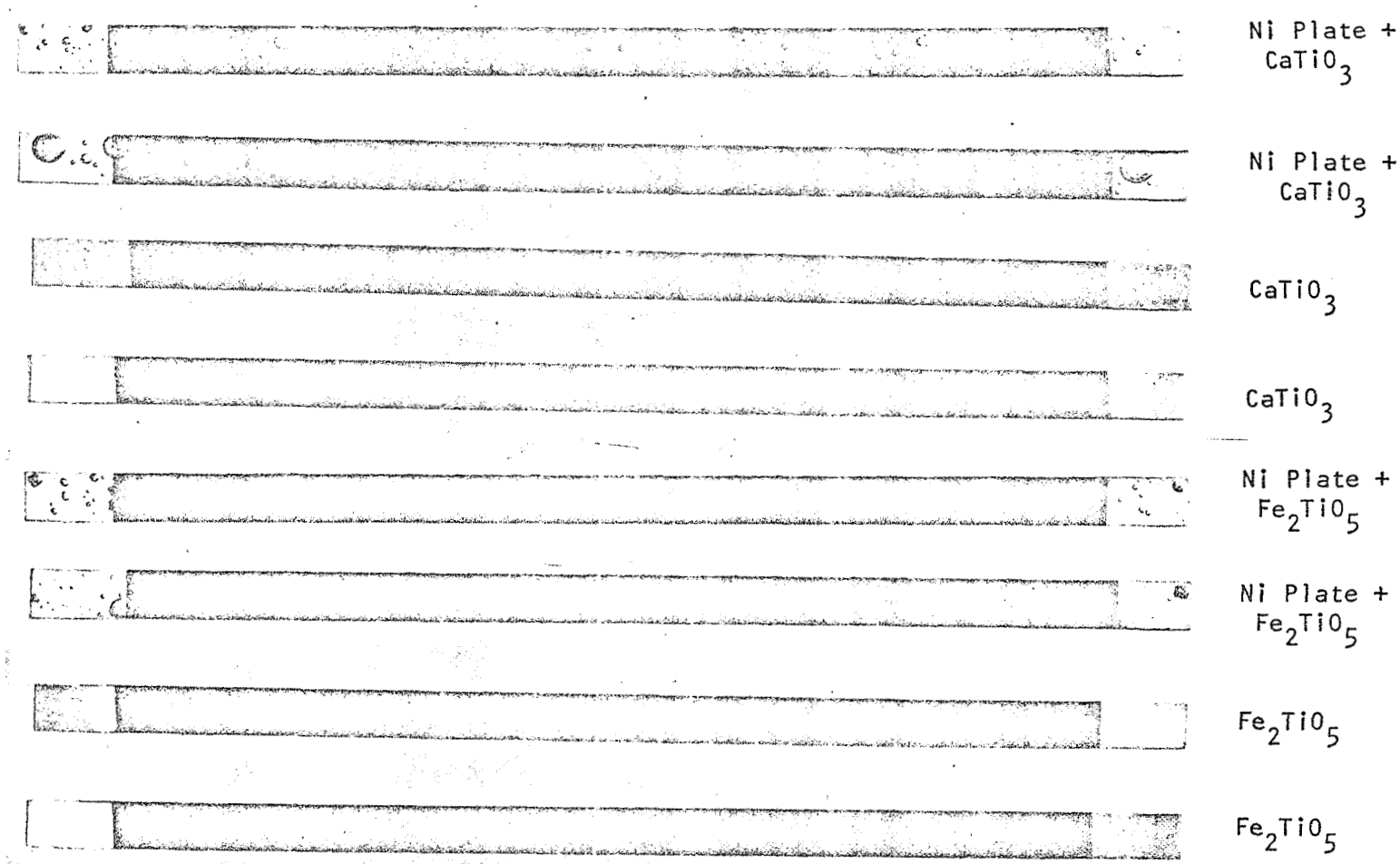


Front Side

1X

Figure 2 OFHC Copper Substrate After Exposure At 1400°F For 1 Hour In Vacuum (~0.1 Micron). Coatings As Noted.

Both High Emissivity Coatings Appear Adherent Even Though All Of The Nickel Plated Substrates Exhibit Blistering At The Base Metal/Plate Interface.



Back Side

1X

Figure 3 OFHC Copper Substrate After Exposure At 1400°F For 1 Hour In Vacuum (~0.1 Micron) Coatings as Noted.

Both High Emissivity Coatings Appear Adherent Even Though All Of The Nickel Plated Substrates Exhibited Blistering At the Base Metal/Plate Interface.

5879 B

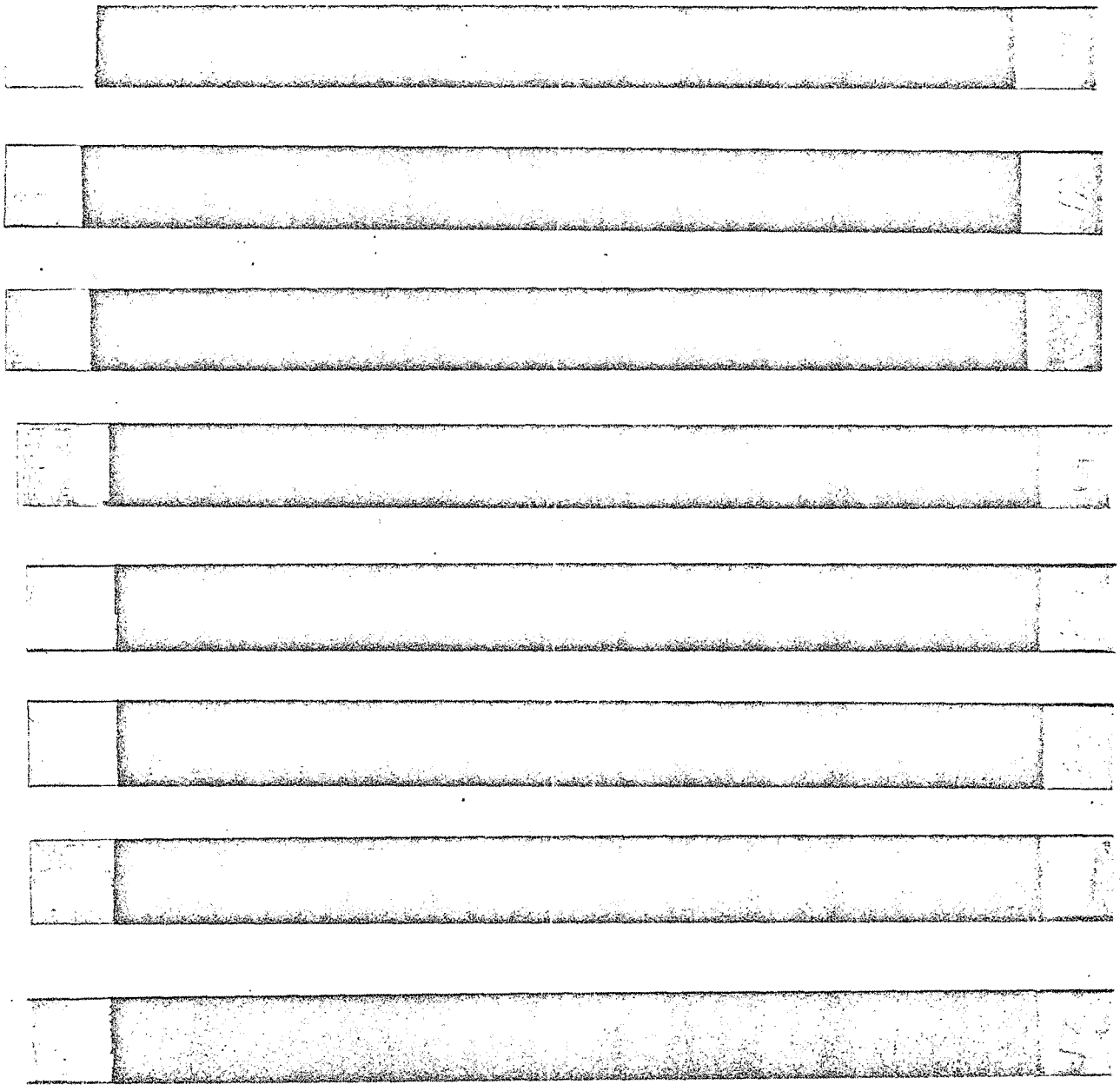


Figure 4 310 Stainless Steel Substrate After Exposure at 1400°F For 1 Hour In Vacuum (~0.1 Micron) Coating As Noted.

5880 a

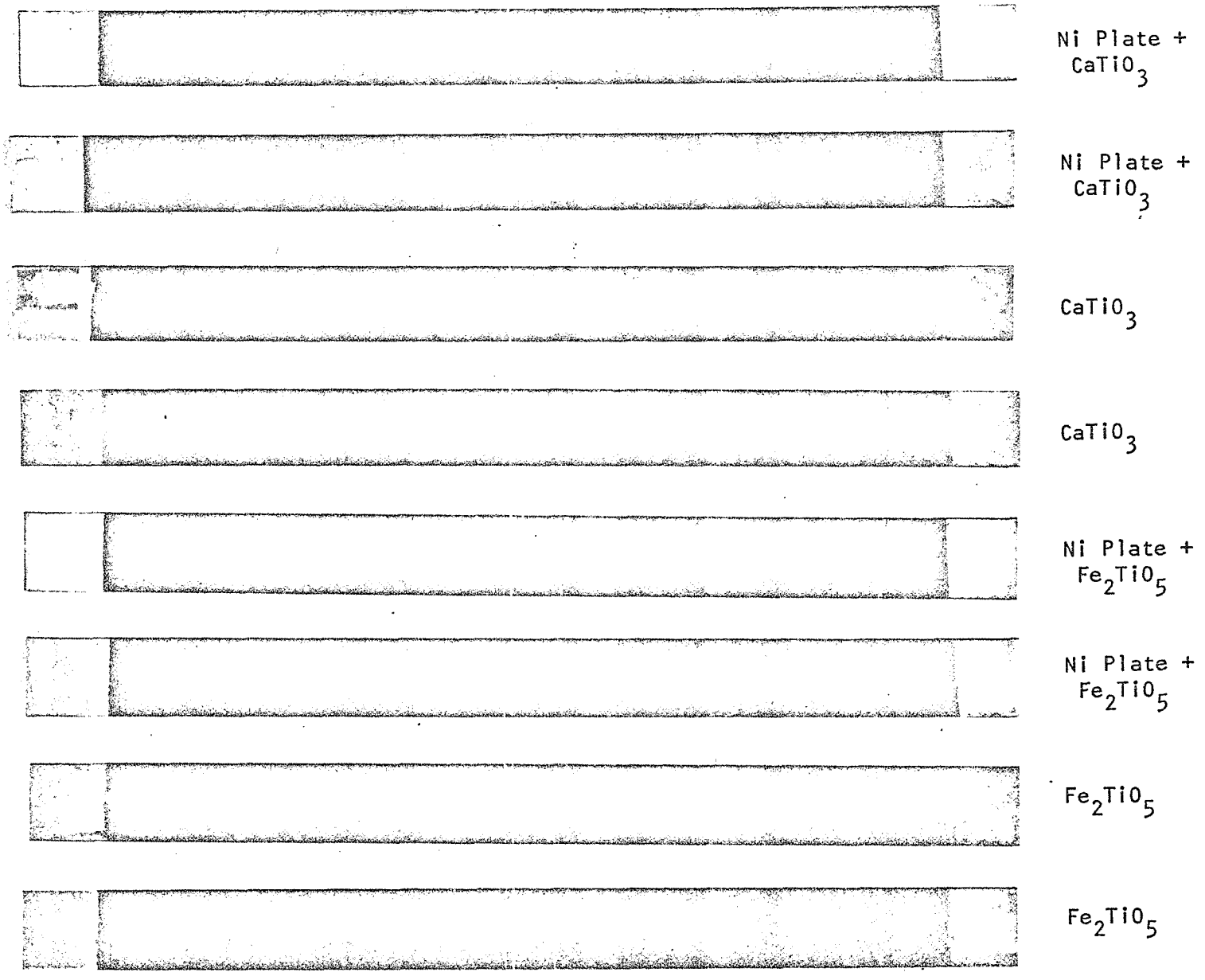


Figure 5 310 Stainless Steel Substrate After Exposure At 1400°F For 1 Hour In Vacuum (~0.1 Micron) Coatings As Noted.

5881 B

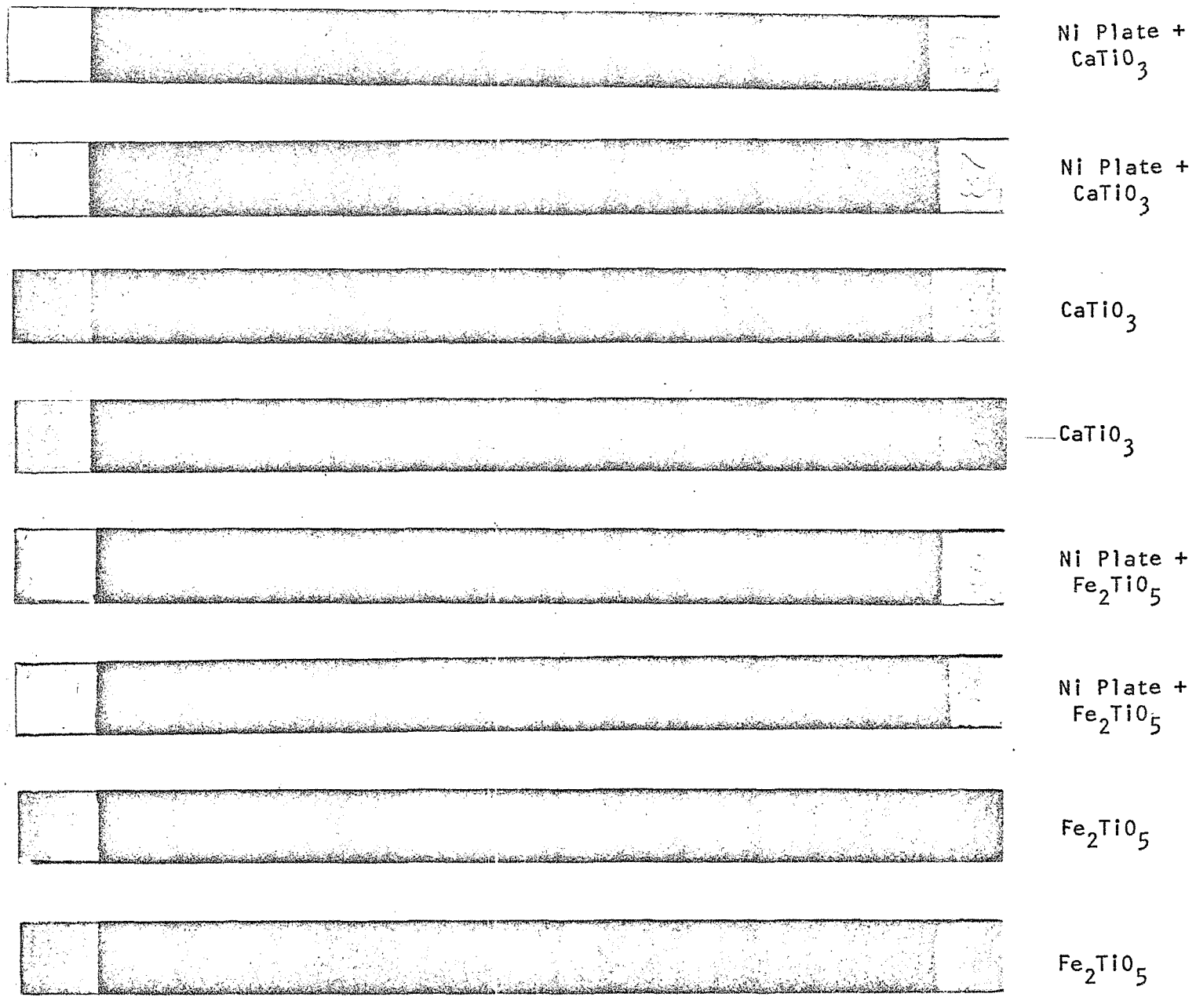
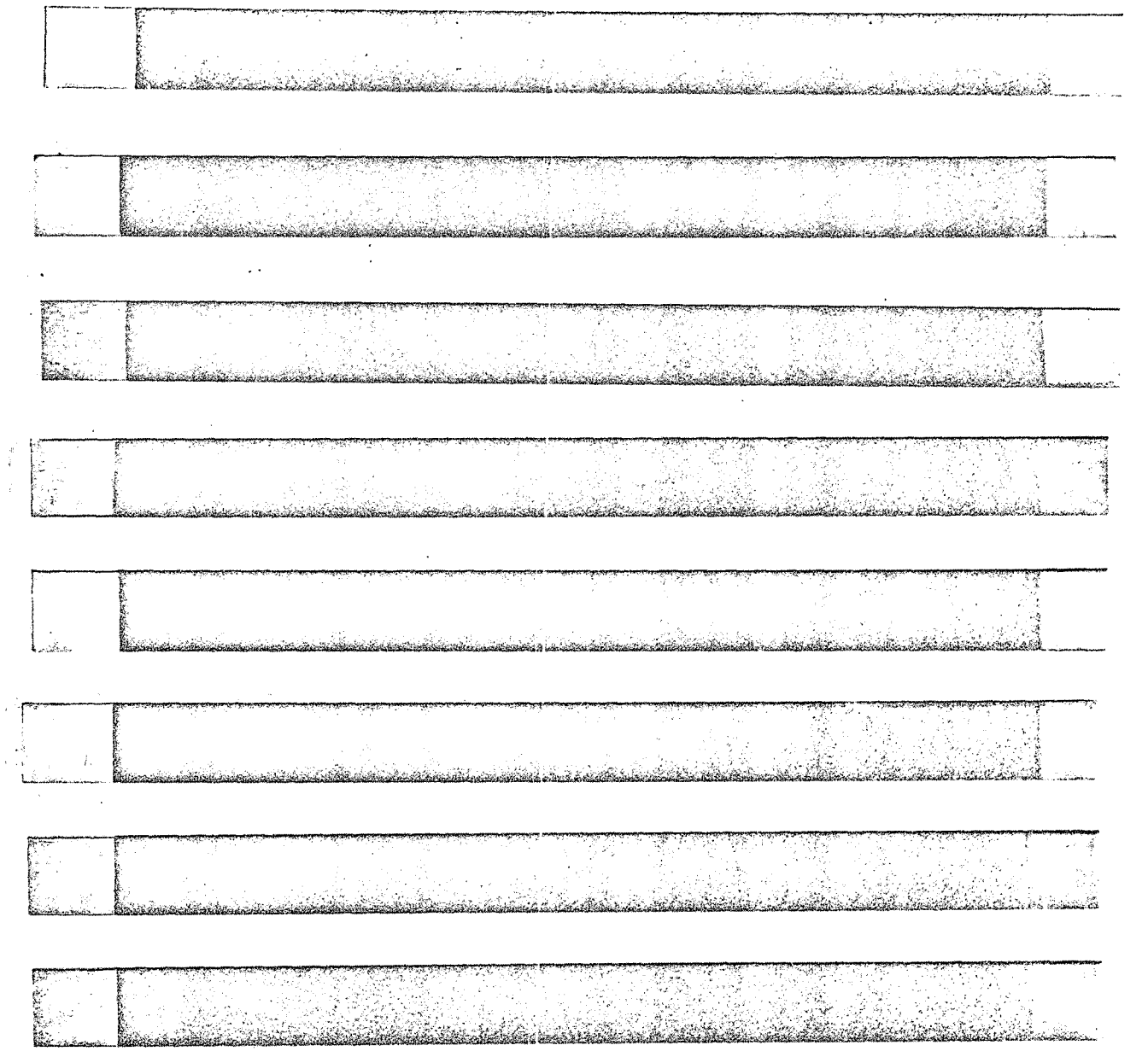


Figure 6 Hastelloy X Substrate After Exposure at 1400°F For 1 Hour In Vacuum (~0.1 Micron) Coating As

5086 B



Back Side

Figure 7 Hastelloy X Substrate After Exposure at 1400°F For 1 Hour In Vacuum (~0.1 Micron) Coatings As Noted.

