NASA-CR-135055
NBSIR 76-1026

STUDIES OF NOBLE-METAL THERMOCOUPLE STABILITY AT HIGH TEMPERATURES

P. D. Freeze and D. B. Thomas

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Interagency Agreement
NASA Order No. C-67546-B, Modification 5

Issued July, 1976

U.S. Department of Commerce
National Bureau of Standards
Institute for Applied Technology
Washington, D. C. 20234

NOTICE

1. Report No.
NASA-CR-135055 NBSIR- 76-1026

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
STUDIES OF NOBLE-METAL THERMOCOUPLE STABILITY AT HIGH TEMPERATURES

5. Report Date
July 1976 (Published)

6. Performing Organization Code

7. Author(s)
P. Freeze and D. Thomas

8. Performing Organization Report No.
NBSIR 76-1026

9. Performing Organization Name and Address
U.S. Department of Commerce
National Bureau of Standards
Institute of Applied Technology
Washington, D.C. 20234

10. Work Unit No.

11. Contract or Grant No.
C-67546-B, Modification 5

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration,
Washington, D.C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes
Project Manager, I. Warshawsky, Technical Consultant, Instrument Development and Applications Office, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, and G. E. Glawe, Technical Monitor

16. Abstract

This report describes two investigatory studies on performance characteristics of noble-metal thermocouples: (1) thermoelectric stability as affected by preferential oxidation of iridium in the system iridium-40% rhodium versus iridium, and (2) the effects of temperature gradients on the emf stability of the systems platinum-13% rhodium versus platinum and iridium-40% rhodium versus iridium, operating in air.

The stability investigation was carried out at three temperatures — 1700, 1850, and 2000°C — by comparing the output of the test thermocouple in air with the output of an identically constructed reference thermocouple in nitrogen. The results show that no calibration shift was observed producing a change in output greater than that corresponding to a 2.0% change in the indicated temperature for all samples tested.

The investigation of gradient effects was carried out by subjecting test thermocouples to both severe and mild gradients for periods up to 200 hours. For the platinum system, the operating temperature was 1500°C with gradients of 1475 and 700°C/cm; for the iridium system, 2000°C with gradients of 700, 1500, and 1975°C/cm. Exposure to temperature gradients was found to introduce significant changes in calibration for both systems.

In both investigations, the thermoelements were examined by means of electron-probe analysis and by metallographic methods to detect chemical and structural changes. Data and micrographs are presented.

17. Key Words (Suggested by Author(s))
drift
high temperature
iridium-rhodium alloy
platinum-rhodium alloy
preferential oxidation
stability
temperature gradient
thermocouples

18. Distribution Statement
Unclassified-Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	57	$4.50

* For sale by the National Technical Information Service, Springfield, Virginia 22151

NASA-C-168 (Rev. 6-71)

TABLE OF CONTENTS

Acknowledgment

The work described was carried out at the National Bureau of Standards under the overall direction of J. Stern, Chief, Instrumentation Applications Section. The Section is a component of the Electronic Technology Division in the Institute of Applied Technology.

The sponsor Project Manager was I. Warshawsky, Chief, Instrument Research Branch , NASA Lewis Research Center. The sponsor Technical Monitor was G.E. Glawe.

STUDIES OF NOBLE-METAL THERMOCOUPLE STABILITY AT HIGH TEMPERATURES

SUMMARY

This report describes two investigatory studies on performance characteristics of noble-metal thermocouples: (1) thermoelectric stability as affected by preferential oxidation of iridium in the system iridium-40% rhodium versus iridium, and (2) the effects of temperature gradients on the performance of the systems platinum-13% rhodium versus platinum and iridium-40% rhodium versus iridium, operating in air.

Preferential Oxidation

The stability investigation was carried out at three temperatures — 1700, 1850, and 2000°C — by comparing the output of the test thermocouple in air with the output of an identically constructed reference thermocouple in nitrogen. All thermocouple reference junctions were maintained at 0°C. The test thermocouple and the reference thermocouple were mounted in test cells incorporated in a high-temperature furnace and designed so that the thermocouple hot junctions would be in an isothermal zone. The results show that no calibration shift was observed producing a change in output greater than that corresponding to a 2.0% change in the indicated temperature for all samples listed. The changes in calibration were found to be affected by test temperature, duration of exposure to elevated temperature, and thermoelement diameter.

Observations tended to confirm that changes in calibration result from preferential oxidation of the iridium component of the alloy element. The results of metallographic studies and qualitative chemical analyses of sample lengths from exposed and unexposed thermoelements tend to corroborate that this mechanism is responsible. Observations showed that the alloy elements experienced considerable grain growth after thermal exposure and became brittle. It should be noted that these studies also revealed the presence of silicon, which, acting as a contaminant, might have contributed in part to the observed changes in thermocouple calibration.

Gradient Effects

The investigation of gradient effects on thermocouple emf stability was carried out by subjecting test thermocouples to both severe and mild gradients for periods of up to 200 hours in an air atmosphere. For the severe-gradient test, platinum-13% rhodium versus platinum thermocouples were exposed to a gradient of 1475°C/cm with the measuring junction at 1500°C. A water-cooled thermocouple mount was used to achieve this gradient. For the mild-gradient test, thermocouples of the same system mounted in an insulating sleeve were exposed to a gradient of 700°C/cm, with the junction at 1500°C. The investigation was successfully extended to the higher junction temperature of 2000°C for the iridium-40% rhodium versus iridium thermocouple system, and thermocouples of this system were exposed to gradients of 1975, 1500, and 700°C/cm. Thermocouple reference junctions were maintained at 0°C.

A Nd:YAG laser was used for all tests as the heat source to raise the thermocouple junction temperature to either 1500 or 2000°C. Thermocouple wire sizes selected for test had diameters of 0.25, 0.51, and 0.81 mm. Thermocouple junctions were formed into either stirrup-type or wedge-type configurations, as appropriate.

Measurements indicate the effects of temperature gradients on thermocouple output are sizable, i.e., exceeding a change in output corresponding to a 2.0% change in the test temperature. The test results indicated that the calibration shifts observed after exposure were affected by junction configuration, wire diameter, and gradient.

Metallurgical and chemical tests were made on selected sample lengths from exposed and unexposed thermoelements. Significant changes were observed in the composition of the alloy elements of both thermocouple systems. These changes are of sufficient magnitude to account for the calibration changes measured, but further work is required to demonstrate a one-to-one correspondence between composition change and calibration shift.

1. INTRODUCTION

Noble-metal thermocouples used to measure temperatures of exhaust gases in advanced propulsion systems are subject to a number of effects resulting from the severity of the operating environment that tend to degrade thermocouple performance. Three such effects have been investigated at the request of and with sponsorship by the National Aeronautics and Space Administration Lewis Research Center. Two of these investigations (NASA Contract Order Number C-67546-B, Modification 5, September 26, 1972) are reported here: (1) thermoelectric stability as affected by preferential oxidation of iridium in the system iridium-40% rhodium versus iridium and (2) the effects of temperature gradients on the performance of the systems platinum-13% rhodium versus platinum and iridium-40% rhodium versus iridium, operating in air. (The third investigation concerned catalysis effects. [1]*)

The stability study was conducted in accordance with the following guidelines:

1. The thermocouple system to be studied is to consist of a positive component of 60% iridium, 40% rhodium paired with a negative component of iridium (iridium-40% rhodium versus iridium**).
2. A determination is to be made of the change in calibration of a thermocouple as a result of preferential oxidation of the iridium constituent in the alloy thermoelement (iridium-40% rhodium) as a result of exposure to long-term heating.
3. The tests are to be made at the highest temperature attainable up to 2000°C.
4. In order to maximize the ratio of surface area to cross-sectional area, the tests are to be conducted with thermocouple wires of the smallest practical diameter available with reliable calibration data.†
5. The test duration is to be 1000 hours of exposure to high temperature, or the time required for a calibration drift equal to the change in thermocouple output (thermal emf) corresponding to a 2.0% change in test temperature, or until failure of the sample.

The gradient study was conducted in accordance with specific guidelines, with modifications suggested by early work and agreed to by the sponsor. The guidelines as revised follow:

1. The thermocouple system to be used in gradient tests is to consist of a positive component of 87% platinum, 13% rhodium paired with a negative component of platinum (platinum-13%

---

* Figures in brackets refer to references in section 5.