1X

A brief summary of the microprobe analysis of both coatings, Fe_2TiO_5 and $CaTiO_3$ follows:

1. There was no diffusion of any element checked (Ni,Cr, Fe,Ca or Ti) into either the coating or substrate of as-coated plated or unplated specimens.

2. There was little (<1 micron) or no diffusion of the elements checked into either the coating or substrate of unplated specimens after thermal exposure at 1400°F.

3. There was little (<1 micron) or no diffusion of the elements checked into or out of the coating of nickel plated copper specimens thermally exposed at 1400°F.

4. Copper diffused into the nickel plate and nickel diffused into the copper in plated substrate specimens during thermal exposure at 1400°F.

5. Nickel from the nickel plate diffused into the Hastelloy X and chromium from the Hastelloy X diffused into the nickel plate in nickel plated Hastelloy X specimens during thermal exposure at 1400°F.

6. Little (<1 micron) or no diffusion of the elements checked into or out of the coating of nickel plated Hastelloy X specimens occurred during thermal exposure at 1400°F.

Typical microprobe traces are shown in Figures 8 through 28. These were selected from over 100 microprobe traces to show elements from both the coating and the substrate before and after thermal exposure. The line between the coating and substrate is not vertical because the stream of electrons used to pulse the surface of the specimen has a finite diameter and, as it crosses the interface, picks up elements from both coating and substrate. If a point source were used, a sharp demarcation would result. Although the height of the trace is an indication of the amount of the element present, no attempt was made to make a quantitative analysis. The microprobe was adjusted to give almost full chart width for the element under study. Figures 29 through 32 are photomicrographs showing the Fe_3TiO_5 coating on unplated Hastelloy X and copper before and after thermal exposure.

Selection of Coating

It appears that a number of "coating-substrate" combinations would satisfy that required thermal control coating performance characteristics. Complications in the coating application would result if a different coating or surface treatment were selectively applied to each of the base metals, Hastelloy X and OFHC copper.

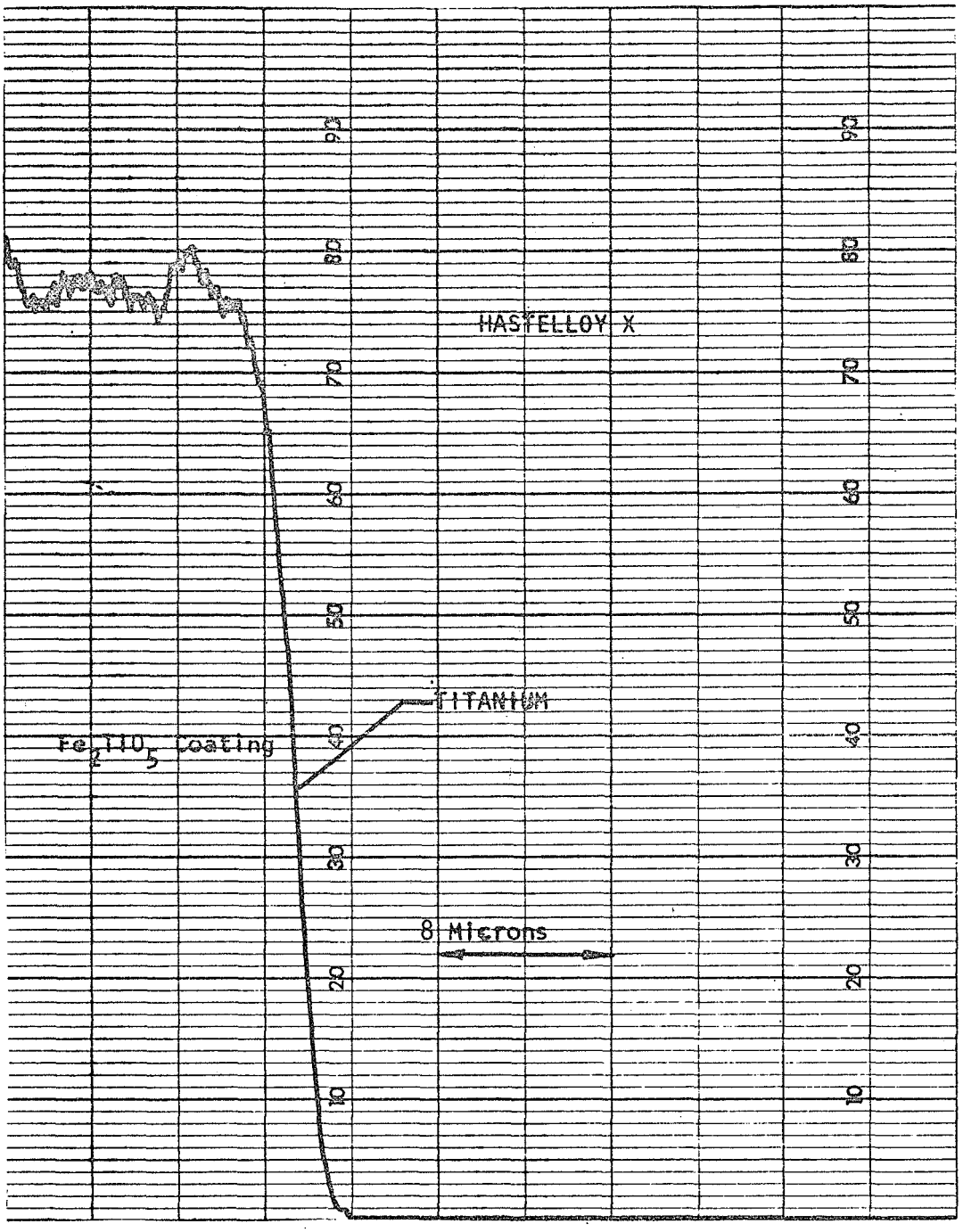


Figure 8 Microprobe Analysis of Titanium in Fe_2TiO_5 Coated Hastelloy X (as coated specimen)

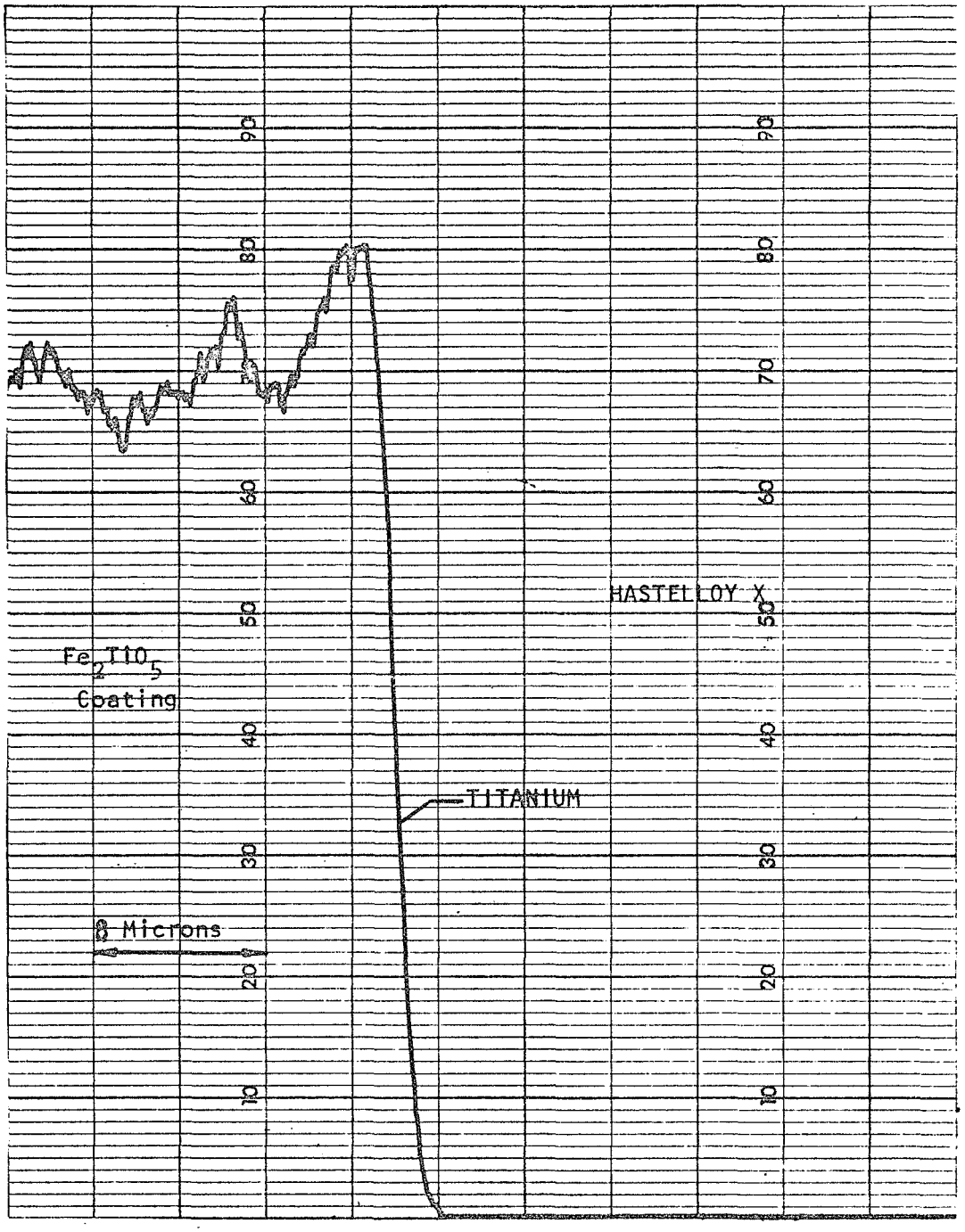


Figure 9 Microprobe Analysis of Titanium in Fe_2TiO_5 Coated Hastelloy X (thermally exposed specimen)

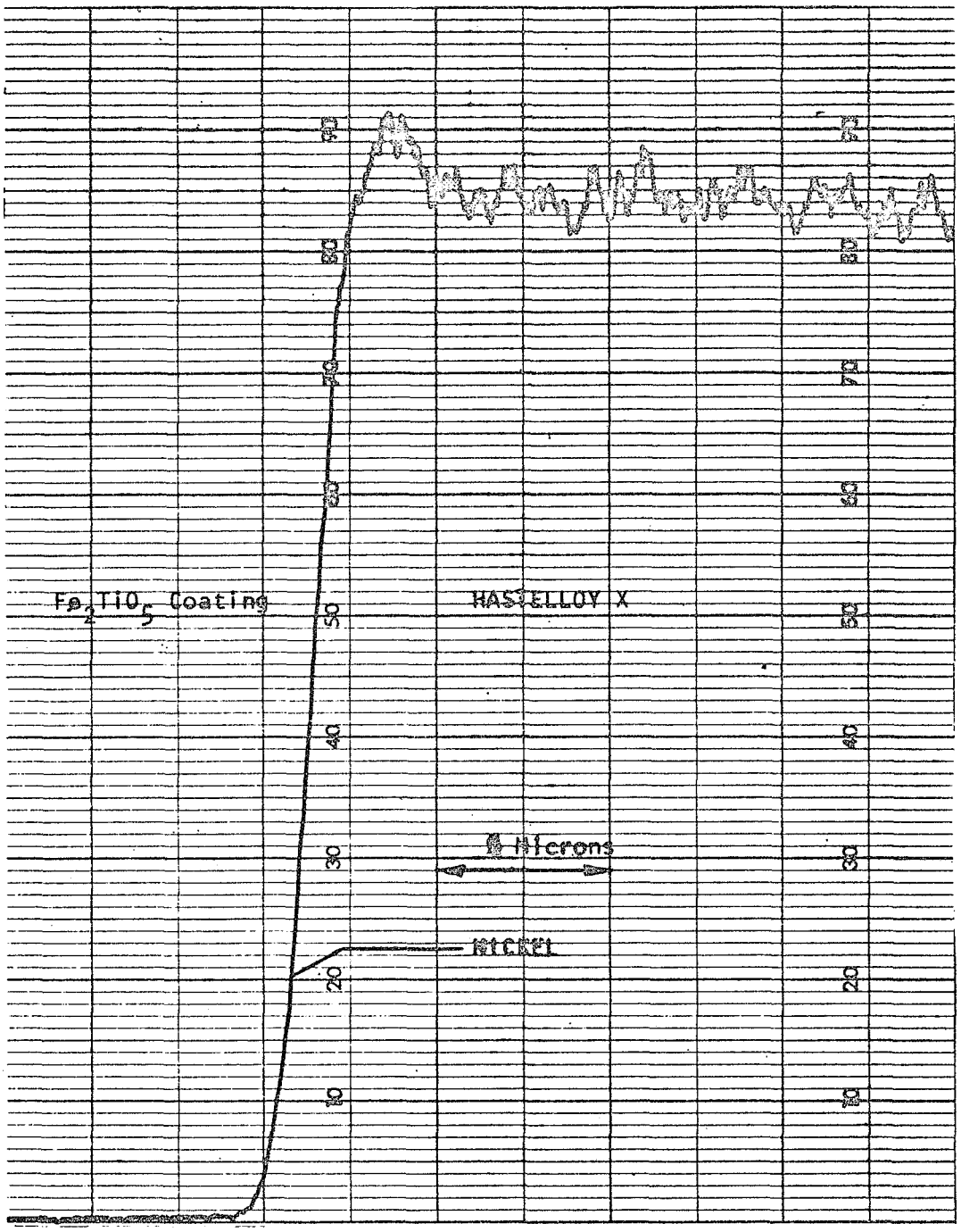


Figure 10 Microprobe Analysis of Nickel in Fe_2TiO_5 Coated Hastelloy X. ((as-coated specimen)

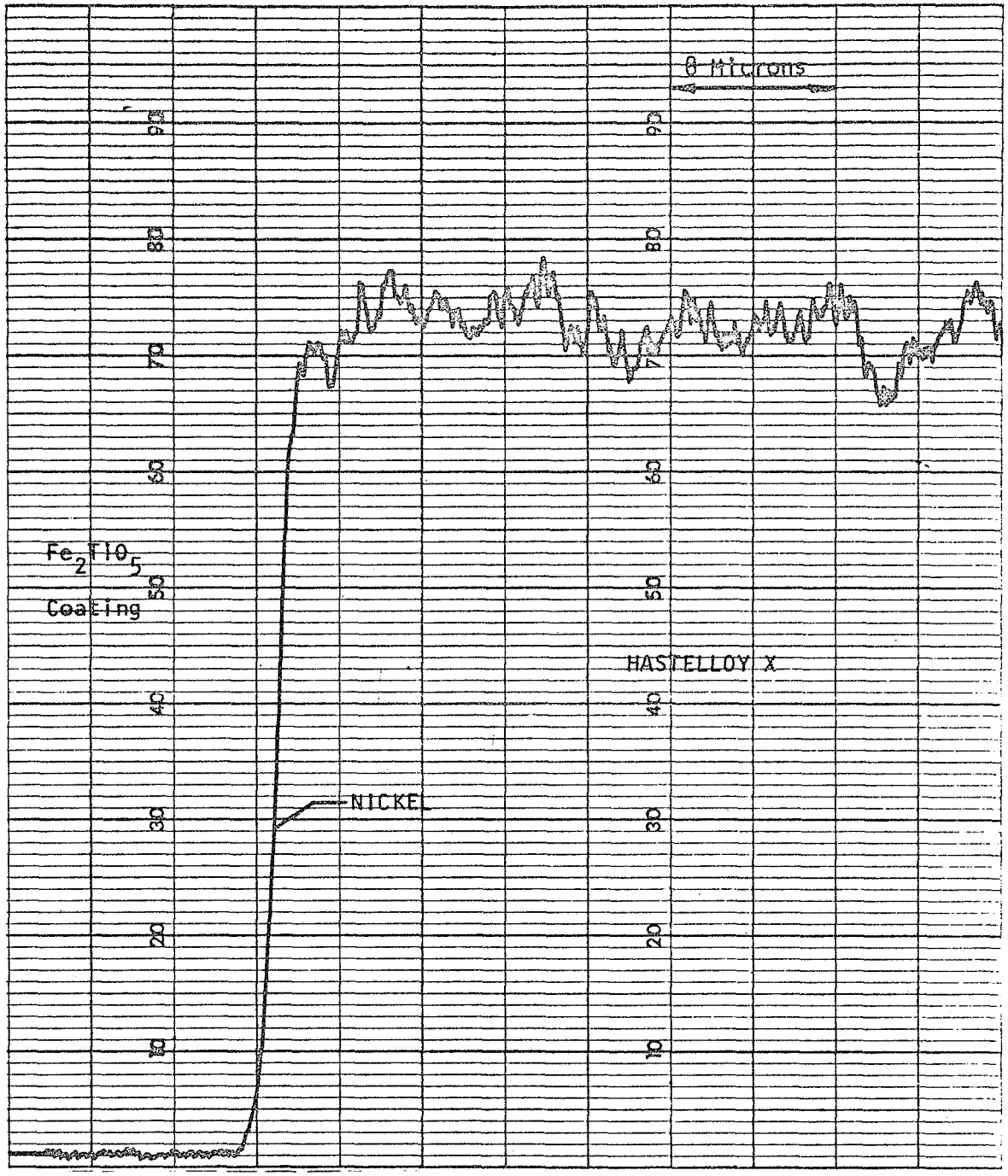


Figure 11 Microprobe Analysis of Nickel in Fe_2TiO_5 Coated Hastelloy X (thermally exposed specimen)

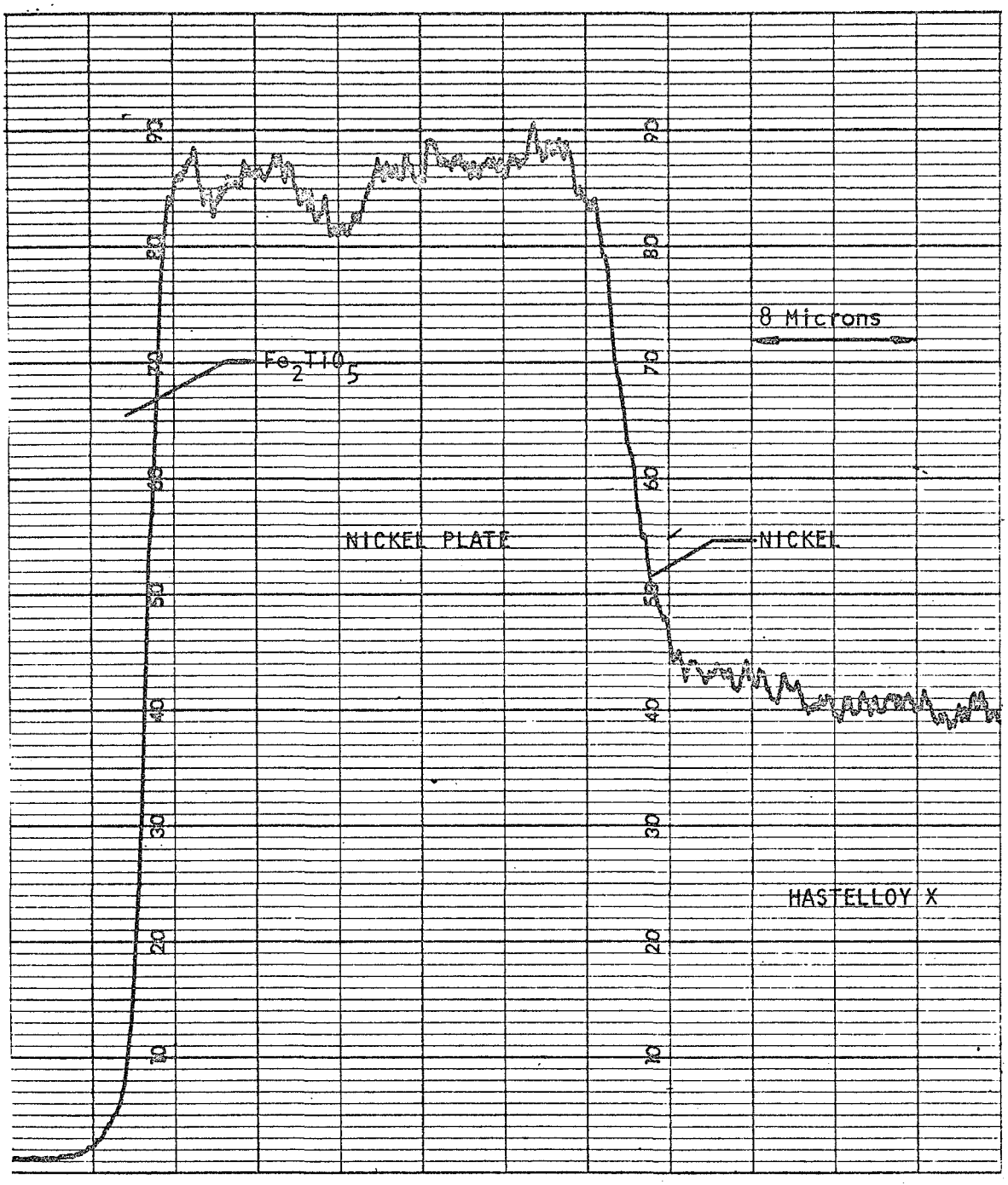


Figure 12 Microprobe Analysis of Nickel in Fe_2TiO_5 Coated, Nickel Plated Hastelloy X (as coated specimen)

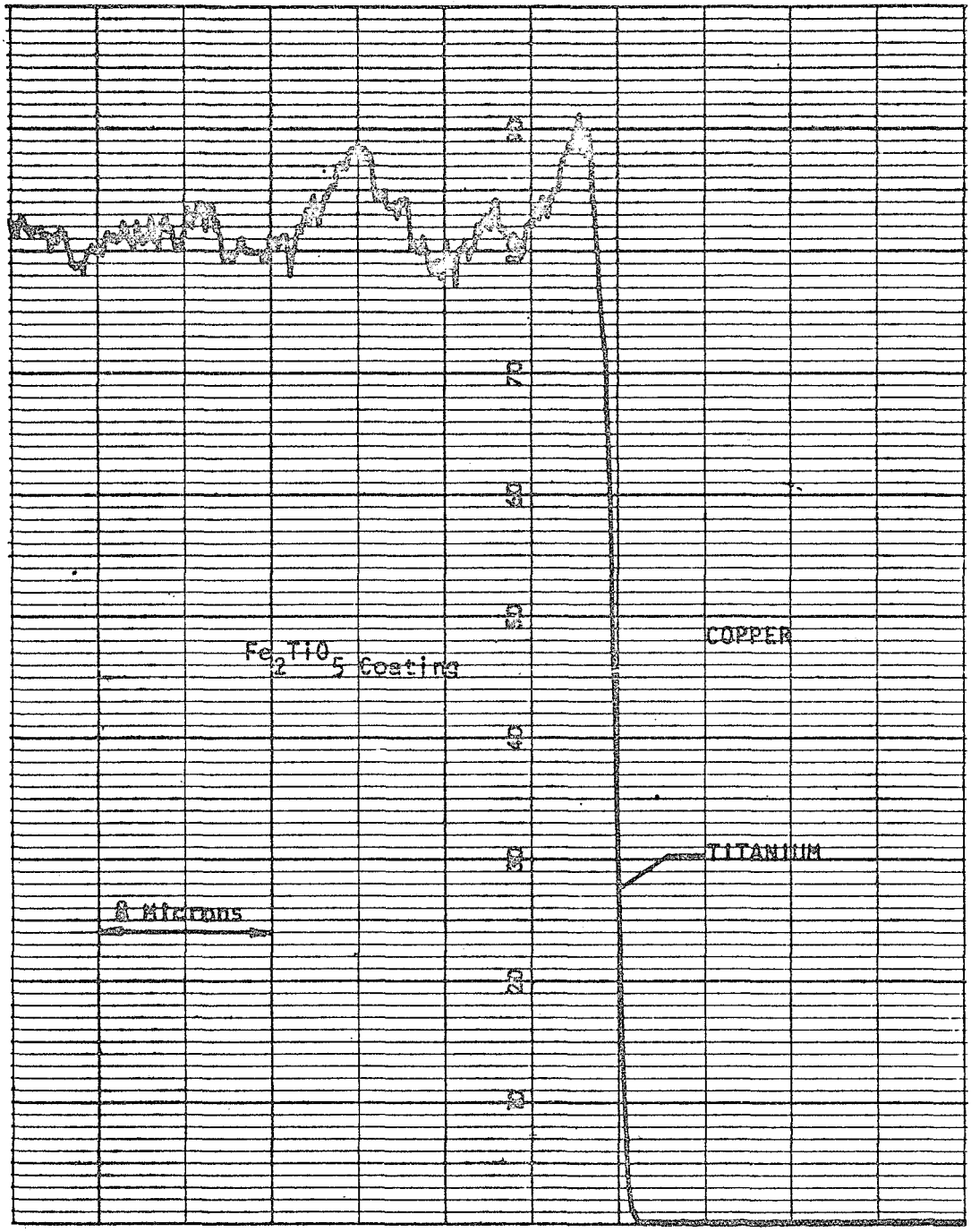


Figure 13 Microprobe Analysis of Titanium in Fe_2TiO_5 Coated Copper (as coated specimen)

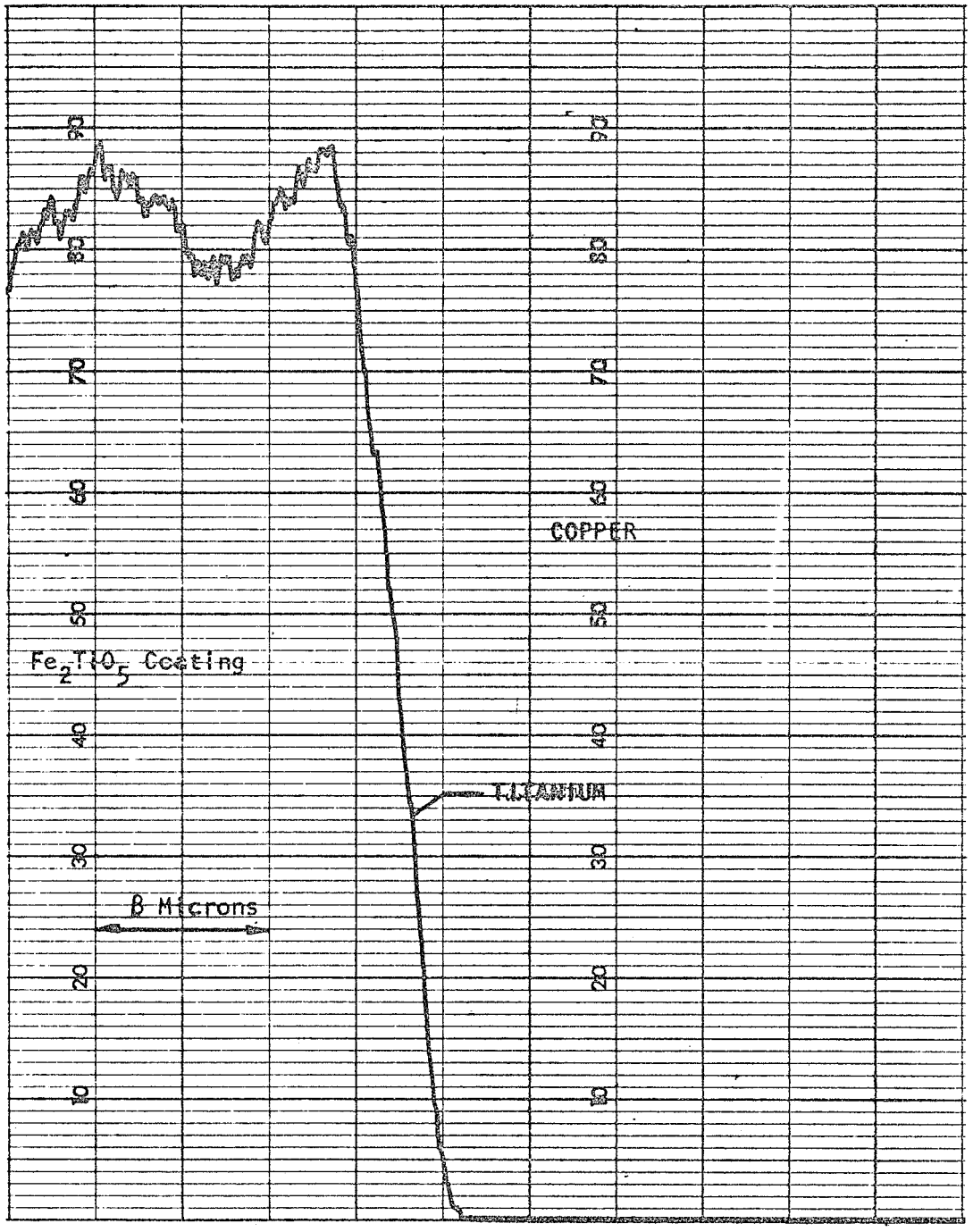


Figure 14 Microprobe Analysis of Titanium in Fe_2TiO_5 Coated Copper (thermally exposed specimen)

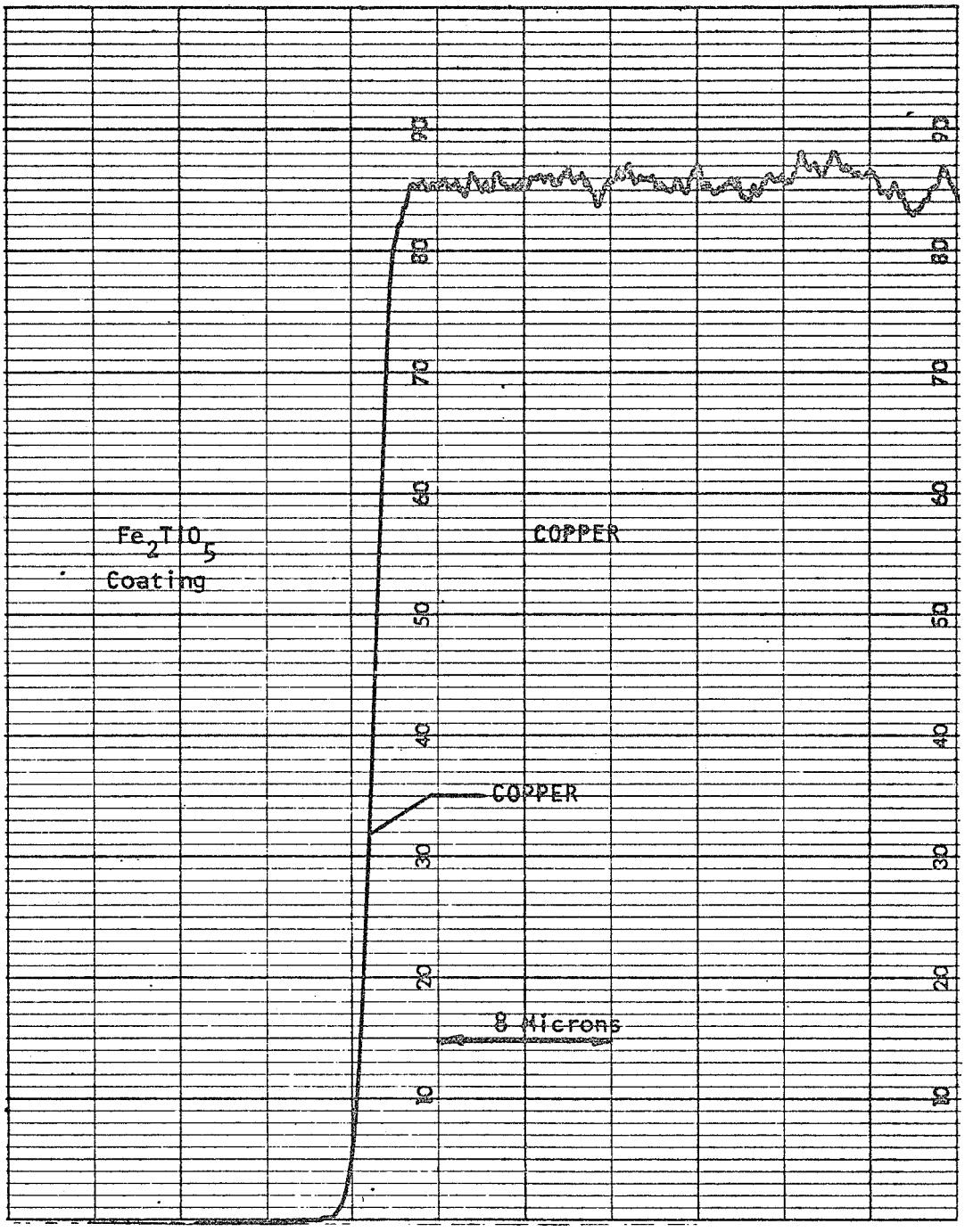


Figure 15 Microprobe Analysis of Copper in Fe_2TiO_5 Coated Copper (as coated specimen)

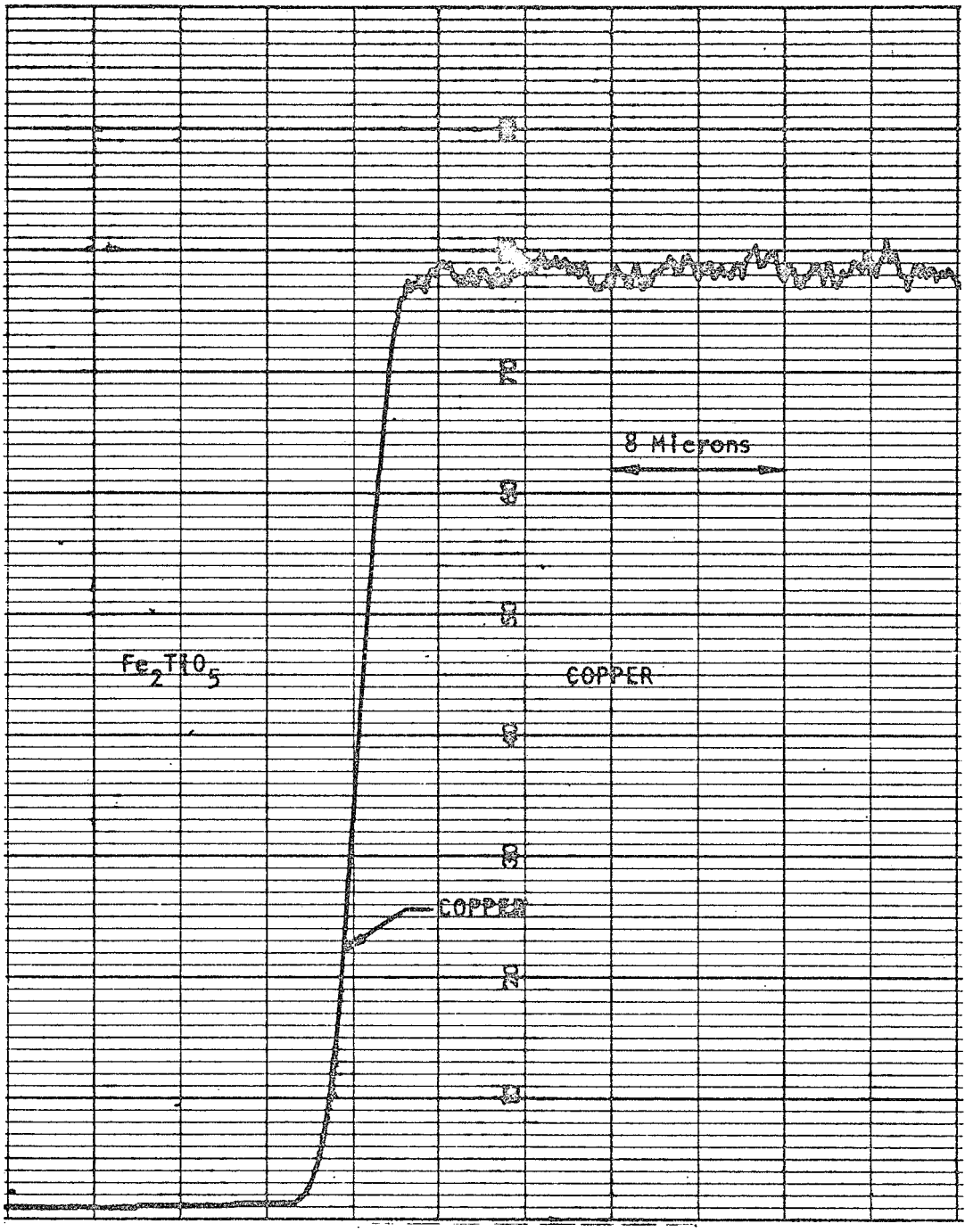


Figure 16 Microprobe Analysis of Copper in Fe_2TiO_5 Coated Copper (thermally exposed specimen)