** In this convention for identifying thermocouple systems, the positive element is given first.

† "Reliable" in the sense that composition is homogeneous along the length of the wire.

rhodium versus platinum) with the hot junction to be at 1500°C in air. If significant calibration changes are found, further tests are to be conducted with the system iridium-40% rhodium versus iridium in air with the hot junction at the highest temperature attainable up to 2000°C.

2. A comparison is to be made of the effect on thermocouple calibration of a severe temperature gradient to that of a mild temperature gradient, with the hot junction at the same temperature in both instances. The specified system is to be platinum-13% rhodium versus platinum.

3. Studies are to be made with thermocouples constructed from wires of the smallest diameter practicable, with an air atmosphere, and at a gas pressure of one atmosphere (10^5 Pa).

4. Test durations are to be 200 hours of exposure at 1500°C (or at 2000°C for the iridium-rhodium system), or the time required for a calibration drift equal to the change in thermocouple output corresponding to a 2.0% change in test temperature, or until failure of the sample.

The number of test samples used in both studies was limited. Analysis of the data yields results that may be used as guidelines for estimating the magnitude of the measurement errors that would occur with exposure of thermocouples composed of the systems used in these studies to conditions similar to the test conditions.

2. THERMOELECTRIC STABILITY OF THE IRIDIUM-40% RHODIUM VERSUS IRIDIUM THERMOCOUPLE

2.1 Background

Feussner in 1933 [2] proposed the use of iridium-rhodium versus iridium thermocouples "for very high temperature." Thermocouples of these materials appeared suitable for use at temperatures up to 2000°C, in oxidizing media. Several alloy combinations were later proposed by various experimenters for the positive component, with the greatest interest being shown in iridium-rhodium alloys containing 40, 50, and 60% rhodium. Thermal emfs of thermocouples made from wires of these compositions versus iridium do not differ widely as a function of temperature. The output of iridium-50% rhodium versus iridium is slightly greater than that of either iridium-40% rhodium or iridium-60% rhodium versus iridium. Carter [3] predicted that exposure to oxygen-rich gases at high temperatures would volatilize iridium preferentially from the iridium-rhodium alloy, which would become relatively richer in rhodium. A change in thermocouple emf results from the loss of iridium from the iridium-40% rhodium alloy and reaches a maximum when the composition becomes iridium-50% rhodium. Additional loss of iridium slightly decreases the thermocouple output, and thus the output of iridium-40% rhodium versus iridium remains more nearly in calibration for a longer time of exposure to high temperatures in the presence of oxygen than that of the other common thermocouple systems based on iridium-rhodium alloys. It is also expected that the high-temperature limit will be somewhat greater for the alloy containing more iridium because of its higher melting temperature.

There is little information available on the calibration drift of thermocouples of iridium-rhodium alloys versus iridium in oxidizing atmospheres. The studies of Rudnitshkii and Tyurin [4] reported changes in thermal emfs for the iridium-60% rhodium versus iridium system for an exposure of 10 hours at 1800°C. The total change did not exceed a change in output corresponding to a change of 0.8% in the measured temperature. Aleksalin et al [5] observed that "at 2000°C the iridium-60% rhodium versus iridium thermocouple allows us with sufficient accuracy to measure the temperature, at least briefly, for a period of 10-20 hours."

2.2 Summary of Test Method

The stability investigation was carried out at three temperatures — 1700, 1850, and 2000°C — by comparing the output of the test thermocouple in air with the output of an identically constructed reference thermocouple in nitrogen.

The thermocouple under test and the reference thermocouple were mounted in test cells incorporated in a high-temperature furnace in such a manner that both thermocouple hot junctions were in an isothermal zone. The design of the furnace was intended to provide a gas flow through the test cells sufficient to prevent any significant impurity concentration from developing around the test thermocouples. The nitrogen used was certified by the supplier to contain less than 2.0% oxygen by weight. The air was certified to contain a total hydrocarbon level of less than 0.5 ppm. The outputs of test and reference thermocouples were measured potentiometrically, and the calibration change (also referred to as "thermal emf drift") was calculated.

2.3 Apparatus

Figure 1 is an overall view of the stability-test apparatus. The cabinet on the left housed controls for the specially constructed furnace which contained the thermocouple test cells. A separate cabinet housed the furnace power supply and associated water-cooling system. The furnace itself was mounted in a supporting structure made from pipe. An oil-diffusion pump with cold trap and valve, which formed part of the vacuum system used to purge the furnace, was also supported by this structure. Two optical pyrometers used to measure furnace temperatures are shown swung away to reveal the upper and lower furnace ports. A precision potentiometer console together with a null-balance galvanometer were used to measure thermocouple emfs (outputs).

2.3.1 Furnace — The furnace is shown in cross section in figure 2. As shown in figure 1, the actual orientation of the furnace was vertical.

The furnace was electrically heated by a split tantalum tube element 10.2-cm in diameter and 80-cm long. This heating element and all other tantalum components were maintained in an atmosphere of helium to prevent oxidation.

The thermocouple test cells were positioned inside the heating element and were suspended through a removable top plate. Each cell was in the form of a zirconia tube, 80-cm long with an outer diameter of 2.5 cm. The tubes were closed at both ends, with removable plugs at the upper ends. A small zirconia gas-supply tube passed through a seal at the top of each cell and extended nearly to the bottom closure. Gas entering each cell through these tubes provided the means by which a controlled atmosphere was established within each cell. For clarity, the gas outlet tubes near the top of each cell are omitted in figure 2.

Positioned between the test cells along the center axis of the furnace and also suspended through the top plate was a control thermocouple well in the form of a tantalum tube, 80-cm long with an outer diameter of 1.3 cm. The bottom end was closed, and provisions for supplying helium were incorporated (not shown in figure 2).

A small tantalum tube (1.9-cm long, 4.8-mm outer diameter, 0.8-mm wall thickness) was mounted transversely through the well just above the bottom closure. This tube was closed at one end; the open end was aligned with a viewing port (sight window) in the furnace wall. In use, the tube served as a blackbody target for the lower optical pyrometer, which was mounted in line with the viewing port.

A second viewing port mounted in the furnace wall made it possible to observe a point on the tantalum well approximately halfway along its length. An optical pyrometer was mounted outside the furnace in line with this viewing port also. Both upper and lower optical pyrometers were arranged to swing aside to permit visual observation through the ports.

To reduce radiation heat losses, the tantalum heating element was surrounded by a shield assembly consisting of six spaced layers of tantalum sheet. This assembly was made in three parts: a cylindrical main shield and top and bottom shields.

All the furnace components were enclosed in a double-wall, cylindrical, stainless-steel pressure vessel, or chamber, with stainless-steel end plates. Water circulated between the walls provided cooling.

A vacuum system was used to purge the furnace chamber prior to gas fill. Major components of this system included a mechanical roughing pump, an oil diffusion pump, a liquid-nitrogen cold trap, and a high vacuum manifold and valve assembly.

Further construction details and a discussion of furnace design considerations are given in [6]. For the work described here, two rather than four test cells were used, although the furnace was designed to accommodate four.

2.3.2 Furnace Control Instrumentation — The furnace control system provided manual and automatic modes of operation. In the automatic mode, a proportional-control unit was capable of maintaining the temperature at the reference thermocouple junction to within ± 0.5% of the set temperature. At temperatures between 1700 and 2000°C, this degree of control established a 46-cm-long hot zone uniform in temperature to approximately ± 1%.

The control unit was an SCR type and supplied heating current to a combination Scott-connected and step-down transformer. The unit received its control signal from the control thermocouple and incorporated a device to limit the maximum current supplied to the furnace to a preselected value. Once this current value was reached during a run, the unit continued to supply it until the limiter was reset.

The tungsten-25% rhenium versus tungsten-3% rhenium control thermocouple output was recorded on a strip-chart recorder.

2.3.3 Potentiometer Assembly — Thermocouple potentials were measured with a five-decade precision potentiometer.* Measurements were taken with a least count of 1 μV. A provision was made to switch the emf of the test thermocouple, the reference thermocouple, or the control thermocouple to the potentiometer assembly or to the console strip-chart recorder.

2.3.4 Optical Pyrometers — Calibrated optical pyrometers were used to infer the zirconia test-cell temperatures at two stations (calibrating and test). Corrections were applied for transmission losses through each of the viewing-port windows. Measurements made at the upper port were corrected to allow for the spectral emittance of the outer surface of the tantalum reference thermocouple well. The measurement precision of these instruments varies with measurement range and depends in part on operator performance as well as on instrument capability. Experience has shown that the following are conservative values for a competent operator: 700 to 1100°C, ± 2°C; 1100 to 1500°C, ± 3°C; and 1500 to 2000°C, ± 5°C.

2.4 Test Thermocouple Materials

The wire from which the test thermocouples were constructed was provided by the selected manufacturer to a specification developed by the sponsor, the NBS, and the manufacturer in consultation. State-of-the-art procedures were to be used in producing three sizes of pure iridium wire for the negative components and of 60% iridium-40% rhodium alloy wire for the positive components. The wires were to be as free from mechanical and structural defects as possible, and the decision was made not to use doping.**

The three wire diameters selected were 0.25, 0.51, and 0.81 mm. To provide a maximized ratio of surface to cross-sectional area consistent with reliable calibration data, there was concern that thermocouples constructed from 0.25-mm-diameter wire might not survive the intended aging temperatures. Accordingly, the two larger sizes of wire were also used. The use of three wire diameters also offered the opportunity of detecting in the results any tendency for a functional dependence on wire size.

---

* The manufacturer's statement of uncertainty is ± (0.005% of reading + 0.1 μV) [low range] or ± (0.005% of reading + 0.3 μV) [middle range]. All measurements were taken in these two ranges.

** Doping refers to the addition of carefully chosen impurities in controlled amounts to the wire. It is often used to tailor thermocouple outputs so that existing, well-established tables of thermocouple emf-versus-temperature may be used. For the study reported here, the use of doped wire would have introduced an uncontrolled factor, as the thermoelectric-stability effects on such wires of the high temperatures used are not known.

Immediately before thermocouple fabrication, wires were immersed in a solution of soapy water and then rinsed in ethyl alcohol. The wires then were annealed for approximately one hour by heating them to a temperature 100°C above the intended aging temperature for the given thermocouple. The wires were heated by passing a current through them while they hung suspended in catenary form in the laboratory. The annealing temperature was monitored with an optical pyrometer. Following annealing, the wires were welded together in an oxygen-hydrogen flame to form thermocouple junctions.

2.5 Test Procedure

The test procedure may conveniently be described as a series of steps, as follows:

1. The zirconia test cells were heated in position in the furnace to 1600°C (measured by the control thermocouple in the well) to remove carbonaceous materials, and the furnace was then permitted to cool slowly* to room temperature. The outside walls of the cells were immersed in an atmosphere of helium, and the inside cell surfaces exposed to a positive flow of air. Prior to heating, the furnace chamber was first vacuum purged and then the helium supply for the chamber and for the control thermocouple well was turned on.

2. Reference and test thermocouples were then installed into the test cells in the "up", or calibrating, position with the junctions in line with the center of the upper viewing port (32 cm from the bottom of each cell).

3. Following another furnace purging, the gas flows for the test cells were turned on: nitrogen into the test cell with the reference thermocouple, and air into the other test cell. As before, helium was circulated through the furnace chamber and the control thermocouple well. The test cell flow rate was adjusted to be 1 cm^3/s.

4. The reference thermocouple (in nitrogen) and the test thermocouple (in air) were annealed in the furnace to minimize any effects on thermocouple output that might have resulted from cold working of the thermocouple wires during fabrication or installation. Annealing was accomplished by heating the furnace to the intended aging temperature for approximately 2 minutes and then permitting it to cool slowly to 1200°C.

5. Starting at 1200°C, measurements of the outputs of the thermocouples were taken at 200°C increments, with an upper limit of 1700°C, 1850°C, or 2000°C, depending on the intended aging temperature of the test. The average duration of a calibration over a temperature range of 1200 to 2000°C was approximately 4 to 5 hours. The data from these measurements were regarded as the base calibration for each thermocouple. The temperatures of the test cells were inferred from direct optical-pyrometer measurements of the outside wall of the reference thermocouple well. A curve was fitted to the base-calibration

---

*At a rate no greater than 400°C/hour.

data for the reference thermocouple; the equation of this curve permitted computation of tables of thermocouple output versus temperature for any desired temperature intervals over the temperature-measurement range. The procedure is described in detail in [7].

6. The reference and test thermocouples were slowly* moved to the "down", or aging, position with the junctions near the plane of the blackbody (1.5 cm from the bottom of each cell). [Both calibration and aging positions of the junctions were well within the isothermal hot zone of the furnace. The purpose of the deeper aging position compared to the calibration position was to ensure that when calibration measurements were made, those portions of thermocouple wires subject to temperature gradients during aging would be outside the furnace at room temperature and therefore not contributing to thermocouple output. As a result, measured changes in output following aging may be attributed to aging alone.]

7. The reference and test thermocouples were maintained at the selected aging temperature for a period originally intended to be about 16 hours, although various experimental difficulties tended to vary the duration of an aging period considerably. The temperature of the junctions was inferred from optical-pyrometer measurements of the blackbody temperature. Measurements of both thermocouple outputs were made at selected intervals.

8. The reference and test thermocouples were slowly** withdrawn from the aging position to the calibrating position. Since iridium and iridium-alloy wires are extremely fragile when at temperatures above 1700°C, great care was required to avoid jerking the wires, which were retracted and inserted manually. Also, any contact between the thermocouple wires and the zirconia tube at high temperatures resulted in instant destruction of the tube and samples. The wires were withdrawn at a rate that permitted them to cool to a few hundred degrees Celsius before emerging into the laboratory air.

9. Measurements of the reference and test thermocouple outputs were made and the calibration shifts were calculated in terms of an equivalent change in test temperature.

10. If the calibration shift was less than an equivalent 2.0% change in test temperature, steps 6 through 9 were repeated until a calibration shift greater than an equivalent 2.0% change in test temperature was detected or until failure of either the reference or the test thermocouple. If the calibration shift was greater than an equivalent 2.0% change in test temperature, the test was terminated.

---

* At a rate of approximately 2 cm/min.

** At a rate of approximately 1 cm/min.

2.6 Microstructural Examination and Chemical Analysis

The work reported here was carried out to test the hypothesis that high-temperature exposure of the iridium-40% rhodium versus iridium system to an oxidizing atmosphere would result in preferential loss of iridium by oxidation and thus a change in alloy composition. Accordingly, selected segments of various thermocouple wires were sectioned, polished, and etched using conventional metallurgical techniques. These specimens were then examined at magnifications from 80X to 1200X with a metallurgical microscope. Specimens were selected from wires of all three diameters, exposed at the three aging temperatures. In addition, specimens were taken from thermocouples exhibiting large changes in thermoelectric output, or obvious external changes in appearance, or both.

An electron microprobe was used to provide quantitative information about the alloy composition of, and the presence of contaminants in, selected areas of some of the specimens studied by microscope. The microprobe was calibrated using a specimen of iridium-40% rhodium alloy thermocouple wire as received from the wire manufacturer. Since the stability study was concerned with indicative changes, this spectrum was accepted as being 60% iridium, 40% rhodium according to the manufacturer's analysis, and thus the decision was made not to attempt a more precise measurement of composition by other techniques. Considerable difficulty was experienced by the operators of the microprobe at the time the thermocouple specimen composition measurements were made. Because of this difficulty, the microprobe results are reported to the nearest percent.

2.7 Results and Interpretation

2.7.1 Thermoelectric Observations — Table 1 presents a summary of the cumulative relative changes in thermoelectric emf with aging time at 1700°C in an oxidizing atmosphere (air) for an iridium-40% rhodium versus iridium thermocouple of 0.81-mm-diameter wire. The reference is the thermal emf of the similar reference thermocouple exposed to the same aging program in a nitrogen atmosphere. Results are given for six calibration temperatures from 1200 through 1700°C for up to 359 hours of aging.

The calibration of the reference thermocouple was relatively stable during the tests, changing by no more than 7 μV at 1700°C and by no more than 10 μV at either 1850 or 2000°C. As described in 2.4, the calibration temperature was measured with an optical pyrometer. In contrast, the test thermocouple emf increased during the first 116 hours of aging and decreased thereafter. Two calibration measurements were taken at 71.5 and 76.5 hours, but only at 1700°C, because of experimental difficulties. At 259 and 359 hours, calibration measurements were also made only at the aging temperature, again because of experimental difficulties. Figure 3, which is a graphic representation of the data in table 1, shows the plot of ΔE versus time at a calibration temperature of 1700°C. It is seen that ΔE rises to a maximum of about 73 μV (~14°C) at 116 hours and then decreases thereafter at the rate of 0.12 μV per hou (0.02°C per hour) to the end of the test at 359 hours. Examination following the test showed that both thermocouples had undergone structural changes which resulted in the wires becoming brittle. This embrittlement was the probable cause of the mechanical failures which occurred as the junctions were being repositioned.