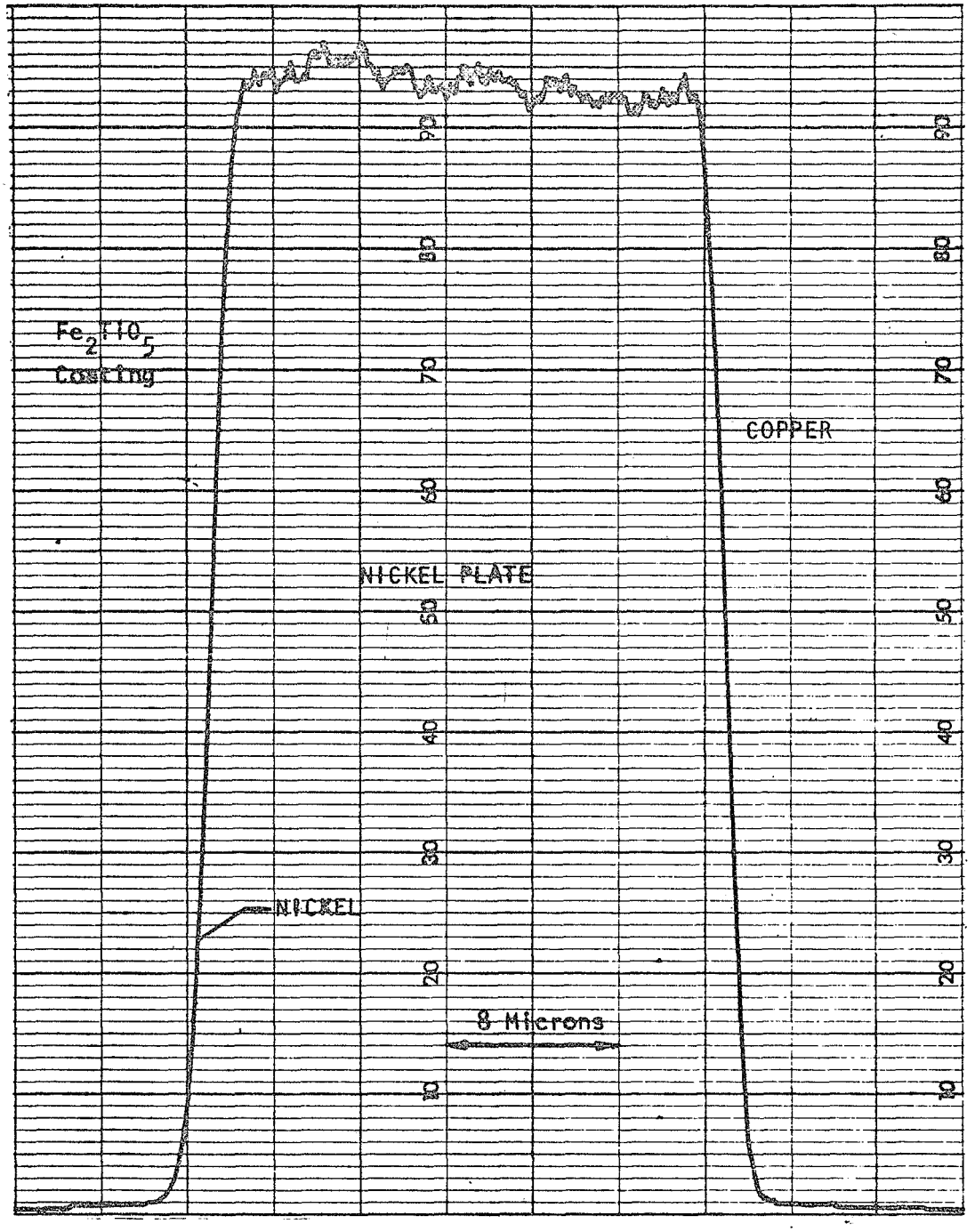


Figure 17 Microprobe Analysis of Nickel in Fe_2TiO_5 Coated, Nickel Plated, Copper (as coated specimen).

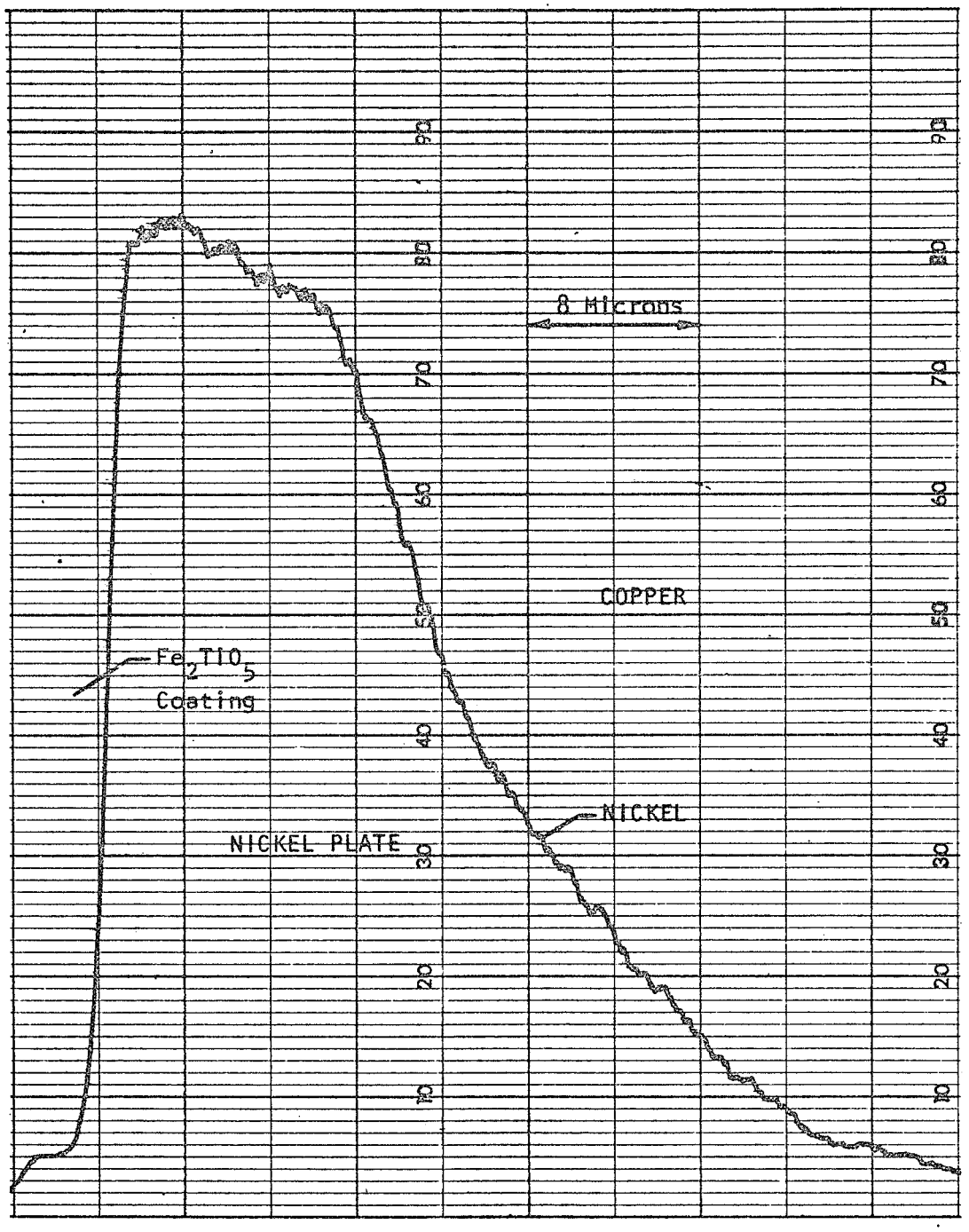


Figure 18 Microprobe Analysis of Nickel in Fe_2TiO_5 Coated, Nickel Plated, Copper (thermally exposed specimen)

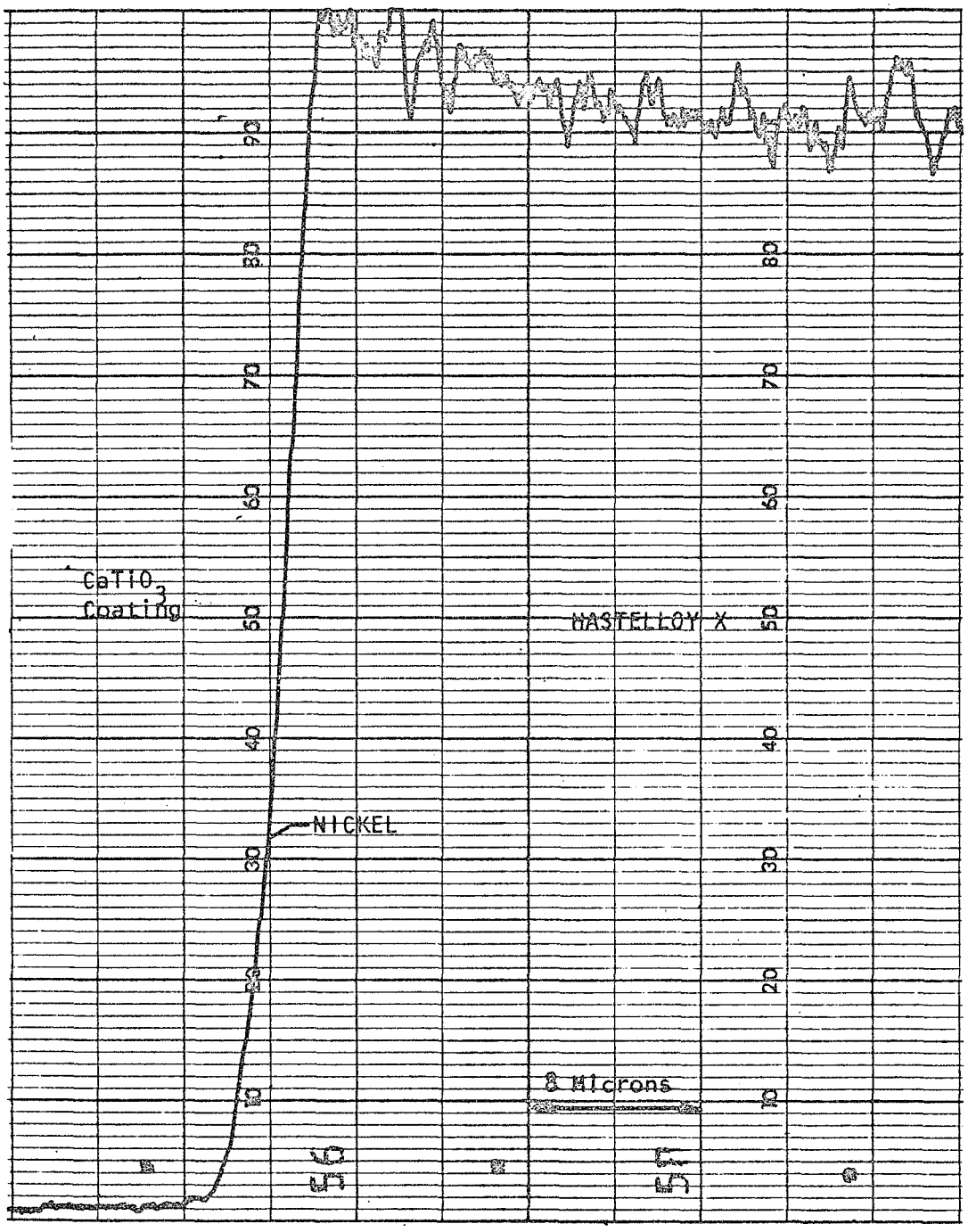


Figure 19 Microprobe Analysis of Nickel in $CaTiO_3$ Coated Hastelloy X (as coated specimen).

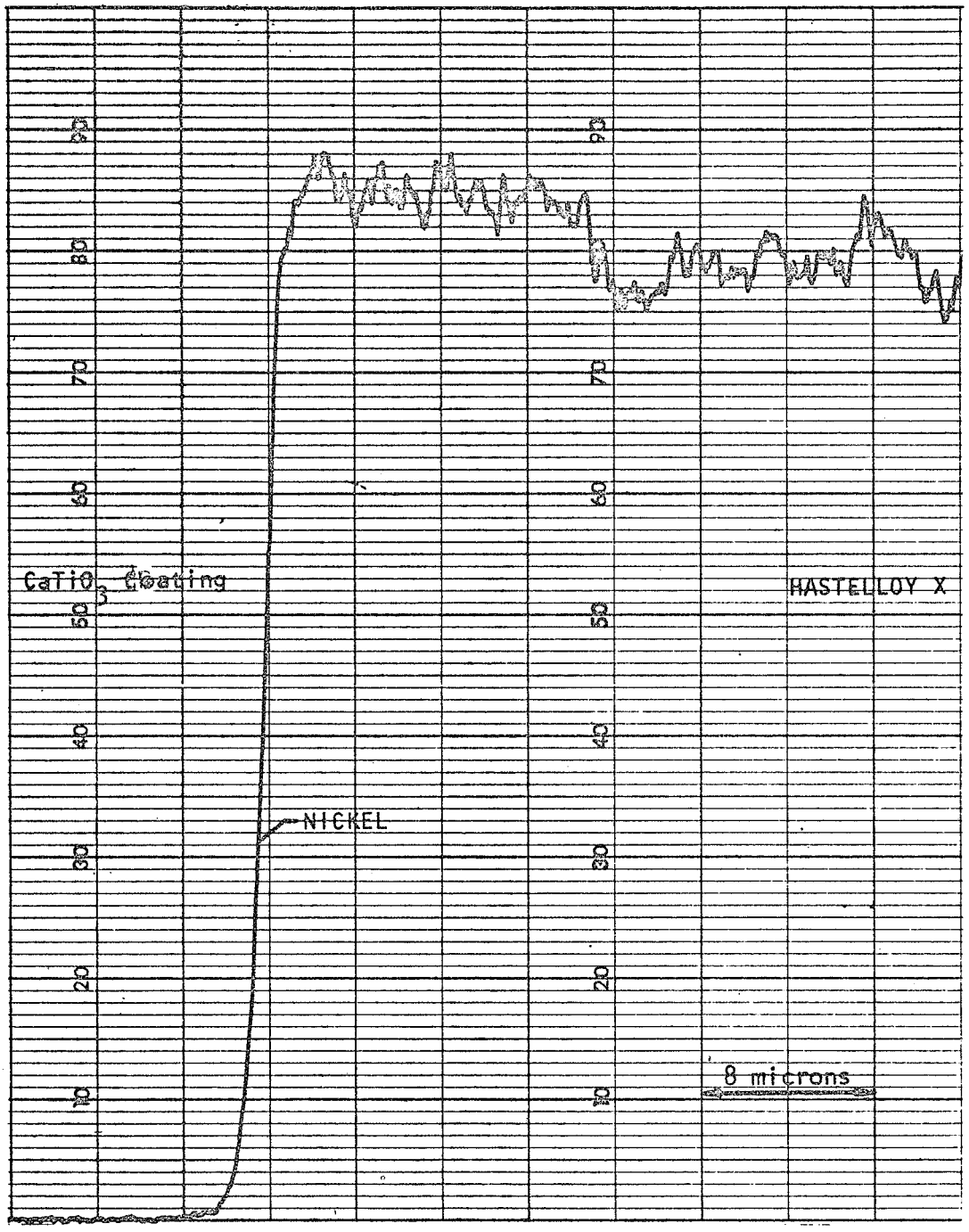


Figure 20 Microprobe Analysis of Nickel in $CaTiO_3$ on Hastelloy X (Thermalloy exposed specimen).

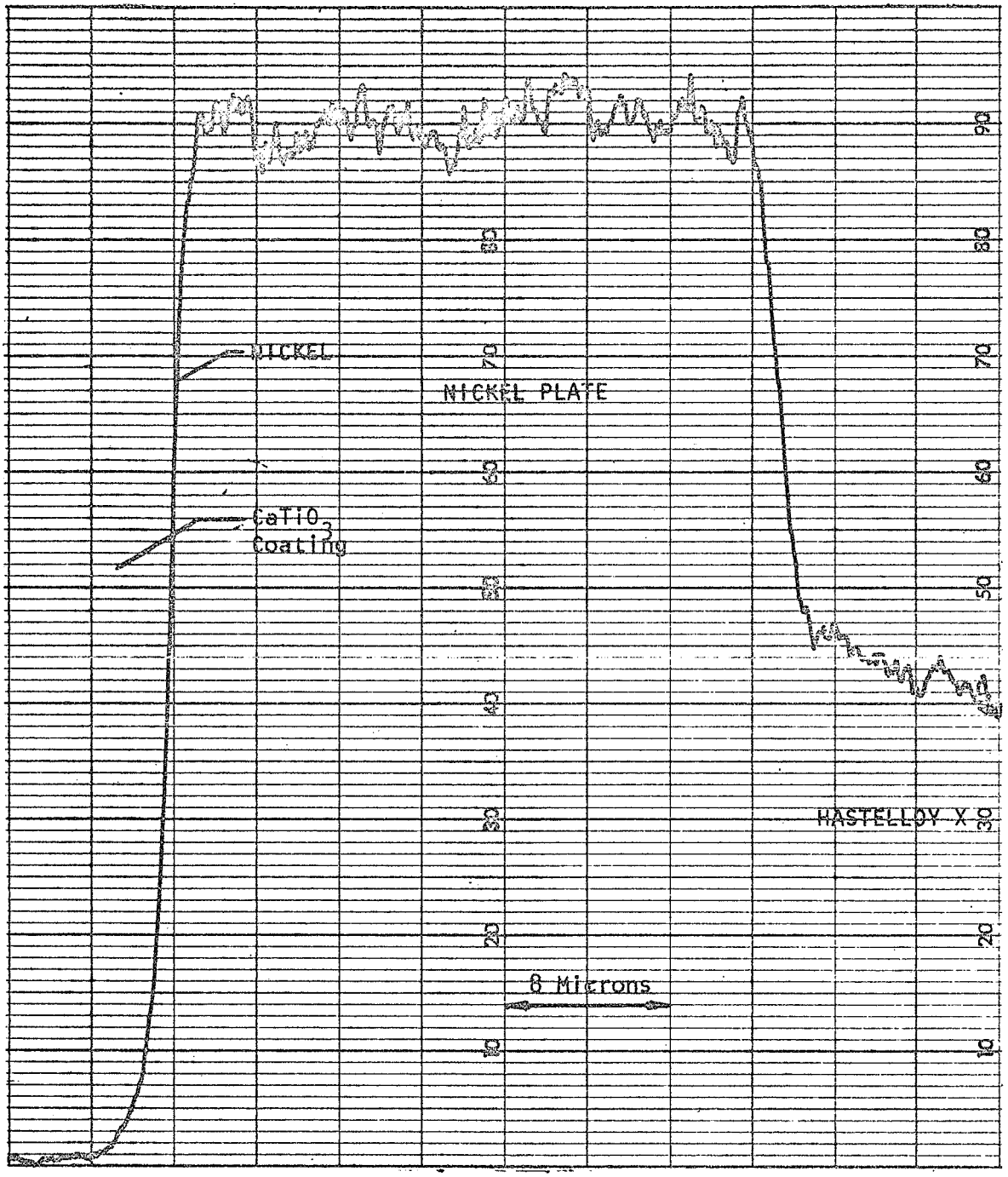


Figure 21 Microprobe Analysis of Nickel in $CaTiO_3$ Coated, Nickel Plated, Hastelloy X (As coated specimen)

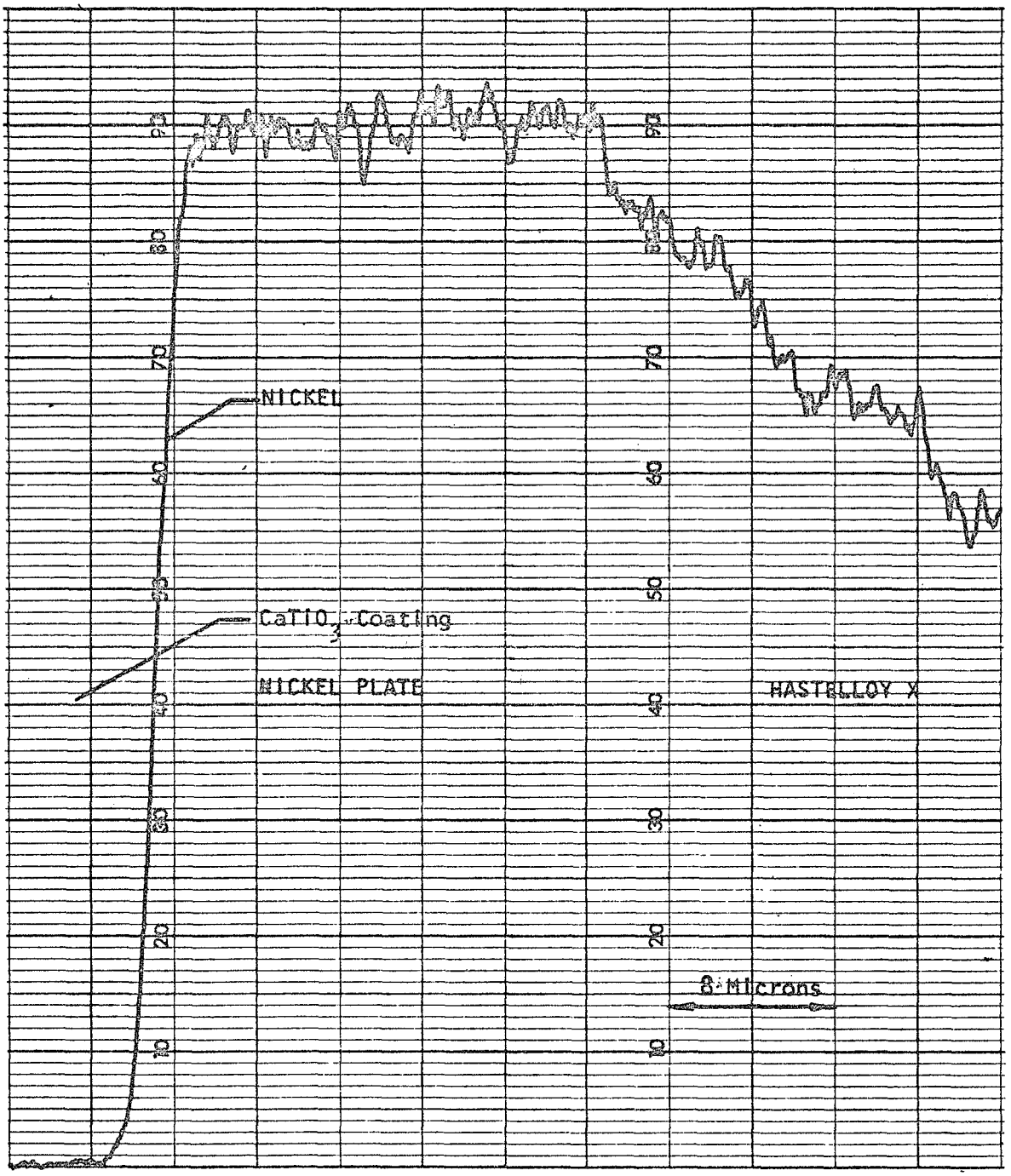


Figure 22 Microprobe Analysis of Nickel in $CaTiO_3$, Nickel Plated, Hastelloy X (Thermally exposed specimen).

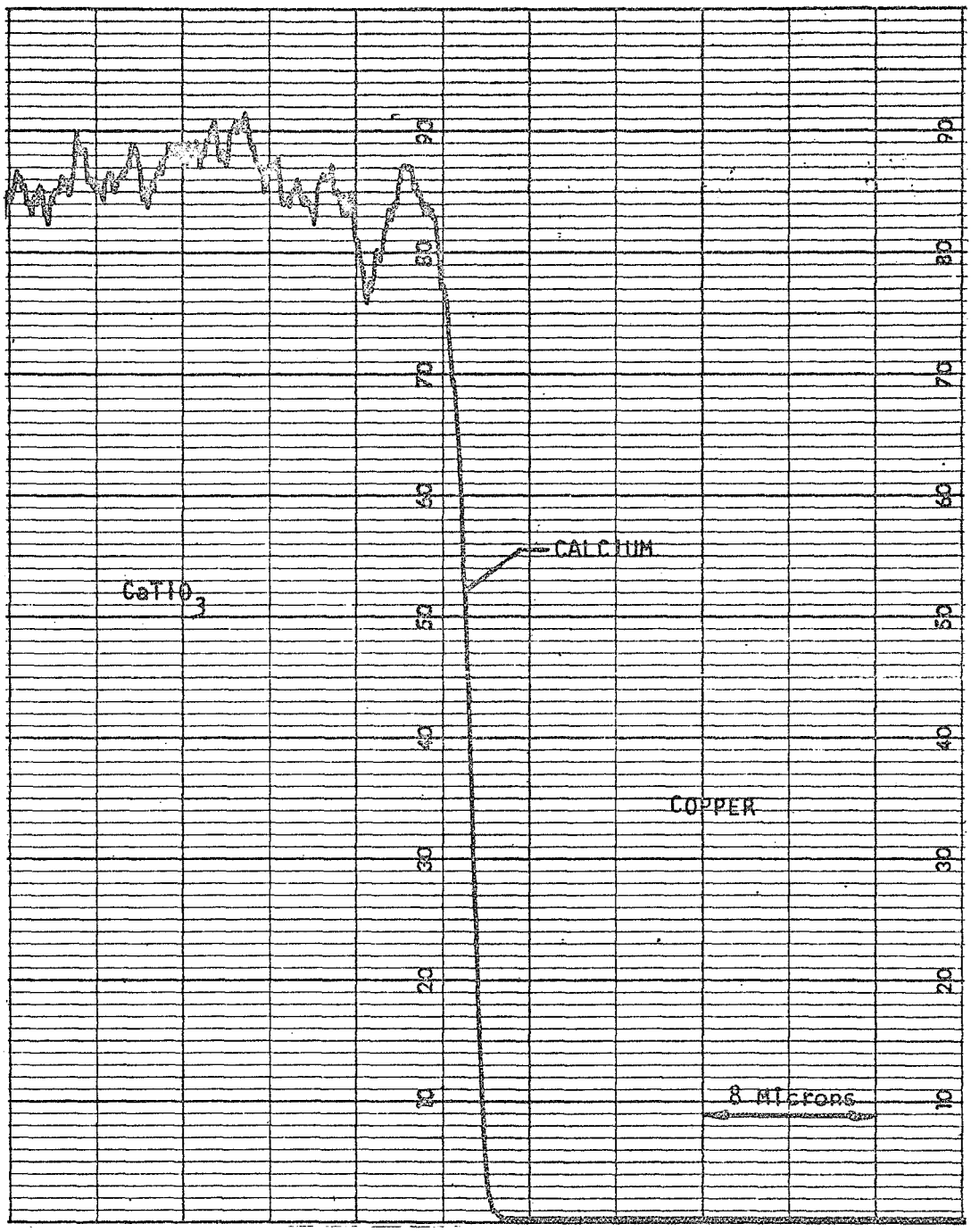


Figure 23 Microprobe Analysis of Calcium in $CaTiO_3$ Coated Copper (Thermally exposed specimen).

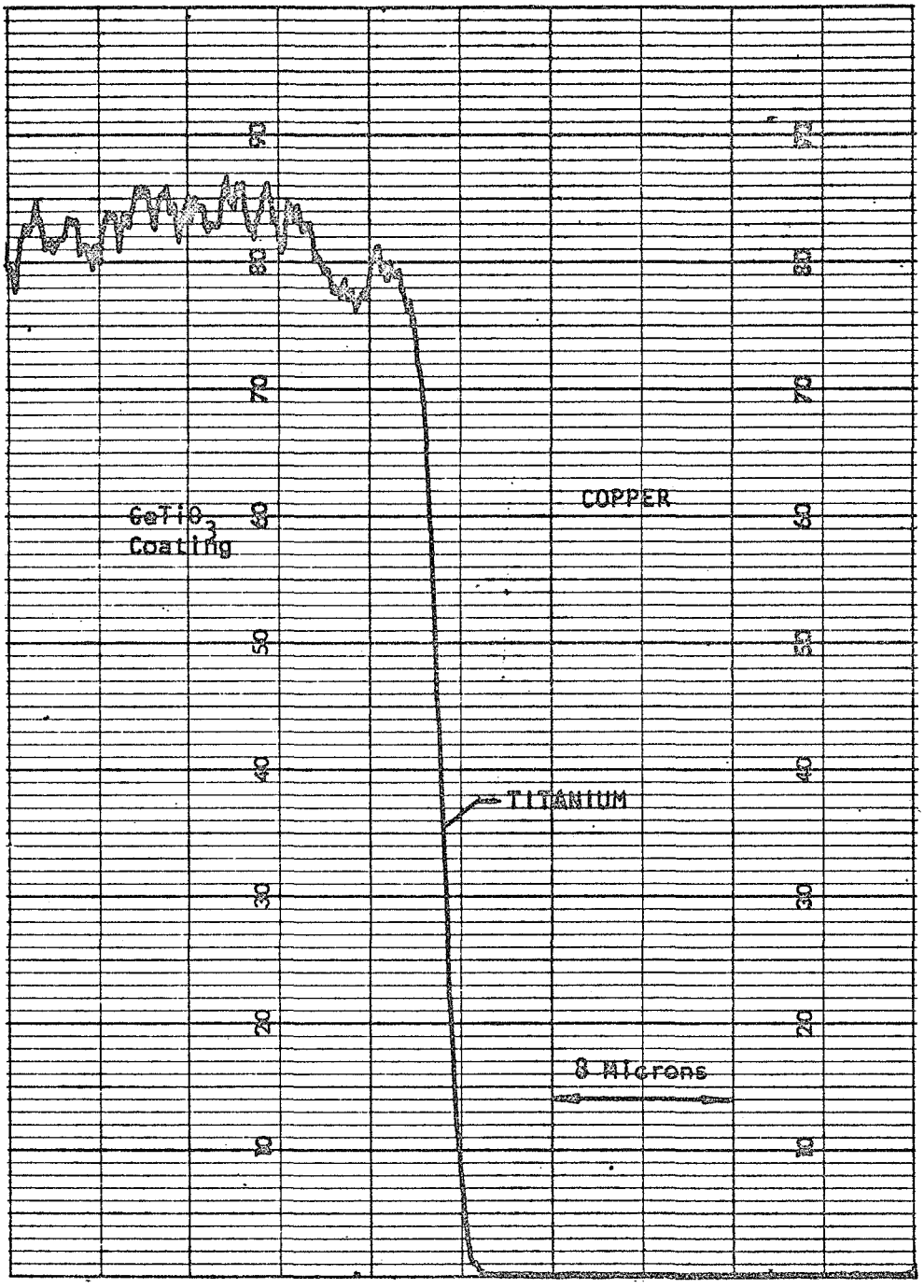


Figure 24 Microprobe Analysis of Titanium in $CaTiO_3$ Coated Copper (Thermally Exposed Specimen)

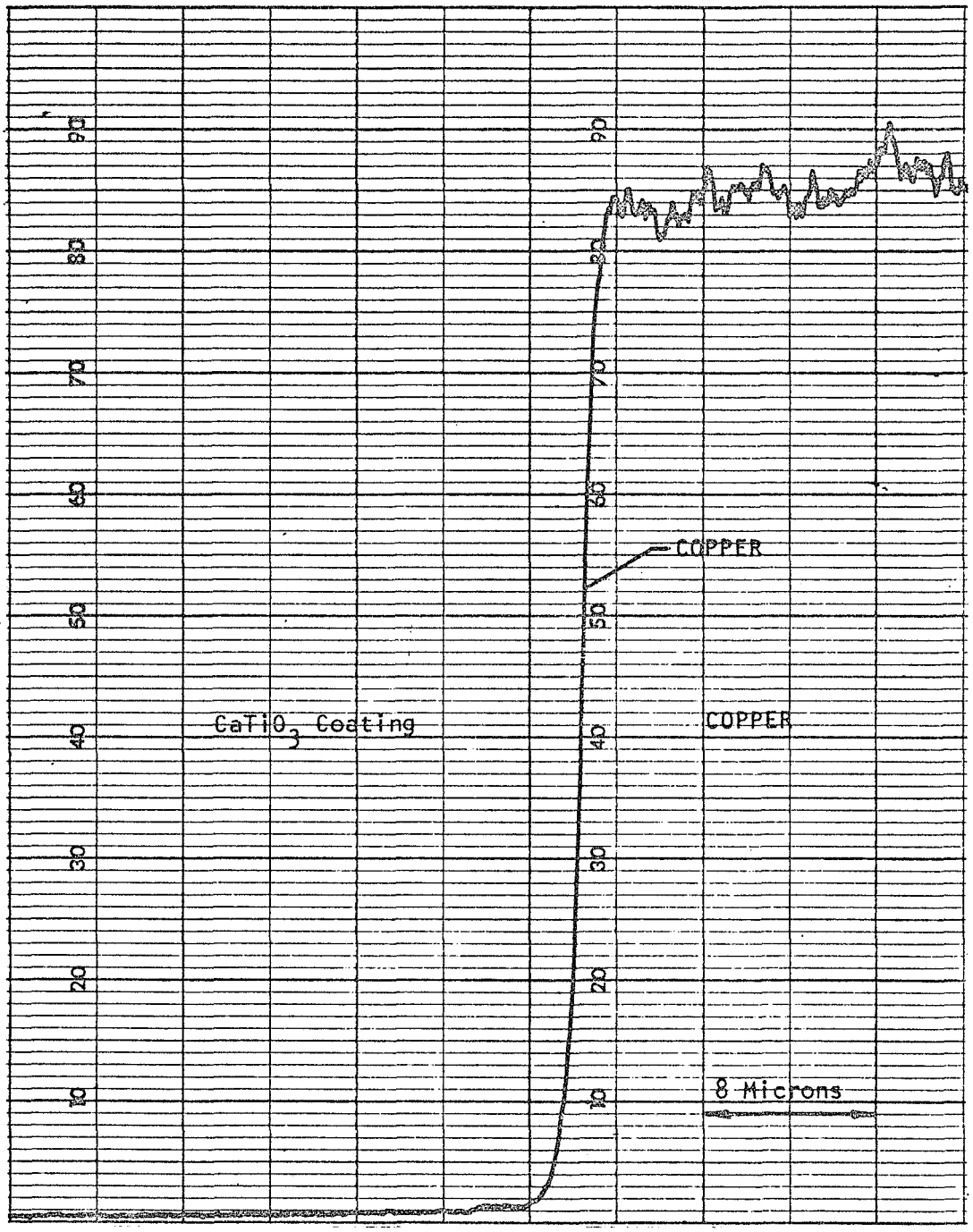


Figure 25 Microprobe Analysis of Copper in $CaTiO_3$ Coated Copper (As coated specimen)

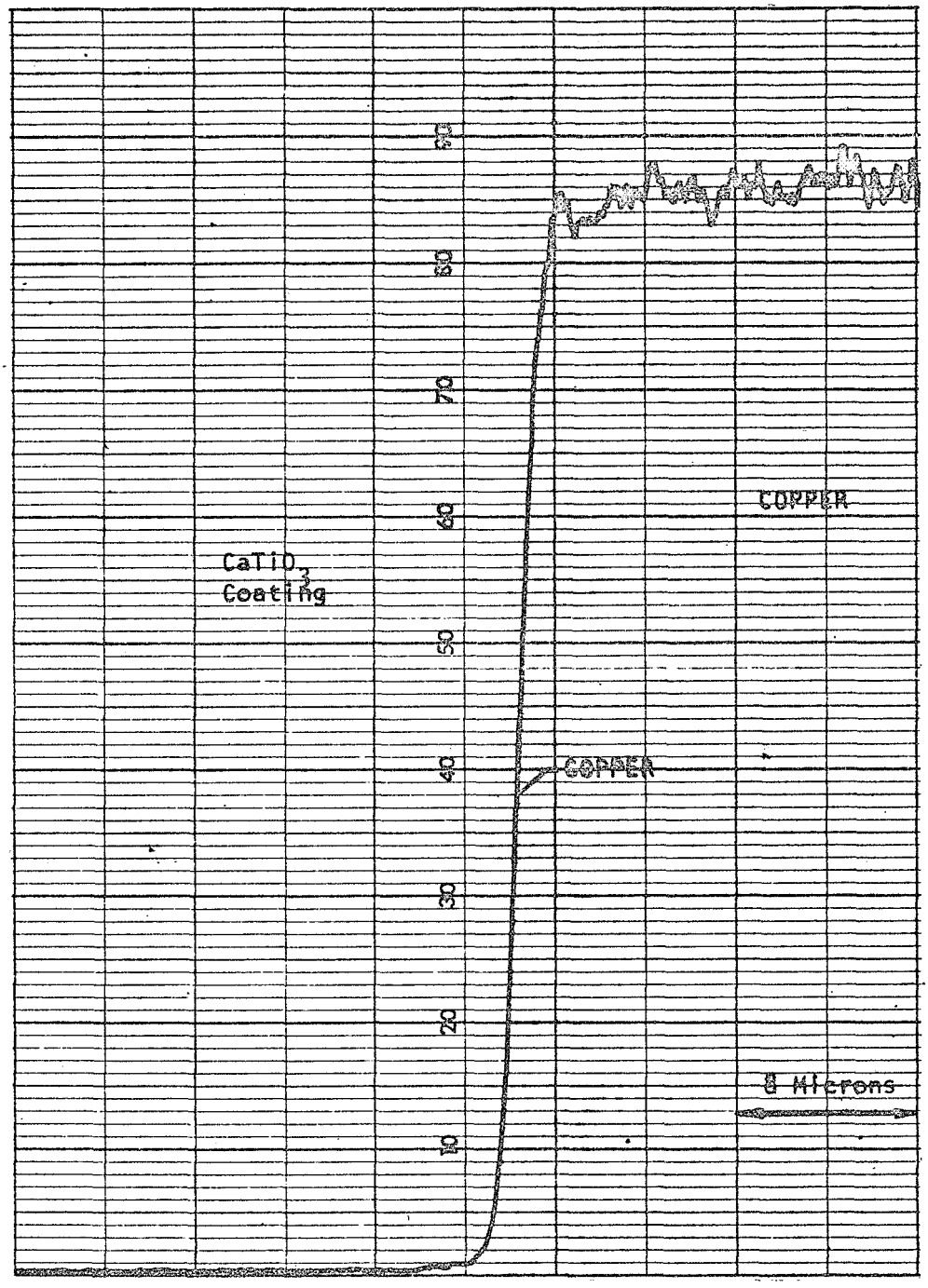


Figure 26 Microprobe Analysis of Copper in $CaTiO_3$ Coated Copper (Thermally exposed specimen)