The data from a single test have been presented in detail as being typical of the results of all the tests. The number of tests successfully conducted for each wire size and aging temperature is given in table 2.

Figure 4 consists of plots of relative change in thermal emf for three thermocouples of 0.81-mm-diameter wire as a function of aging time at 1850°C. The plots are for calibration at 1850°C as determined by the optical pyrometer. Relative change in thermal emf is defined as the difference between the thermal emfs of the test thermocouple in air and the reference thermocouple in nitrogen. In general, the thermal emfs of the reference thermocouples changed little, so that the change in the relative thermal emf may be considered to reflect the behavior of the test thermocouples. As shown, after the first 10 hours all three test thermocouples experienced greater changes in thermal emf than did the reference thermocouples. The observed changes in thermal emf corresponded to a change in the 1850°C aging temperature of less than 1.2%, before failure. The maximum spread in the three relative emfs occurred at 70 hours and was 33 μV, corresponding to 6.1°C. The average rate of drift during the first 70 hours was 0.2°C per hour.

Figure 5 is a plot of relative change in thermal emf of a single thermocouple of 0.51-mm-diameter wire as a function of aging time at the highest test temperature of 2000°C. The plot is of five calibrations made at 2000°C. Relative change in thermal emf has the same meaning as for figure 4. After about an hour at 2000°C, the test thermocouple experienced greater changes in thermal emf than did the reference thermocouple. The observed maximum relative thermal emf of 85 μV at 8 hours corresponded to a change in the 2000°C aging temperature of 15.7°C, or less than 0.8%. The rate of drift during 8 hours of heating was 2°C per hour, ten times higher than that for the 0.81-mm-dilameter wire at 1850°C. Failure occurred in the subsequent aging period.

Figure 6 consists of plots of changes in thermal emf of three thermocouples of the three different wire sizes as a function of aging time at 1850°C. The calibration temperature was also 1850°C. Failure occurred in the thermocouple made from the smallest wire first, at less than 10 hours. The thermocouple made from the largest wire lasted beyond 100 hours. These data, together with the results of other tests, indicate that thermocouples made from smaller-diameter wire have shorter lifetimes in high-temperature environments. There also is a tendency for such thermocouples to experience a higher rate of change of thermal emf compared to thermocouples made from larger wires. The rates of drift are 2.9, 1.7, and 0.2°C per hour, respectively, for the 0.25-, 0.51-, and 0.81-mm-diameter wires, for the aging times indicated.

Figure 7 consists of plots of changes in the thermal emfs of three thermocouples of 0.81-mm-diameter wire as a function of aging time at three temperatures. Each thermocouple was calibrated at its aging temperature. The changes in thermoelectric output occur at a greater rate and the lifetime is markedly reduced as the aging temperature increases from 1700 to 2000°C. The average drift rates were 0.1, 0.2, and 1.5°C per hour at temperatures of 1700, 1850, and 2000°C, respectively.

2.7.2 Microstructural and Chemical Studies — Two thermocouples of 0.81-mm-diameter wire, for which test results were presented in table 1, were among those chosen for microstructural examination and chemical analysis. As described, these thermocouples withstood 359 hours of exposure to an aging temperature of 1700°C, the longest exposure time for any set of thermocouples, prior to failure. Specimen lengths of wire were cut from each element of the two thermocouples for microstructural examination starting about 0.3 mm from each junction and extending to about 2.4 cm from the junction. Such samples are identified as "near junction". Adjacent to the junction of the thermocouple exposed to air, the alloy component showed evidences of oxidation and melting along the wire surface. About 7.5 cm from the junction, a reddish-brown coating was also observed on the surface of this component.

Figure 8 presents micrographs of the sectioned iridium-40% rhodium component of the test thermocouple. Photographs a, b, and c were taken with a magnification of 100X; d, at 1200X. The changes in structure appear greater than those experienced by the other components in either atmosphere and suggest the possibility that this alloy may have experienced a change in composition as well as structural deterioration. Photograph 8a shows a longitudinal section of the alloy wire microstructure in regions not exposed to any high temperature, for reference. Photograph 8b shows a longitudinal section of the alloy wire that was exposed to high temperatures in an air atmosphere. The microstructure reveals a grain-boundary phase and large, smooth-cornered grains, whose presence indicates that melting had occurred. Photograph 8c is a longitudinal section of the same wire about 2.4 cm from the thermocouple junction showing erosion of the surface and voids near the surface. Considerable grain growth is also shown. Photograph 8d is an enlargement of the grain-boundary phase in 8b.

Table 3 gives the results of composition analyses of the specimens shown in figure 8. The specimen shown in 8a was taken as a reference, with a composition of 60% iridium and 40% rhodium by weight.

The changes in composition of the alloy component in the nitrogen atmosphere were found to be negligible, and only a slight enlargement of grain size was observed. However, the alloy component in the oxidizing atmosphere changed considerably. The composition analyses of phases enclosed by the grain boundaries near the thermocouple junction of the sample heated in air, photographs 8b and 8d, showed no great change in composition except in the areas near the wire surface, where the iridium content dropped to about 20% and the rhodium content increased to 75%. In these regions the presence of a significant amount of silicon was detected. From the sample taken farther from the junction, shown in 8c, voids were observed near the surface. There was an accompanying enrichment of rhodium near the wire surface, which is consistent with the hypothesis that iridium had been oxidized and removed from the surface.

A possible source of silicon contamination was the magnesia-stabilized zirconia test cells. Spectrochemical analysis of the wire specimens revealed an estimated silicon content of 0.1 to 1.0% by weight. However, a greater concentration, approximately 5.0%, was found (by microprobe analysis) near the grain boundaries of wire samples closest to thermocouple junctions. The presence of silicon will result in the formation of a low-melting eutectic with either iridium or rhodium [8].

Figure 9 consists of four micrographs at a magnification of 80X of specimens that experienced some structural deterioration. These specimens are longitudinal sections, and the widths of the polished surfaces shown in the figures do not necessarily correspond to the product of the wire diameter and the magnification. Following exposure to high temperature, some specimens were found to be considerably deformed and enlarged, especially near the tip. Figure 9a is a photograph of an iridium specimen taken from a reference thermocouple aged for 88 hours at 1850°C in nitrogen; photograph 9b is of an iridium specimen taken from a test thermocouple aged for 88 hours at 1850°C in air; photograph 9c is of an alloy specimen from the reference thermocouple; and photograph 9d is of an alloy specimen from the test thermocouple. The wire diameter was 0.81 mm. Photograph 9a shows a very large grain size, which indicates that grain growth had occurred. A slight surface erosion of metal is evident near the tip of the sample, at the right. These factors could have contributed to a structural weakening of the wire. Photograph 9b shows larger grains at the tip than at the shank. Some surface erosion is also in evidence. Photograph 9c shows erosion of metal at the surface. This photograph also shows a grain-boundary second phase and fine precipitate throughout the structure. It is probable that the grain-boundary phase was a liquid contaminant or an oxygen-deficient oxide at the test temperature, and that the precipitate in the grains was a sub-oxide precipitated during cooling. This is suggested by the rounded appearance of the grain-boundary corners. The lighter coloration of the oxide phase indicates a lack of oxygen.

Photograph 9d shows considerable surface erosion, a second phase at the grain boundaries, and fine precipitate throughout the structure. It seems probable from the coloration of the oxide phase that the oxide liquid was less oxygen-deficient than that for the specimen shown in 9c.

The possibility also exists that the observed structural deterioration of specimens from the reference thermocouple resulted from contamination of the nitrogen atmosphere with oxygen. During the final cooling phase of the test, immediately prior to thermocouple failure, the test cells were subjected to severe thermal shock, resulting in cracks in the reference cell and permitting the entry of air. The precipitate areas found in the grain structure of the specimens from the reference thermocouple probably resulted from certain oxides that solidified during the rapid cooling which followed failure of the test cell.

Measurements of thermocouple output made after 88 hours of aging of these two thermocouples showed changes that were in reasonable agreement with those obtained with other thermocouples tested under like conditions.