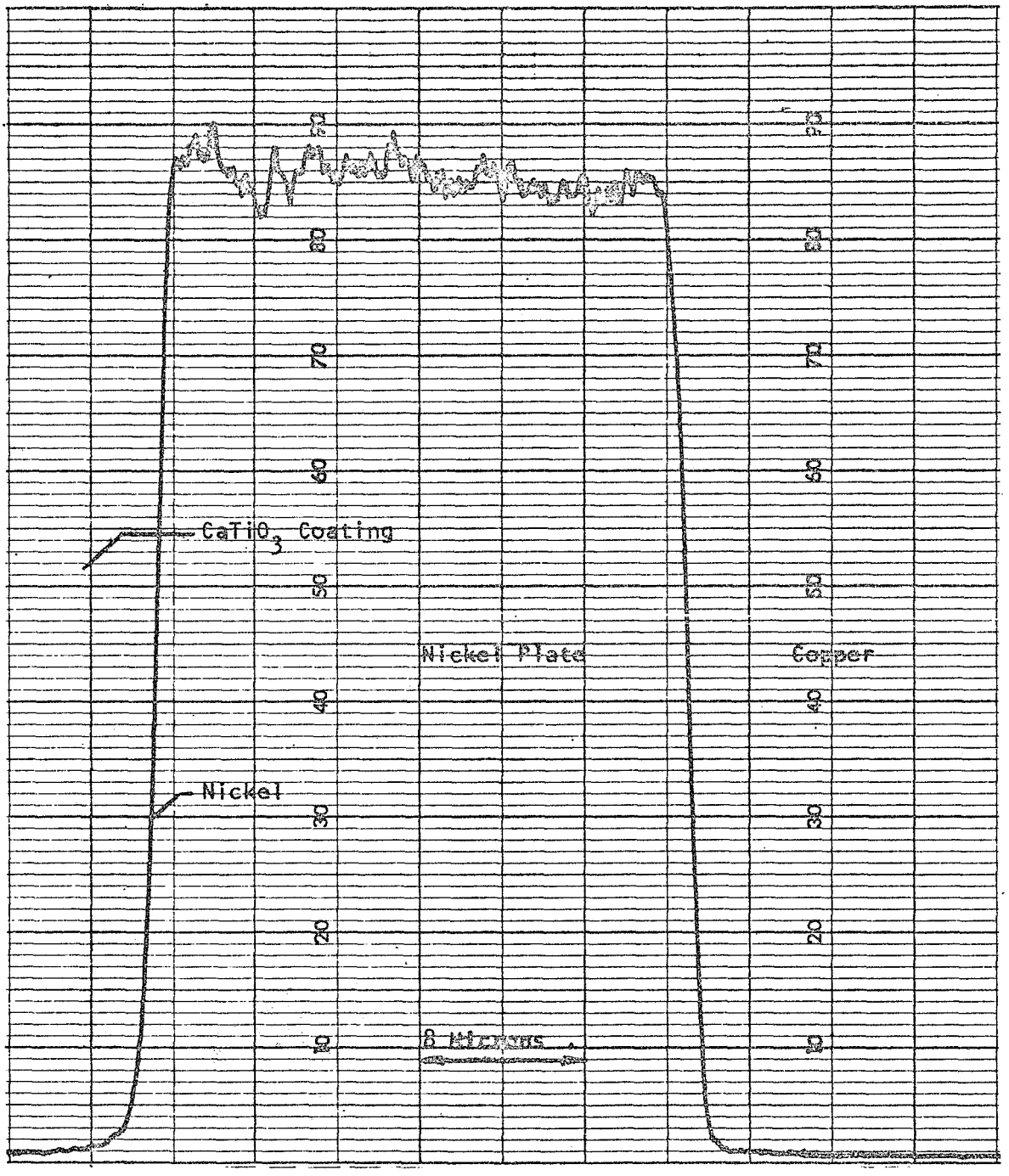


Figure 27 Microprobe Analysis of Nickel In $CaTiO_3$ Coated, Nickel Plated Copper (As received specimen).

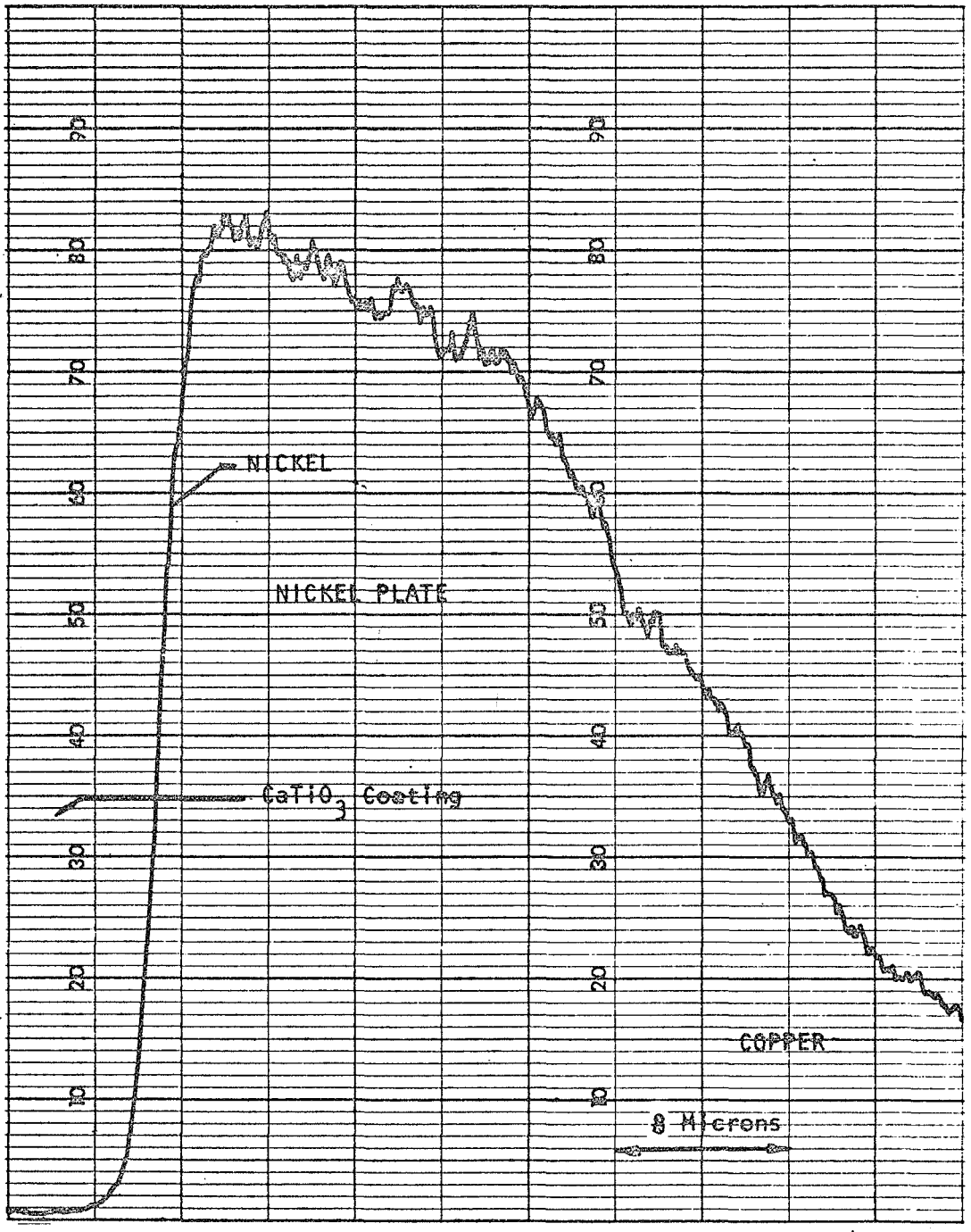


Figure 28 Microprobe Analysis of Nickel in $CaTiO_3$ Coated, Nickel Plated Copper (Thermally exposed specimen).

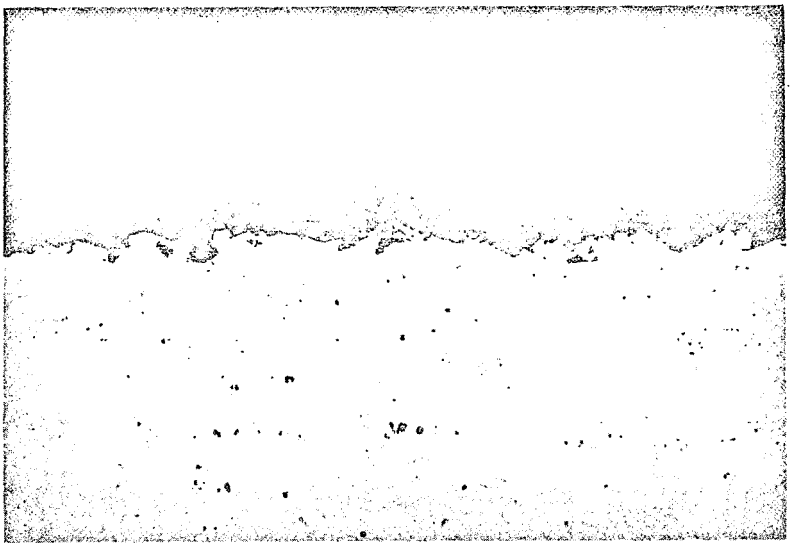


Figure 29 Fe_2TiO_5 On Hastelloy X, as Coated.

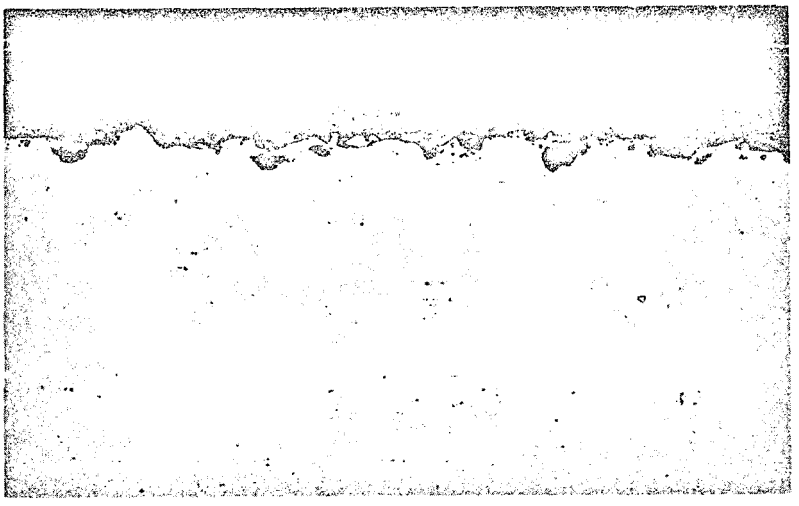


Figure 30 Fe_2TiO_5 on Hastelloy X, Thermally Exposed.

250X

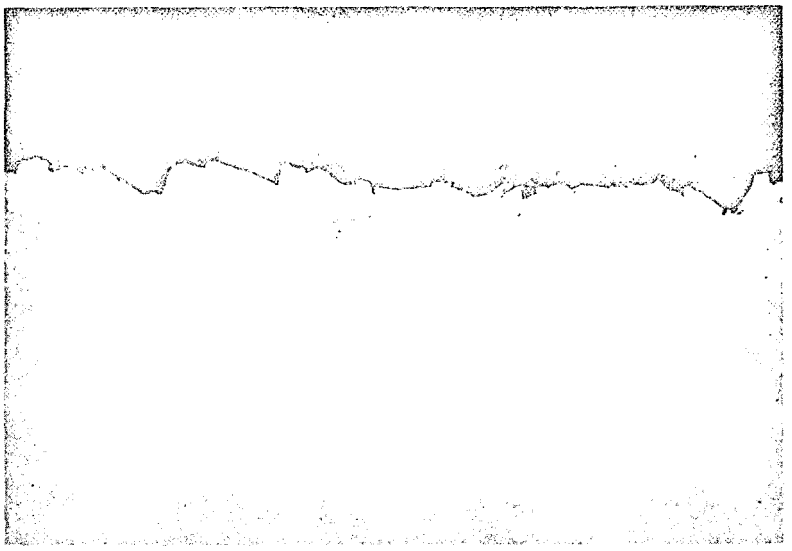


Figure 31 Fe_2TiO_5 on Copper, As Coated.

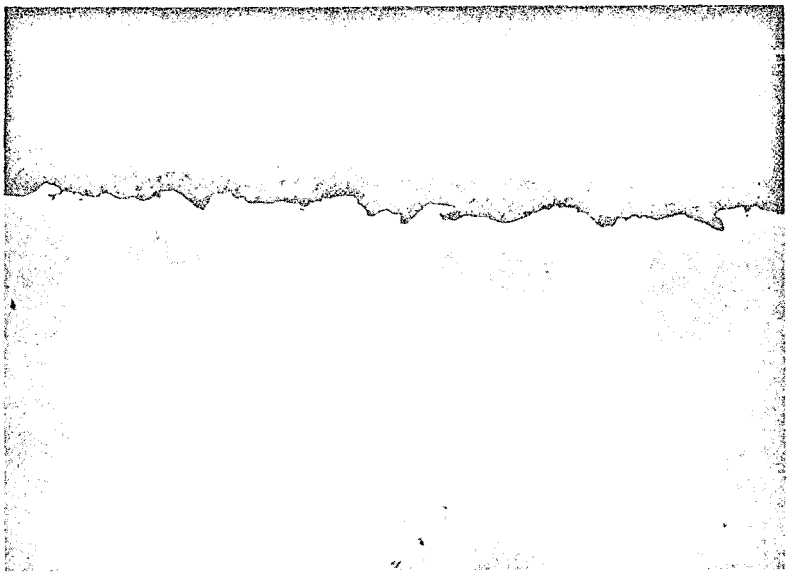


Figure 32 Fe_2TiO_5 on Copper, Thermally Exposed.

250X

5884 B

Because of this fact, the microprobe analysis results and the required application of the coating to the scroll and fin hardware (in contrast to flat, uniform test specimens), the iron titanate coating and the bare substrate Hastelloy X and OFHC copper system was chosen.

Application Procedure

The procedure for the application of the high temperature thermal control coating, iron titanate (Fe_2TiO_5) to the HEPS scroll and fin assembly was developed at the TRW Colwell Engineering Center with the assistance of Mr. Charles Ammann, Development Chemistry Section of Pratt & Whitney Aircraft Division of United Aircraft Corporation, East Hartford, Connecticut and is contained in Appendix B.

Hardware Test Results

Upon the recent completion of the DVR space simulation system test at the Roanoke, Virginia Test Facility of Virginia Polytechnic Institute, examination of the scroll and fin assembly revealed the coating to be uniform in appearance and adherent to all scroll areas. Some small localized areas on the fin were void of the iron titanate coating. The most probable cause of this condition was the "contaminated surface skin" of the OFHC copper fin. This contamination was not removed prior to the application of the high temperature thermal control coating because of the advanced position of the scroll and fin assembly in the fabrication sequence. The post-test condition of the assembly and the test results gives every indication that properly prepared base materials and strict control of the application of the high temperature thermal control coating did provide an adherent coating and did serve to lower component operating temperatures.

Low Temperature Thermal Control Coating

A thorough literature survey, a review of applicable TRW documents containing generally unpublished data, and a visitation with personnel of the Space Power Systems Division at the NASA-Lewis Research Center yielded only two low temperature ($< 400°F$) coatings, (DC92-007 and IITRI-Z93) which appeared promising. The Z93 coating, which was then employed at NASA Lewis on a space program, appeared to present a number of hardware application problems. These were the milling of the paint just prior to its application, extreme cleaning procedure and handling of the substrate to be coated, the necessity of five applications of the paint on five successive days to provide for optimum surface cured coating thickness, relatively close control of temperature and humidity in the application environment, and finally the total inability of the final applied coating to be repaired after contact with oil, fingerprints, processing soil, etc. These considerations made the Z93 coating incompatible with the hardware designed for use in this program.

Selection of Low Temperature Coating

DC 92-007 has been used by TRW in certain classified programs with excellent results. The coating has proved to be easy to apply and to be capable of being repaired or cleaned if necessary. This coating was chosen for HEPS components.

Application of Low Temperature Coating

A specification was prepared (TAP-PS-465) to cover the application of the DC 92-007 coating. A copy of the specification is shown in Appendix C.

Elevated Temperature Emissivity and Absorptivity Measurements of DC 92-007 Coating

Available data did not provide sufficient information regarding emissivity characteristics and absorptivity at its probable use temperature in the HEPS program. Consequently, tests were run on coated specimens.

The solar absorptance as a function of ultraviolet irradiation and the hemispherical emittance were measured for DC 92-007 coated type 6061 aluminum specimens by TRW Systems, Thermophysics Section personnel. The material was maintained at an elevated temperature during ultraviolet irradiation and during hemispherical emittance measurement.

The sample was exposed to ultraviolet irradiation while it was maintained at 205°C within a vacuum chamber with a pressure of 10^{-6} torr or less. The vacuum chamber is a fused silica "test tube" as shown in Figure 33. This "test tube" is transparent in the ultraviolet region where the xenon compact arc source emits energy. An external temperature controlling system is used to circulate fluid to the platen on which the sample is mounted. The sample temperature was monitored with a thermocouple which was attached to the substrate aluminum. Solar absorptance measurements were made between and after ultraviolet exposures while the sample remained in the vacuum in which the sample was irradiated (in situ)[3]. The exposure time was approximately 100 hours. The irradience was equal to the solar ultraviolet irradience. Solar absorptance measurements were made at 50 hour intervals.

The solar absorptance was determined by measuring the spectral directional reflectance from 0.28 to 2.5 microns in the Beckman DK2A Spectrophotometer with integrating sphere of the Edwards, et al., design[4]. The sample is shown inserted in the integrating sphere in Figure 34. This reflectance was integrated over the solar irradiance[5] to obtain solar absorptance. For opaque samples, the absorbed (α) energy plus the reflected (ρ) energy equals the incident energy; hence,

$$\alpha_\lambda + \rho_\lambda = 1$$

The absorptance is, therefore, calculated from reflectance measurements by the relation

$$\alpha_\lambda = 1 - \rho_\lambda$$

The hemispherical emittance was measured in the TRW Systems Calorimetric Hemispherical Emittance Device. This measurement is performed by determining the power density required to maintain the sample at equilibrium temperature in a liquid nitrogen-cooled vacuum chamber. The emittance was measured at the temperatures given in Table 3. The sample was maintained at 401°F for approximately

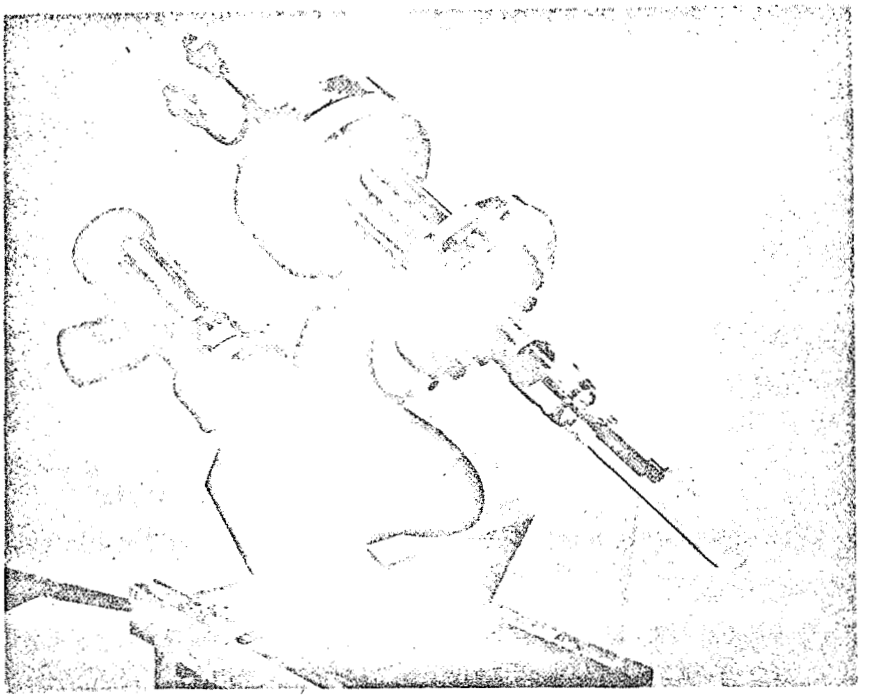


Figure 33 In Situ Vacuum Test Chamber Containing Sample.

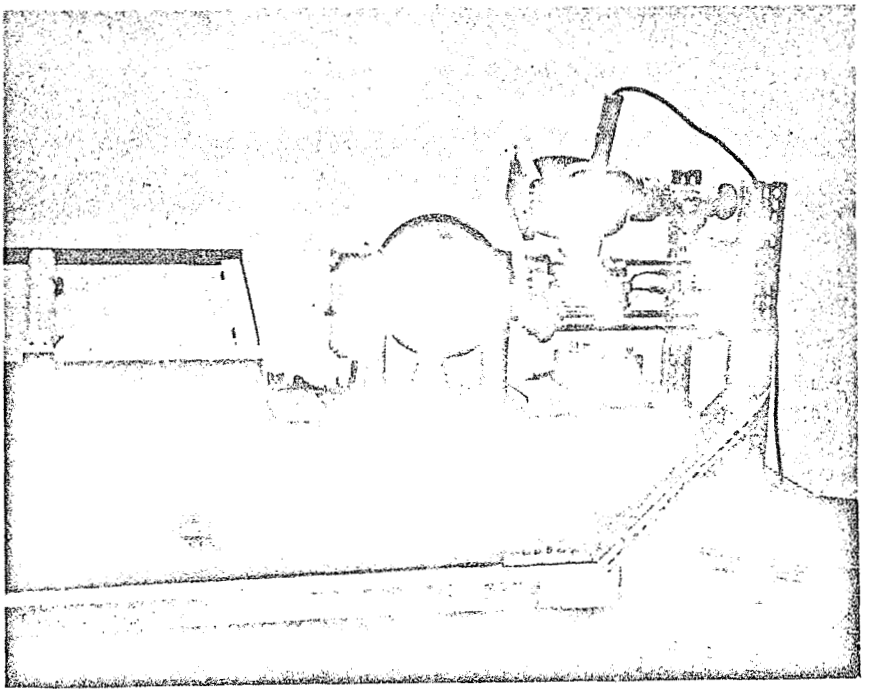


Figure 34 In Situ Vacuum Test Chamber in Measurement Position

TABLE 3

SOLAR ABSORPTANCE FOLLOWING ULTRAVIOLET IRRADIANCE (1 UV SUN) ON SAMPLE AT 401°F, DC 92-007

	SOLAR ABSORPTANCE
Initial	0.22
After 50 Hours	0.30
After 100 Hours	0.44

HEMISPHERICAL EMITTANCE DURING AND FOLLOWING ELEVATED TEMPERATURE (401°F) MAINTENANCE IN VACUUM, DC 92-007

FOLLOWING INDICATED HOURS AT ELEVATED TEMPERATURE	TEMPERATURE OF MEASUREMENT	HEMISPHERICAL EMITTANCE
Initial	196°F	0.84_7*
Initial	397°F	0.79_3
50 Hours	397°F	0.78_7
100 Hours	394°F	0.79_0

*Although the accuracy of the measuring instruments does not justify three significant figures, the third figure is retained, depressed, so as to indicate trends.

100 hours. Emittance measurements were made at 50 hour intervals.

The method of measurement used with the TRW Systems Calorimetric Hemispherical Device (Figure 35) has been fully analyzed by Bevans and Nelson[6]. The sample consisted of two 4-inch by 4-inch sheets of sample material which was bonded to a thin 4-inch by 4-inch heater. The sample "sandwich" was then instrumented with six thermocouples. The entire test assembly was suspended by the heater leads within a liquid nitrogen-cooled copper container (with a high absorptance paint on the inside) within a pyrex bell jar evacuated to a pressure of 10^{-6} torr or less. Electrical power measurements and temperature measurements allow a direct calculation of hemispherical emittance since:

$$\varepsilon_H = \frac{P_{elec}}{A\sigma (T_s^4 - T_\infty^4)}$$

where ε_H = hemispherical emittance

P_{elec} = electrical power to heater

A = specimen area

σ = Stefan-Boltzmann constant

T_s = specimen temperature

T_∞ = wall temperature of container

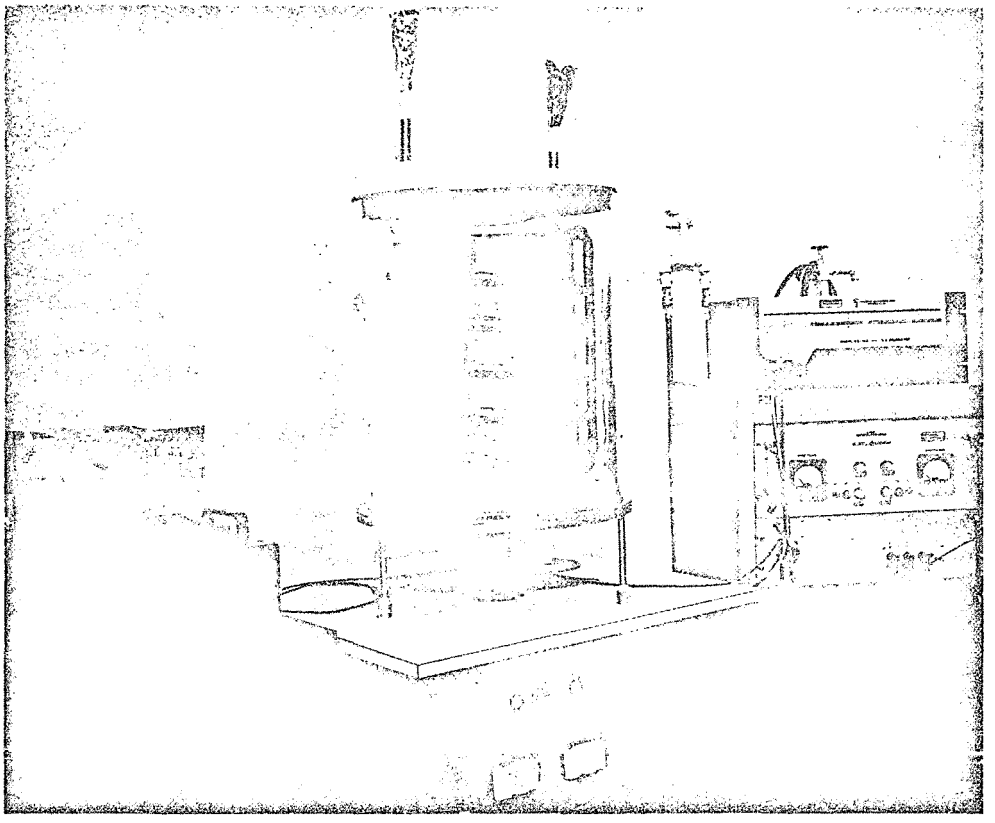


Figure 35 Calorimetric Hemispherical Emittance Apparatus.

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1. R. E. Cleary, et al, Determination of the Emissivity of Materials, Report PWA 3278, Final Report under Contract NAS 3-4174, June 30, 1968.

2. L. Missel, Electroplating in Industry, Metal Finishing, February 1965.

3. W. D. Miller and E. E. Luedke, In Situ Solar Absorptance Measurement, An Absolute Method, Proceedings of Eleventh SAMPE Symposium, April 1967.

4. D. K. Edwards, et al, Integrating Sphere for Imperfectly Diffuse Samples, J.Opt. Soc. Am. 51:1279-88 (1961).

5. F. S. Johnson, The Solar Constant, J. Meteorol. 11:431-439 (1954).

6. K. E. Nelson and J. T. Bevans, Errors of the Calorimetric Method of Total Emittance Measurement, NASA SP-31, pp. 55-65 (1963).

7. Norelco Product Bulletin RC 339-Rev. 264 3MF.

8. Norelco Product Bulletin RC 439-3M-464-0M.

9. Electron Microprobe X-ray Analyzer, Applied Research Laboratories Product Bulletin, November 1965.

APPENDIX A

ELECTRON BEAM MICROPROBE ANALYSIS[7,8,9]

The electron beam microprobe provides a method for nondestructive elemental analysis of extremely minute volumes at the surface of a solid sample. With this instrument, it is possible to conduct a chemical analysis of a sample approximately one to two microns in diameter, and one micron in depth, representing approximately one micro-microgram of material. The analysis can be either qualitative, or, if sufficient standards are available, quantitative.

Figure 36 shows the electron beam microprobe utilized. Figure 37 shows a schematic of the electron optics in the microprobe. Through the use of two magnetic lenses (condenser and objective), and alignment coils, a finely focused beam of electrons is directed at the specimen surface exactly on the spot to be analyzed. This electron bombardment causes characteristic X-rays to be emitted by the atoms affected by the electron excitation.

Crystals of appropriate materials are employed to diffract the generated characteristic X-rays into their component wave lengths. The selected X-rays are focused into X-ray detectors. Figure 38 illustrates the manner in which the goniometer and X-ray detector are mounted in relation to the specimen in the electron beam microprobe utilized. Only those X-rays exciting the specimen surface at an angle of 15.5° pass through the the entrance window into the goniometer.

The X-ray photons entering the detector are converted into pulses of electrical energy. The number of pulses is directly proportional to the intensity of the X-radiation entering the detector, which in turn bears a relationship to the mass concentration of the element producing the X-rays. The pulses of energy from the detector can be utilized in various types of read-out systems.

Analyses can be conducted on all elements above the atomic number of 4.

The electron beam microprobe utilized was designed to allow for three different modes of operation, which are;

1. Spectral Scan With this method, the area of interest is positioned under the electron beam and the analyzing goniometer is set to scan the elemental range of interest. The X-ray detector and the diffracting crystal are mounted so that characteristic X-rays with wave lengths between 1.4 and 14 angsrom units (2θ angles from 0 to 88°) can be detected. A peak of radiation obtained at a specific goniometer angle indicates the presence of a particular element. The amount of radiation detected (i.e. height of peak) is a function of the amount of that particular element in the area of interest.

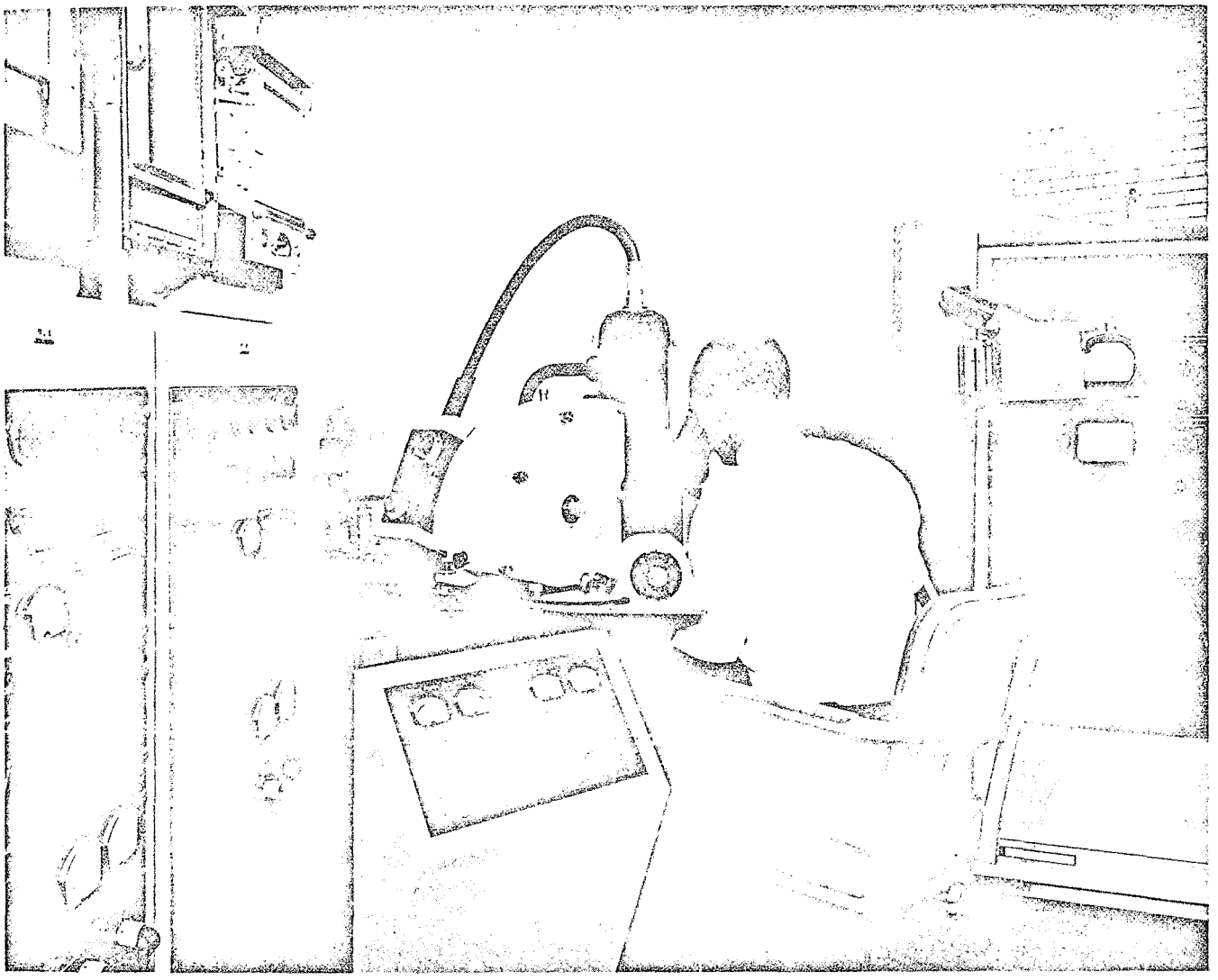

Figure 36 Electron Beam Microprobe Utilized in This Study.

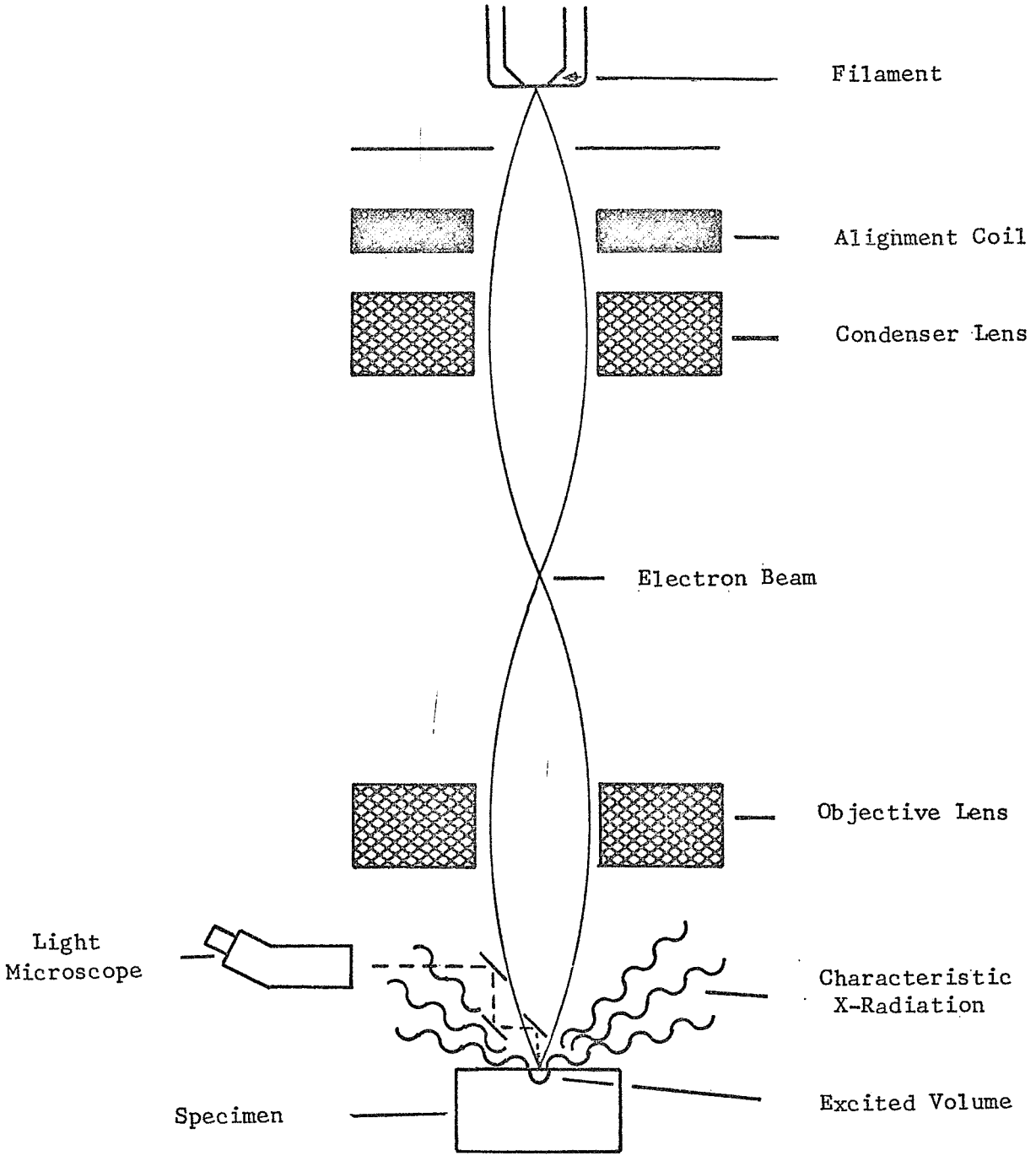

Figure 37 Schematic Showing the Electron Optics of the Electron Beam Microprobe.