Figure 10 consists of four micrographs at a magnification of 80X and illustrates changes in microstructure that may occur following exposure to a high-temperature oxidizing environment. Photograph 10a is of a specimen taken from an unheated portion of a thermocouple alloy component; photograph 10b is of a specimen taken from the same thermocouple component, but from a portion exposed to 2000°C, in air. Similarly, photograph 10c is of a specimen taken from an unheated portion of the iridium component of the same thermocouple, and photograph 10d is of a specimen taken from a portion of the same iridium component exposed to 2000°C, in air. The aged specimens were both taken from portions of wire from 2 to 4 cm from the junction. Wire diameter was 0.81 mm. Gross surface erosion is evidenced in 10b compared with 10a. Photograph 10b also shows a grain-boundary second phase and a fine precipitate throughout the structure.

To detect any changes in alloy composition, and specifically to determine if the phases shown in 10b were rhodium rich (as might have been expected if iridium had been depleted by oxidation), an electron microprobe traverse was carried out from the wire surface to the center. Along this distance of some 0.40 mm, measurements showed that the iridium concentration (by weight) had varied from 28% at the wire surface to 63% at the center. The corresponding change in the rhodium concentration varied from 61% to 36%.

Comparison of photographs 10c and 10d shows little effect on the iridium component from exposure to a high-temperature oxidizing atmosphere. There is an indication that a slight increase in grain size occurred, but as the specimens are from widely separated portions of the iridium wire, this conclusion remains tentative.

2.7.3 Interpretation of Combined Thermoelectric and Microstructural Results — Changes in thermocouple calibration observed following aging of thermocouples at temperatures of 1700, 1850, and 2000°C in an oxidizing atmosphere indicate some instability of the iridium-40% rhodium versus iridium thermocouple at these temperatures. The mechanism that has been proposed to account for these calibration shifts has been that of preferential oxidation of iridium in the alloy component. An initial loss of iridium would be expected to increase thermocouple output until the alloy component composition became about 50-50; any further loss of iridium would then decrease output, as the alloy became effectively more and more rhodium enriched. The direction of the observed thermoelectric changes is consonant with this hypothesis. No calibration shift was observed producing a change in output greater than that corresponding to a 2.0% change in test temperature. Unfortunately, no set of test and reference thermocouples withstood an aging time of more than 360 hours, and that performance was exceptional (the thermocouples involved were made from 0.81-mm-diameter wire; aging temperature was 1700°C). Premature mechanical failures of thermocouples suggested that the wires were embrittled because of structural changes such as grain growth and the formation of new phases and boundaries. Subsequent microstructural examination of related specimens verified that, in some tests, such changes had in fact taken place. Microchemical analysis by means of an electron microprobe was also carried out for some specimens. The resulting composition data suggest that the preferential-oxidation hypothesis may be correct, but are not conclusive.

2.8 Stability Test Conclusions

The following conclusions, based on results with the limited number of thermocouples tested, are presented for the stability investigation for the iridium-40% rhodium versus iridium thermocouple system in a high-temperature oxidizing environment.

1. No calibration shift was observed producing a change in output greater than that corresponding to a 2.0% change in temperature during the lifetime of the thermocouple.

2. Calibration changes and thermocouple lifetime appear to be functionally dependent on aging temperature, aging time, and wire size. The rate of calibration change is seen to be strongly dependent on aging temperature: a higher temperature corresponds to a greater rate.

3. Under the test conditions, no test thermocouple pair had a lifetime exceeding 360 hours.

4. Observed calibration shifts and structural and chemical changes are consonant with the preferential-oxidation hypothesis.

5. The structural changes observed included marked grain growth which may account for the considerable degree of embrittlement that occurred.

3. GRADIENT STUDIES

3.1 Background

A number of practical measurement applications, such as the measurement of gas temperatures in aircraft turbines, require that the transducer sensing element be exposed to thermal gradients of up to several thousand degrees Celsius per centimeter. The thermally generated potential, or output, developed by a thermocouple constructed from homogeneous components is in principle a function of the thermocouple materials and of the junction temperature. However, inhomogeneities along thermocouple wires may be developed, for example, by cold working that may occur in the course of fabrication and in normal use, both in the laboratory and elsewhere. The thermal emf, or output, generated by a thermocouple with inhomogeneous components depends not only on the component materials and the junction temperature, but also on any temperature gradients that may exist along the wires. Effects that may be negligible as a result of the presence of mild gradients may become appreciable for severe gradients and seriously limit measurement accuracy. The purpose of the work reported here was to explore the effects of gradients on the emf stability of selected thermocouple systems from 700°C/cm to nearly 2000°C/cm, with junction temperatures up to 2000°C.

3.2 Summary of Test Method

Test thermocouples were fabricated in either stirrup or wedge configuration, as shown in figure 13. Thermocouples of the system platinum-13% rhodium versus platinum were prepared for tests with gradients of 700 and 1475°C/cm, with a junction temperature of 1500°C. For tests extending the gradient severity to nearly 2000°C/cm, another thermocouple system was required. Thermocouples of iridium-40% rhodium versus iridium were prepared for tests with gradients of 700, 1500, and 1975°C/cm, with a junction temperature of 2000°C. To investigate effects of wire size, thermocouples of platinum-13% rhodium versus platinum were fabricated from wires 0.25, 0.51, and 0.81 mm in diameter. Iridium-40% rhodium versus iridium thermocouples were all made from 0.51-mm-diameter wire.

The test thermocouple was mounted in a test chamber open to the laboratory atmosphere. A continuous infrared laser beam was focused onto the thermocouple junction, and the resulting gradient could be controlled by adjusting the distance between the water-cooled mount and the junction and by regulating the cooling-water flow through the mount. Thermocouple temperatures were measured with a calibrated optical pyrometer, and the thermocouple emf was measured with a precision potentiometer assembly. The number of tests successfully conducted for each thermocouple system, wire size, gradient, and configuration is given in table 4.

3.3 Apparatus

Figure 11 is an overall view of the gradient-test apparatus. The cabinet on the left constituted the precision potentiometer console that was used to measure test thermocouple emfs and, indirectly, temperatures in the test chamber by means of the optical pyrometer. An interference filter prevented reflected laser radiation from entering the pyrometer. The test thermocouple junction was mounted in the test chamber and positioned to be at the focus of the laser beam by means of an x-y translation stage. The beam from the 60-W, continuous, Nd:YAG laser was focused by a glass lens mounted in a tube. Dual laser controls were mounted in a small console; a separate cabinet housed the laser power supply and cooling system.

3.3.1 Test Chamber — The test chamber is shown in cross section in figure 12. The chamber, constructed of brass, was double walled, with provisions for cooling water to flow between the walls. Overall, the chamber was 5 cm in diameter and 20 cm in height. The support for the chamber also carried an x-y translation stage with micrometer adjustments. Both horizontal and vertical adjustments were provided to position the test-thermocouple junction into the focused laser beam. The beam was focused by a lens mounted in a two-piece tube that was supported at one end by the chamber and at the other end by the laser head. The test thermocouple was mounted in an aluminum oxide insulator, and the insulator mounted in what is identified in figure 12 as the "thermocouple probe".* The mount was water cooled. The lower ends of both the brass mount and the aluminum oxide insulator are shown in cross section in figure 13. Ports in the chamber gave optical access to the mounted junction for the focused laser beam and for the optical pyrometer.

The test chamber was vented at top and bottom so that laboratory air could flow freely into and out of the chamber. During tests, convective flow was established which ensured that a continuous supply of fresh air surrounded the junction and wires.

3.3.2 Laser Heat Source — The test-thermocouple junction was heated by the focused beam of an infrared (wavelength of 1.065 μm) Nd:YAG continuous laser with a maximum beam power of 60 W. Major components of the laser system included the laser head, with lamps, elliptical cavity, and laser rod; an optical bench to support the head; a dual laser control station; lamp power supplies; and water-cooling equipment.

---

*The design of the mount simulates that of thermocouple probes used with aircraft propulsion systems.