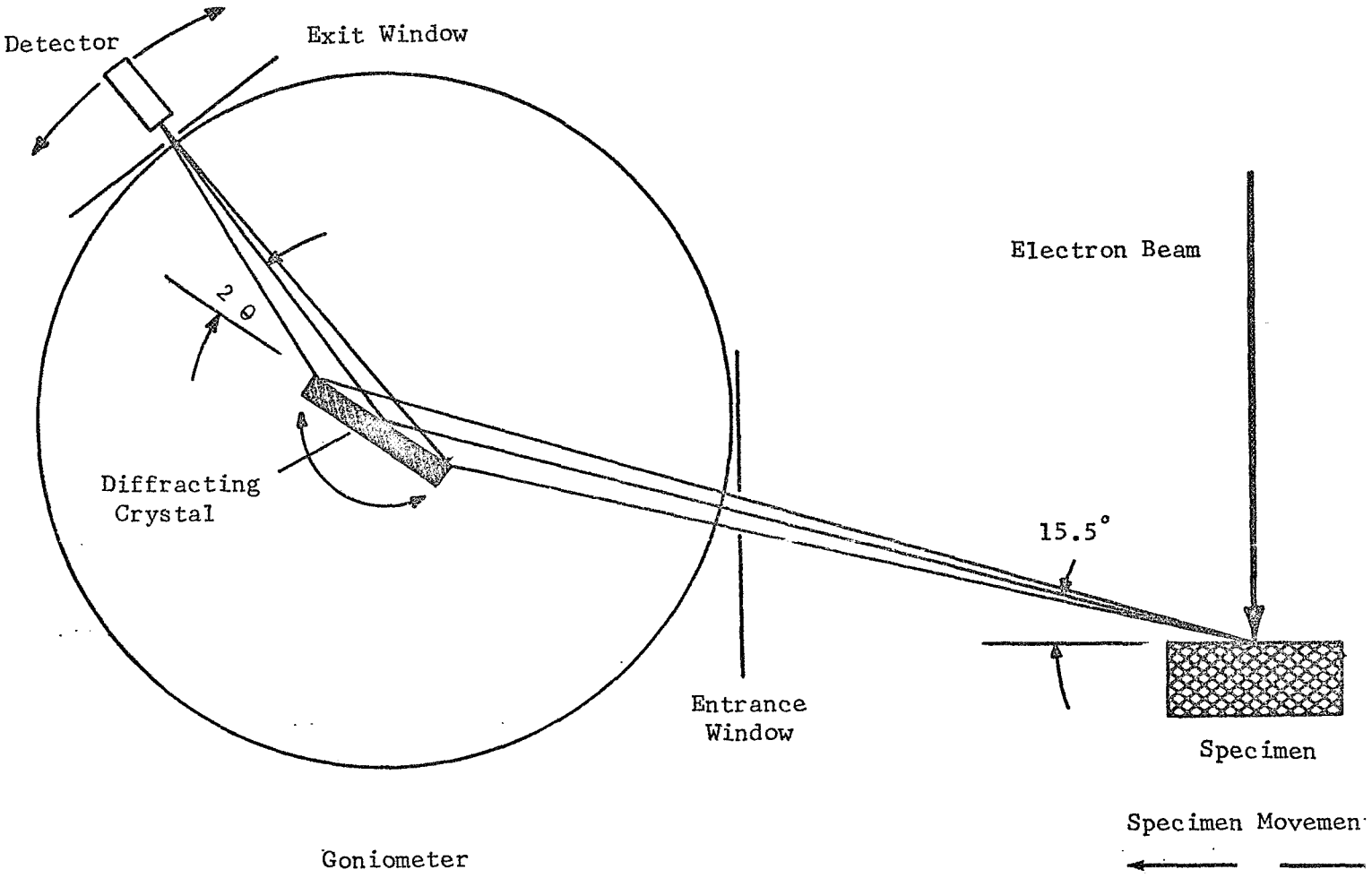

Figure 38 Schematic Showing the Mounting of the X-ray Detecting Goniometer on the Electron Beam Microprobe.

2. Surface Scan This mode of operation allows for the determination of variations in composition of a given element across a sample. With this mode, the goniometer is set at the specific 2θ angle required for this element and the sample is moved under the beam. Movement of the sample can be either in the X or Y direction, or a combination X-Y direction. A recorder is utilized to monitor the variation in element composition (X-ray intensity) as a function of distance across the sample.

3. Electron Beam Scanning With electron beam scanning, the electron beam is deflected in the X and Y directions along the sample surface. The deflection of the electron beam can be conducted in two ways: (a) in the X direction with the electron beam continually scanning along a given line on the sample surface; or (b) in both the X and Y directions in a manner similar to the movement of the electron beam across a television screen (raster). The mode of operation is illustrated in Figure 39.

   During electron beam scanning, the goniometer is set at the proper 2θ angle for the element to be analyzed. The X-ray intensity, through suitable electronic circuitry is displayed on an oxcilloscope screen. Through this type of operation, the concentration of a given element in a specific area can be determined.

   In addition to obtaining elemental analyses, an electronic display of the surface structure being scanned can be obtained. This display is obtained by either measuring the sample current at each X-Y point or measurement of the back-scattered electron current from each X-Y point. An approximate discrimination between elements can be made, since the higher the atomic number, the more the electrons are scattered back from the specimen surface. The more the electrons are scattered back from the surface the lower the sample current. Thus, depending upon the polarity of the sample and the monitoring mode, the brightest areas on the oscilloscope screen could indicate light elements and gradations down through grays into black would indicate heavier elements. Conversely, with the opposite polarity, the brightest areas would indicate heavy elements, and the dark or black areas would indicate either light elements or holes. Both the sample current and back-scattered electron current provide an electronic picture of the sample surface. The only difference is that with the same polarity one is the negative image of the other.

   Magnification of the sample area being viewed and analyzed can be obtained by reducing the X and Y axis of deflection of the electron beam while the screen area viewed on the oscilloscope remains constant. Magnifications from 400 up to 2400 times can be obtained by this method. Photographs of the images displayed on the oscilloscope screen can be obtained with a Polaroid camera fitted to the oscilloscope.

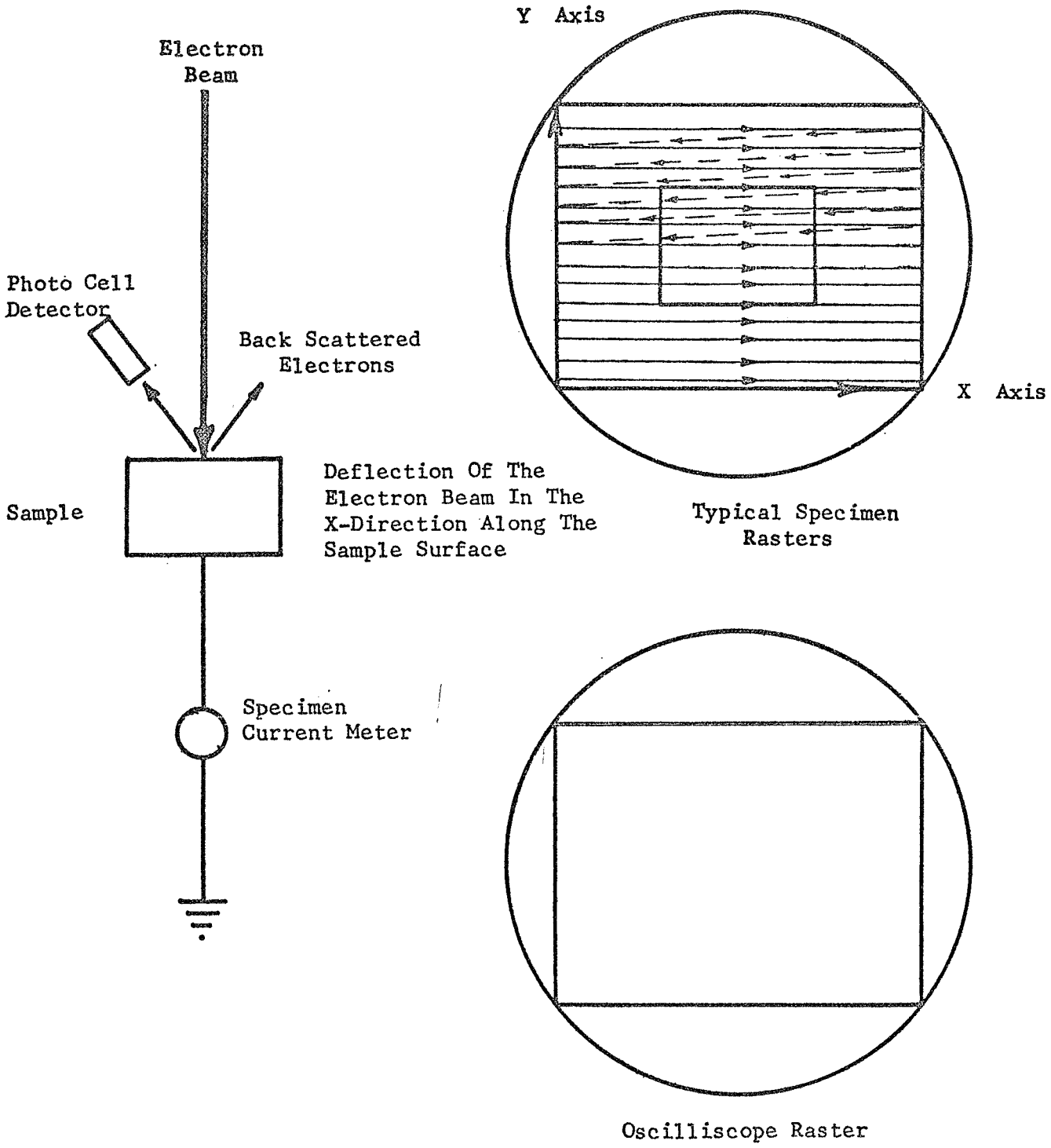

Figure 39 Schematic Showing the Electron Beam Scanning Mode of Electron Beam Microprobe Operation.

APPENDIX B

EQUIPMENT LABORATORIES MATERIALS TECHNOLOGY	TRW INC. 23555 EUCLID AVENUE · CLEVELAND, OHIO 44117 DEVELOPMENT PROCESS SPECIFICATION	TAP-DPS-1074 SHEET 1 OF 4 ISSUED 6-2-69 REVISED

APPLICATION OF THERMAL CONTROL COATING - IRON TITANATE (Fe_2TiO_5)

1.0 SCOPE:

1.1 This specification covers the equipment and the materials for the application of one type of thermal control coating.

2.0 APPLICABLE DOCUMENTS:

2.1 The following document provides information relevant to the ascribed thermal control coating.

2.1.1 Pratt & Whitney Aircraft Report PWA-3278, Final Report - Determination Of The Emissivity Of Materials, June 30, 1968 (Prepared for National Aeronautics & Space Adminstration - Contract NAS3-4174).

3.0 EQUIPMENT:

3.1 Dermitron Model D-2 Non-Destructive Thickness Tester

Vendor: Unit Process Assemblies, Inc., Woodside, New York

3.2 Plasma Flame Console & Power Supply Model F40

Vendor: Thermodynamics Inc., Lebanon, New Hampshire

3.3 Plasma Torch Metco 2M

Vendor: Metco Inc., Westbury Long Island, New York

3.4 Trinco Dry Blaster - Split Level Model Serial No. 2594-9

Vendor: Trinity Tool Co., Detroit,Michigan

3.5 Sylvester Powder Hopper - Serial No. 137

Vendor: Sylvester & Co., Cleveland, Ohio

4.0 MATERIALS:

4.1 Aluminum Oxide Grit No. 24, Bastite Grain

Vendor: Carborundum Company, Niagara Falls, New York

4.2 Gloves, Clean White Disposable (cotton or nylon)

Vendor: Various

4.3 Iron Titanate Powder (Fe_2TiO_5) - FCT-11H (-200, +325 mesh)
Vendor: Continental Coatings Corporation, Cleveland, Ohio

4.4 Vinyl Tape 3M No. 470
Vendor: Minnesota Mining & Manufacturing Co., St. Paul, Minnesota

5.0 SURFACE PREPARATION:

5.1 The substrate surface to be coated shall be thoroughly degreased in clean trichloroethylene.

5.2 During all subsequent processing the parts shall be handled with clean white disposable gloves. Under no circumstance shall parts be touched with bare hands or exposed to dirt or oil after completion of the degreasing operation. NOTE: If parts are inadvertently contacted by hands, oil, dirt, etc. -- repeat degreasing per Paragraph 5.1 and all subsequent processing operations.

5.3 All areas not to be coated shall be masked with 3M Vinyl Tape No. 470.

5.4 Dry blast all areas to be coated with clean filtered air and aluminum oxide grit No. 24 to a surface roughness of 80-125 RMS. NOTE: Do not re-use grit. Conventional air blast equipment can be used to perform this operation.

6.0 THERMAL CONTROL COATING APPLICATION:

6.1 Immediately after grit blasting, adequately fixture the part using trichloroethylene vapor degreased austenitic or austenitic-like material.

6.2 Apply, by plasma spraying, approximately 0.5 mil iron titanate (Fe_2TiO_5) coating on all substrate surfaces to be coated. This initial, thin coating layer serves as a contamination barrier for the substrate material.

6.3 Continue to apply sufficient coating until the thickness requirements of the applicable blueprint are satisfied.

6.4 Verify coating thickness using a Dermitron Model D-2 thickness tester and the standard test coupons established in Section 8.0.

6.5 Remove all masking materials.

6.6 The coated part shall be protected from contamination by sealing in 5 mil polyethylene(or equivalent) film.

7.0 PLASMA SPRAY EQUIPMENT PARAMETERS

7.1 The following processing parameters are recommended for the application of iron titanate (Fe_2TiO_5) coating per Paragraphs 6.0 - 6.4.

7.2 Plasma Flame Console and Power Supply Model F40.

7.2.1 Voltage - 32 v.

7.2.2 Amperage - 500 a.

7.2.3 Plasma gas - Argon at 60 C.F.H.

7.3 Plasma Torch Metco 2M.

7.3.1 Torch to work distance -- approximately 3"

7.3.2 Torch direction to work -- normal

7.4 Sylvester Powder Hopper - Serial No. 137

7.4.1 Hopper flow index - 18

7.4.2 Hopper gas - Argon at 15 C.F.H.

8.0 QUALITY CONTROL:

8.1 Dimensional:

8.1.1 A minimum of two flat test coupons (approximately 2" x 4" x thickness), representative of each alloy type and section thickness, shall be coated in accordance with the above procedure (Paragraphs 5.0 through 6.4).

8.1.2 Determine the coating thickness with a micrometer.

8.1.3 Obtain two coated coupons which represent the extremes of the allowable thickness range as specified by the applicable blueprint. These test coupons shall serve as thickness gage standards for the Dermitron non-destructive thickness tester.

8.1.4 Verify the applied coating thickness on all part areas.

8.2 Visual:

8.2.1 The coating shall be uniform, adherent, and free from defects and shall cover all surfaces of the part where specified. The color shall range from brownish-red to dark grey.

8.3 Adherence:

8.3.1 The coating shall remain adherent and not exhibit a flaking tendency when a sharp edge of a knife or chisel is impacted at the coating-substrate interface. A properly applied coating will exhibit a tendency to powder or crumble.

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Materials Application

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EQUIPMENT LABORATORIES Materials Technology	TRW INC. 23555 EUCLID AVENUE · CLEVELAND, OHIO 44117 PROCESS SPECIFICATION	TAP- PS-465 SHEET 1 OF 3 ISSUED 12-10-68 REVISED

APPLICATION OF THERMAL CONTROL COATING 92-007

1.0 SCOPE:

1.1 This specification covers materials, preparation of materials and application of one type of thermal control coating.

2.0 APPLICABLE DOCUMENTS:

2.1 The following documents provide information relevant to the ascribed thermal control coating.

2.1.1 Dow Corning Bulletin 08-226, Dow Corning 92-007 Thermal Control Coating, July 1966.

2.1.2 Dow Corning Bulletin 08-177, Dow Corning 1200 and 4094 Primers, September 1965.

2.1.3 Dow Corning Report No. #-369, Pigmenting Dow Corning 92-009, April 14, 1966.

2.1.4 Dow Corning Report No. E-237, Spraying Room Temperature Vulcanizing Silicone Rubbers, August 13, 1965.

3.0 MATERIALS:

3.1 Dow Corning 92-007 Thermal Control Coating, Dow Corning Corporation.

3.2 Dow Corning 1200 Primer, Dow Corning Corporation.

3.3 n-Heptane, Moisture Free, Reagent Grade, Diluent.

3.4 Toluene, Moisture Free, Reagent Grade, Diluent or Solvent.

3.5 Drierite (calcium sulphate pellets), or equivalent desiccant.

4.0 FORMULATION:

4.1 The Dow Corning 1200 Primer shall be applied in the as-received condition.

4.2 A typical batch formulation of Thermal Control Coating is comprised as follows:

Dow Corning 92-007	300 parts by weight
n-Heptane (diluent)	50 parts by weight
Toluene (diluent)	25 parts by weight

4.3 Certain precautions should be observed:

4.3.1 All materials should be kept free from moisture.

4.3.2 To insure moisture free diluent or solvent -- a drying compound, such as calcium sulphate, should be added in sufficient amount to cover the bottom of the storage container. A change of color of commercial drying compounds from blue to pink indicates water pick-up. Additional drying compound should be introduced into the solvent diluent until no further color change occurs over a 24 hour period.

4.3.3 All containers with primer and formulation ingredients should be kept closed when not in use.

4.3.4 Addition of diluents to the 92-007 coating material should be made without introducing moisture laden air. This can be accomplished by adding the diluents and rolling the mixture in a closed container or agitating in a paint shaker.

4.3.5 The storage life (in closed containers) of both the 92-007 coating and the 1200 primer is a maximum of six months from the date of manufacture when stored below 90°F.

5.0 SURFACE PREPARATION:

5.1 The substrate surface to be primed shall be thoroughly solvent cleaned with a soft cloth soaked in moisture-free toluene.

6.0 PRIME COAT APPLICATION:

6.1 Dow Corning 1200 Primer shall be applied within one hour after solvent cleaning.

6.2 The coating shall be applied evenly by spraying to a dry film thickness of approximately 0.3 mil.

6.3 The primer shall be allowed to air dry, preferably at room temperature (60-80°F) and 50% relative humidity for at least 30 minutes.

6.4 Primer 1200 is supplied in a flammable solvent and shall be applied in a well ventilated area. It should be kept away from heat, sparks and open flames.

7.0 THERMAL CONTROL COATING APPLICATION:

7.1 The 92-007 coating shall be evenly applied by spray application.

7.2 Conventional paint-spray equipment can be used to apply this material as formulated in Paragraph 4.2.

7.2.1 Typical application parameters are:

Spray gun distance from substrate surface	12-18 inches
Air gun pressure	60 psi
Spray passes over substrate	5-7
Thickness build up (dry) per pass	0.4-0.6 mil
Drying between passes	15 sec/mil
Final dry film thickness	3.0-4.5 mils

7.3 Spray coating should be adjusted so that at least 15 seconds drying shall take place between each 1 mil dry coating application.

7.4 The coated substrate may be handled 2-4 hours after coating, but a 5-day cure shall be allowed before exposing to space environmental conditions.

7.5 Thermal control coatings contain flammable solvents. Adequate ventilation should be provided away from heat and open flames. Avoid prolonged exposure to vapor, and prolonged or repeated skin contact.

7.6 The cured structure coating should be protected from contamination by sealing in 5 mil polyethylene (or equivalent) film.

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