3.3.3 Optical Pyrometer Measurements — The thermocouple junction temperature was measured with an optical pyrometer. The measuring scale of the instrument was not used. Instead, to improve the precision of the pyrometer for temperatures up to 2000°C, the pyrometer was calibrated and used on a basis of temperature versus pyrometer filament current. A 2.0-Ω rheostat was connected in series with the pyrometer slide wire to provide a more sensitive means of setting filament current. The filament current was measured by using a standard resistor with a nominal value of 1 Ω and a precision potentiometer assembly.* Measurements were taken with a least count of 1 μV. Appropriate corrections were applied to the optical pyrometer measurements to compensate for the spectral emittance of the thermocouple materials, for window transmission losses, and for transmission losses imposed by the interference filter. The spectral emittance values used for the thermocouple materials were obtained from [9]. Although the actual spectral emittances of the thermocouple materials during testing may have deviated slightly from the reference [9] values (due to alloy composition changes or surface structure changes), these deviations were probably quite small. Also, no oxide or contamination coatings were observed on the thermocouple junctions during or after testing.

3.3.4 Thermocouple EMF Measurements — Thermocouple emfs were measured using the precision potentiometer assembly. A mechanical switch permitted either the thermocouple output or the pyrometer current to be selected for measurement.

3.4 Test Thermocouple Materials

The wire from which the test thermocouples were constructed was obtained from a commercial manufacturer. The thermocouple system first used was platinum-13% rhodium versus platinum. The sponsor had stipulated thermocouple construction from wires of the smallest "practicable" size. As with the stability study, there was concern that thermocouples fabricated from very small wires might not survive the tests, and therefore the same selection of wire diameters was made. Accordingly, thermocouples were fabricated in either stirrup or wedge type (as shown in figure 13) from wire with diameters of 0.25, 0.51, and 0.81 mm. Fabrication procedures were those described in 2.4. The use of three wire diameters offered the opportunity of detecting in the results any tendency for a functional dependence on wire size. The two thermocouple configurations are typical of those used in practical applications**, and their incorporation in the test program was intended to detect any marked performance advantage one design had over the other when subject to gradients of 700 to 1975°C/cm.

Since early test results revealed that significant calibration changes were occurring, the range of gradients tested was extended to nearly 2000°C/cm

---

* The manufacturer's statement of uncertainty is ± (0.01% of reading + 0.2 μV) [low range] or ± (0.01% of reading + 2.0 μV) [middle range]. All measurements were taken in these two ranges.

** The stirrup type provides improved heat transfer from the surrounding gas to the junction, compared to the wedge type; the wedge type provides greater mechanical strength in a high-velocity stream.

with thermocouples of iridium-40% rhodium versus iridium, as the sponsor had requested. For this work, only one wire size was to be used. Experience in the stability study had shown that 0.25-mm-diameter wires had a short lifetime as components of thermocouples subjected to 2000°C. Therefore, the choice was made to use 0.51-mm-diameter wire for the extended tests. A slight modification of both stirrup and wedge thermocouple configurations was required to permit a 2000°C junction to be achieved. A tapered hole was ultrasonically machined into the welded junction through the center of the bead until the diameter of the hole at the surface reached 0.4 mm. Depending on the exact form of the junction, the hole penetrated about two thirds of the way through it. Such holes are indicated by the small irregular circles in the junctions in figure 13. Multiple reflections of the focused laser beam in the hole increased the energy transfer from the beam to the junction. Other than the machining of the hole, fabrication procedures were the same as those described in 2.4.

Before testing, all thermocouples were annealed in air to improve calibration stability with heating. Platinum-13% rhodium versus platinum thermocouples were heated to 1450°C for one hour, and allowed to cool; iridium-40% rhodium versus iridium thermocouples were heated to 2100°C for two minutes, and allowed to cool.

3.5 Test Procedure

As with the stability study, the test procedure may conveniently be described as a series of steps, as follows:

1. The test thermocouple was mounted in an aluminum oxide insulator.
2. The insulator was installed in the water-cooled mount for all tests except those for intended gradients of 700°C/cm. The junction was adjusted to project approximately 1 cm beyond the lower end of the mount.

   An additional control parameter for setting gradients was cooling water flow through the mount. For tests with intended gradients of 700°C/cm, the insulator was installed in a mount that had no water-cooling. The thermocouple junction was adjusted to extend approximately 2.5 cm beyond the lower end of the insulator.

   For all gradients, the exact distance was determined by trial and error for each combination of junction temperature and wire diameter.
3. The mounted test thermocouple was installed into the test chamber in such a manner that the plane of the wires was perpendicular to the laser-beam path. If the thermocouple junction had a conical hole, the thermocouple was oriented so that the hole faced the laser.
4. A check was made to ensure that the tube enclosing the laser-beam path was in place and that the interference filter was also in place.
5. The laser was turned on at a low power setting, and the focused beam spot observed through the optical pyrometer. The spot size was on the order of a few tenths of a millimeter in diameter.

6. Vertical and horizontal adjustments were made to bring the center of the thermocouple junction into the focused beam. If the conical hole was present in the junction, fine adjustments were made to bring the beam into the hole.* [No lens focusing was ordinarily necessary. The initial focus adjustment was made on a trial-and-error basis.]

7. The laser-beam power was adjusted to bring the junction temperature to either 1500 or 2000°C (depending on the test) as determined by the optical pyrometer.

8. At a convenient distance from the junction, the temperature (T-low) of the wire was measured with the optical pyrometer, and the gradient computed. If the desired gradient had not been achieved, adjustments were necessary. After each adjustment, the junction temperature and T-low were measured and the gradient computed. This procedure was iterated until the desired gradient was achieved within ± 10°C/cm for gradients of 700°, 1475, and 1500°C/cm, and within ± 15°C/cm for a gradient of 1975°C/cm. For intended gradients other than 700°C/cm, adjusting the cooling-water flow through the mount provided a means for achieving the desired gradient. If the adjustment required was greater than that provided by the cooling-water flow or for gradients of 700°C/cm, the thermocouple had to be remounted with either a greater or a lesser projection of the junction beyond the mount, and steps 3 through 8 repeated.

9. Thermocouple emf was monitored to determine when the thermocouple achieved thermal stability. An optical-pyrometer measurement of junction temperature was taken to provide an initial calibration for the thermocouple.

10. Measurements of junction temperature were taken at intervals of time and adjustments in laser power made if needed. In some tests, particularly those with a junction temperature of 2000°C and with gradients of 1975°C/cm, the junction bead was partially eroded. In other tests, heating of the junction resulted in a bending of the thermocouple wires with a consequent displacement of the junction. These changes usually required either vertical or horizontal adjustment of the junction position, or both.

11. The operations of step 8 were repeated, except that no adjustment was made of the thermocouple projection beyond the mount. Once a test was underway, this adjustment would have terminated the test. Tests with gradients of 700°C/cm, with no water-cooling adjustment available, tended to be less sensitive to projection distance than tests with more severe gradients, and therefore the gradient tended to remain within the given limits.

If the change in thermocouple emf corresponded to an equivalent change in junction temperature of less than 2.0%, the test continued with iterations of steps 10 and 11. If the change in emf was equal to or greater than an equiva-

---

*In some instances it was necessary to focus the beam on the side of the conical surface to achieve a temperature of 2000°C.

2.0% change in junction temperature, the test was terminated, as specified by the sponsor. The test was also terminated after 200 hours of thermocouple exposure to heating or by thermocouple failure. The heating periods for the test thermocouples were not continuous (that is, not longer than a seven-hour period) because of restrictions imposed by laser operation.

3.6 Surface and Microstructural Examination and Chemical Analysis

Mechanisms judged likely to account for calibration changes in the thermocouples tested in this work include gross mechanical damage, resulting from exfoliation of surface layers and from hot-gas erosion; microstructural changes, such as the formation of new phases and boundaries; and chemical changes in alloy-component composition or micro-composition.

Three types of examination and analysis were suggested by these possibilities: (1) Selected thermocouple junctions, with a few centimeters of component wire attached, were examined under a low-power microscope, with magnifications on the order of 10 to 15X. (2) Specimens were prepared from some junctions and wires whose external appearance or condition suggested the possibility of internal changes. These specimens were sectioned, polished, and etched using conventional metallurgical techniques and then examined in a metallurgical microscope at intermediate magnifications on the order of 100X. (3) As with the stability study, an electron microprobe was used to provide quantitative information about alloy composition and the presence of contaminants for selected areas of some of the specimens studied by microscope. The remarks given in 2.6 concerning the calibration of the microprobe instrument apply here also, except that comparative measurements were possible to 0.1%.

3.7 Results and Interpretation

3.7.1 Thermoelectric Observations — Table 5 presents a summary of the cumulative changes in thermoelectric output with exposure to a junction temperature of 1500°C and to either a "mild" gradient of 700°C/cm or to a "severe" gradient of 1475°C/cm in an oxidizing atmosphere (air) for eight platinum-13% rhodium versus platinum thermocouples made from wire diameters of 0.25, 0.51, and 0.81 mm. Four thermocouple junctions were of the stirrup configuration, and four were of the wedge configuration. The data show that two of the thermocouples experienced emf changes corresponding to more than an equivalent 2.0% change in the junction temperature.

Figure 14 presents a comparison between the test performance of two platinum-13% rhodium versus platinum thermocouples, one stirrup, one wedge, alike in all respects other than junction configuration. The test conditions were a junction temperature of 1500°C and a gradient of 1475°C/cm; wire size was 0.51 mm. The plots are typical of the results in that the wedge thermocouple experienced a continuous decrease in thermoelectric emf at an average rate of 0.5°C per hour (corresponding to an equivalent 1.8% change in the junction temperature after 52 hours), while the emf of the stirrup thermocouple decreased about 0.2°C per hour for the first 50 hours, and then decreased rapidly at about 2.4°C per hour for the next 10 hours. At 60 hours, the emf had changed by the equivalent of 2.0% of the temperature.

The larger emf instability exhibited by the wedge thermocouple, compared to that of the stirrup thermocouple, may have resulted from dissimilar temperature profiles along the wires for the two configurations.* Because of the effects of convective heating, the temperature gradient was probably more severe near the water-cooled region of the wedge thermocouple as compared to the respective gradient for the stirrup thermocouple. Following the test, impurities and volatilized materials were observed on the thermocouple wires at distances of approximately 0.7 to 1.0 cm from the measuring junction of both thermocouple configurations. The presence of these contaminants may have contributed to the greater emf instability in the wedge thermocouple, since the gradient along the contaminated portion of this thermocouple was more severe than the gradient along the contaminated portion of the stirrup thermocouple. Small fluctuations, such as are shown in figure 14, may have resulted from thermocouple instabilities as well as from experimental error.

Table 6 presents the test results from three platinum-13% rhodium versus platinum thermocouples of different wire sizes exposed to a junction temperature of 1500°C and a gradient of 1475°C/cm in an oxidizing atmosphere (air). Each thermocouple was of the stirrup configuration. The emf of the thermocouple of 0.81-mm-diameter wire did not show fluctuations of more than the equivalent of a change of 6.8°C after 200 hours of heating, except for two deviations corresponding to changes of 11.3 and 8.6°C at 25 and 30 hours, respectively. The thermocouple of 0.51-mm-diameter wire showed no major emf drift for the first 50 hours, but then showed a change corresponding to 31.2°C after 60 hours of heating. The thermocouple of 0.25-mm-diameter wire showed a drift of 0.8°C per hour until failure after 34 hours. The net emf change at 34 hours was equivalent to 26.2°C. For both junction configurations, the emfs of thermocouples fabricated from smaller wires consistently changed more rapidly than the emfs of thermocouples fabricated from larger wires.

Figure 15 presents plots of the test performance of four iridium-40% rhodium versus iridium thermocouples fabricated from 0.51-mm-diameter wire and exposed to a junction temperature of 2000°C and to gradients of 700°C/cm (two thermocouples), 1500°C/cm (one thermocouple), and 1975°C/cm (one thermocouple).

One of the thermocouples (A) exposed to the gradient of 700°C/cm behaved in a peculiar manner not typical of others. This thermocouple experienced a nearly steady decrease in thermoelectric output, with the thermoelectric emf decreasing sharply before failure, which occurred at the junction center. The other three thermocouples showed behavior similar to each other. During the first few hours of the test, the emfs of these thermocouples increased relative to the initial calibration. Then some fluctuation in output occurred around a more-or-less stable value significantly above the initial calibration; and finally the emfs decreased to below the initial calibration value until failure occurred.

3.7.2 Surface, Microstructural, and Chemical Studies — Figure 16 presents photographs at a magnification of 15X of the two thermocouples of figure 14.

---

*The gradient was intended to be the same for both configurations. The average gradient calculated from the measuring junction to the water-cooled region was in fact the same for the two configurations within the limits of experimental error; however, the rate-of-change of gradient along the wires differed for the two configurations.

The wedge-type thermocouple experienced more severe crystallization changes, as evidenced by the recrystallization along the wires leading from the junction, although some recrystallization may be detected on the stirrup wires also. The greater changes in crystalline structure may contribute to the less stable thermoelectric behavior of the wedge configuration.

Figures 17 and 18 present micrographs (at 90X) of specimens taken from the alloy component (figure 17) and the platinum component (figure 18) of a platinum-13% rhodium versus platinum thermocouple exposed to a junction temperature of 1500°C and a gradient of 1475°C/cm. Wire diameter was 0.51 mm. The exposure time before failure was 60 hours. The emf values of this thermocouple are given in table 6. In each figure, photograph a shows a section taken 1.0 cm from the junction; b, 0.5 cm from the junction; and c, 0.05 cm from the junction. The temperatures at these points along the wires may be estimated to be 25, 760, and 1425°C, respectively, asssuming a somewhat linear gradient. The photographs of the specimens closest to the junction show marked grain growth compared to the grain size in cooler areas. There is no evidence of severe surface erosion.

The alloy component of this thermocouple was appropriately sectioned and analyzed with an electron microprobe to determine if composition changes had taken place. Table 7 gives the results of two traverses, one longitudinally along the wire extending from the junction bead to approximately 2.5 mm away, the other, within a few micrometers of the bead across a radius starting at the wire surface and moving toward the wire center, with one point at the opposite surface for comparison. Also shown in table 7 are two surface composition measurements made at the same time from an untested thermocouple. Significant changes occurred in the composition of the alloy component, with an effective platinum enrichment. The radial traverse showed a continuous decrease in rhodium content from the wire center to the wire surface, although the low concentration of 7.5% rhodium measured at one surface (at the start of the traverse) was not repeated at the opposite surface (9.5%). Both values represent a large change from the 12.6% rhodium content measured in the untested wire.

At times during the tests described in 3.7.1 and figure 15 with iridium-40% rhodium versus iridium thermocouples, a considerable amount of dark smoke was observed. Probably the smoke was evidence of significant iridium volatilization. If iridium were continuously lost from the alloy component, the thermocouple output might be expected to increase initially, stabilize for a short period, and then decrease to below its initial value, according to the preferential-oxidation hypothesis discussed in connection with the stability study. The thermoelectric emf changes shown in figure 15 for three thermocouples were, in general, consonant with the predicted behavior. Failure for these thermocouples occurred in the iridium component, close to the junction. Figure 19 presents four photographs at a magnification of 12X of the components of two of these thermocouples, one exposed to a gradient of 700°C/cm, the other, to a gradient of 1975°C/cm. The junction temperature was 2000°C. All photographs show that the wires had been severely eroded near the junction. The photographs also show that cooler portions of the wire were covered with a dark, spiny deposit. Analysis of this deposit showed that its major constituent was iridium, with traces of less than 1% of rhodium, copper, aluminum, and zinc.

3.8 Gradient Test Conclusions

The following conclusions, based on results with the limited number of thermocouples tested, are presented for the investigation of the effects of selected thermal gradients on thermocouple performance in an oxidizing atmosphere for two thermocouple systems: platinum-13% rhodium versus platinum, and iridium-40% rhodium versus iridium.

1. The maximum calibration shifts of some of the test thermocouples were greater than a corresponding change in the test temperature of 2.0%.

2. Calibration changes and thermocouple lifetime appear to be functionally dependent on wire size, junction temperature, and, to a lesser extent, gradient severity. Thermocouples fabricated from larger wires tend to change less and to have longer lifetimes compared to thermocouples fabricated from smaller wires.

3. Thermocouples with stirrup configuration tended to be more stable with exposure to a specific gradient than those with wedge configuration; however, there was no significant difference in lifetime.

4. Observed thermoelectric changes in thermocouples of the system iridium-40% rhodium versus iridium are consonant with the preferential-oxidation hypothesis.

5. Significant structural and chemical changes were observed near the junction of platinum-13% rhodium versus platinum thermocouples. Measured rhodium depletion amounted to as much as 40% at one site of one specimen (from 12.6% by weight to 7.5%).

4. REMARKS AND RECOMMENDATIONS

Inherent and severe problems exist in noble-metal thermocouple applications involving exposure of junction and component wires to high-temperature oxidizing environments. In particular, for iridium-40% rhodium versus iridium thermocouples, these problems include lack of thermoelectric stability, loss of mechanical strength as embrittlement occurs, and short lifetime at high temperatures and with severe gradients present along wires.

Some of these deleterious effects may be counteracted by operational procedures which minimize thermocouple exposure to adverse environments, but a more satisfactory solution is required, especially for the expanding field of hot-gas measurements.

Two lines of attack are proposed for future work.

1. Protective coatings offer a means for shielding thermocouple junctions and wires from chemical attack, such as preferential oxidation, and from mechanical erosion. Performance criteria for coatings need to be developed, including conceptual methods of test. Experimental work would include

test-method development and evaluation of the effectiveness of specific coatings.

2. A thermocouple system having only pure-element (unalloyed) components would not be subject to thermoelectric instability because of preferential volatilization or oxidation. Work is required to investigate new thermocouple systems with pure-element components or with alloy components that are oxidation resistant at high temperatures.

The gradient study has also revealed the presence of serious problems for thermocouples of the systems studied in applications involving exposure in oxidizing atmospheres to thermal gradients of the order developed in the tests. The tests indicate the presence of large structural and compositional changes, but correlations between these changes and the emf stability of the thermocouples have not been demonstrated. The following further work is recommended:

3. Continue tests with enough thermocouples for each system, wire size, and configuration to provide data for reasonable statistical evaluation.

4. Extend tests to include a non-oxidizing atmosphere to eliminate changes resulting from preferential oxidation. Other test atmospheres may also be of interest with respect to specific thermocouple applications.

5. REFERENCES

[1] Freeze, P.D., Thomas, D.B., Edelman, S., and Stern, J., Study of Performance Characteristics of Noble Metal Thermocouple Materials to 2000°C, NASA-CR-120990 (August 1972).

[2] Feussner, O., New Noble Metal Thermoelements for Very High Temperatures, *Elektrotech. Z.* 54, pp. 155-156 (February 1933) [in German].

[3] Carter, F.E., Discussion concerning paper: The Tungsten-Iridium Thermocouple for Very High Temperatures by W.C. Troy and G. Stevens, *Trans. Am. Soc. Metals* 42, pp. 1151-1152 (1950).

[4] Rudnitshkii, A.A., and Tyurin, I.I., New Alloys for High Temperature Thermocouples, trans. from U.S.S.R. *J. Inorganic Chem.* 5, Part 1 (Feb. 1960), Chemical Society (London, England).

[5] Aleksalin, I.A., et al, Problems of Investigating Thermoelectric Alloys Stable to Oxidation up to 2000°C, trans. from Russian, Wright Technology Division, AD 662573 (Wright-Patterson Air Force Base, Ohio, 1967).

[6] Freeze, P.D., Thomas, D.B., Edelman, S., and Stern, J., Development of Test Facilities — Noble Metal Thermocouple Research Program 1000-2000°C, NASA-CR-72861 (January 1971).

[7] Blackburn, G.F., and Caldwell, F.R., Reference Tables for Thermocouples of Iridium-Rhodium Alloys versus Iridium, *J. Res. Nat. Bur. Stand. (U.S.)* 68C, No. 1, pp. 41-59 (January-March 1964).

[8] Hansen, M., The Constitution of Binary Alloys, pp. 874 and 1155, McGraw-Hill Book Co. (New York, NY, 1958)

[9] Handbook of Physics and Chemistry, 55th ED., p. E229, CRC Press, Inc. (Cleveland, Ohio, 1975).

6. LIST OF FIGURES

TABLE 1

RELATIVE CHANGES IN THERMAL EMF WITH AGING TIME AT 1700°C IN AN OXIDIZING ATMOSPHERE (AIR) FOR AN IRIDIUM-40% RHODIUM VERSUS IRIDIUM THERMOCOUPLE OF 0.81-mm-DIAMETER WIRE. THE REFERENCE IS THE EMF OF A SIMILAR THERMOCOUPLE EXPOSED TO THE SAME AGING PROGRAM IN A NITROGEN ATMOSPHERE.

	ΔE, emf for Thermocouple in Air minus emf for Thermocouple in Nitrogen (μV)									
Aging Time (hours)	0.0	16.5	33.0	49.5	71.5	76.5	82.0	116	259	359
Nominal Calibration Temperature (°C)										
1200	2	8	11	14	---	---	13	19	---	---
1300	5	12	16	21	---	---	20	21	---	---
1400	7	20	22	29	---	---	28	33	---	---
1500	11	22	24	37	---	---	35	40	---	---
1600	10	28	35	49	---	---	48	52	---	---
1700	6	34	42	68	72	70	69	73	58	47

Note 1: The thermocouple in air always had the greater output.

Note 2: The changes in thermal emf, ΔE, may be converted to an equivalent temperature. The thermoelectric power (dE/dT) over the range 1200 to 2000°C is approximately 5.4 $\mu V/°C$.

TABLE 2

STABILITY TESTS CONDUCTED
(number of test thermocouples for which data were successfully obtained)

Wire Size (mm)	0.25	0.51	0.81
Aging Temperature (°C)			
1700	1	2	1
1850	1	1	3
2000	1	1	1

Note: All tests were terminated by failure of either the reference thermocouple or the test thermocouple, or both.

TABLE 3

COMPOSITION ANALYSIS OF IRIDIUM-40% RHODIUM SPECIMENS TAKEN FROM A THERMOCOUPLE MADE OF 0.81-mm-DIAMETER WIRE AND AGED FOR 359 HOURS AT 1700°C

Specimen Description	Shown in Photograph	Composition by Weight (%)	
		Iridium	Rhodium
Unheated Reference	7a	60	40
Heated in Air - Near Junction	7b	59	39
Heated in Air - Uniform Zone	7c	58	38
Heated in Air - Grain Boundary	7d	20	75
Heated in Nitrogen - Near Junction		61	39

TABLE 4

GRADIENT TESTS CONDUCTED

(number of thermocouples for which data were successfully obtained)

Thermocouple System	Platinum-13% Rhodium vs Platinum*						Iridium-40% Rhodium vs Iridium**	
Thermocouple Design	Stirrup			Wedge			Stirrup	Wedge
Wire size (mm)	0.25	0.51	0.81	0.25	0.51	0.81	0.51	0.51
Gradient (°C/cm)								
700	------	1	------	------	1	------	2	------
1475	1	1	1	1	1	1	------	------
1500	------	------	------	------	------	------	2	------
1975	------	------	------	------	------	------	2	1

* Junction temperature 1500°C.

** Junction temperature 2000°C.

TABLE 5

CALIBRATION CHANGES IN EIGHT PLATINUM-13% RHODIUM VERSUS PLATINUM THERMOCOUPLES, MADE IN TWO CONFIGURATIONS, FROM THREE WIRE SIZES, AND EXPOSED TO A JUNCTION TEMPERATURE OF 1500°C AND TO GRADIENTS OF 700 AND 1475°C/cm

Thermocouple Configuration	Wire Diameter (mm)	Temperature Gradient (°C/cm)	Total Test Duration** (hours)	Elapsed Test Time at Which ΔT max Occurs (hours)	ΔT max, Maximum Deviation From Initial Calibration Expressed in Terms of Equivalent Temperature Change * (°C)	ΔT, Deviation at Termination of Test from Initial Calibration, Expressed in Terms of Equivalent Temperature Change (°C)
Stirrup	0.81	1475	202	25.2	-11.7	+ 2.8
Wedge	0.81	1475	74.6	74.6	-26.6	-26.6
Stirrup	0.51	1475	60.5	60.5	-31.2	-31.2
Wedge	0.51	1475	51.8	51.8	-26.9	-26.9
Stirrup	0.25	1475	33.9	33.9	-26.2	-26.2
Wedge	0.25	1475	14.8	14.8	-29.8	-29.8
Stirrup	0.51	700	182.8	56.2	-17.7	-14.2
Wedge	0.51	700	61.2	61.2	-30.9	-30.9

* + indicates that thermocouple emf became greater than the initial calibration value at 1500°C;
 - indicates that thermocouple emf became less.

** A test was terminated with failure of the test thermocouple at approximately 200 hours, or when the calibration change corresponded to more than a 2.0% equivalent change in junction temperature (= 30°C for 1500°C junction temperature). Six thermocouples reached a maximum deviation from the initial calibration at the maximum lapsed test time, as may be seen by the fact that entries for these thermocouples are identical in the fourth and fifth columns from the left (and also in the sixth and seventh).

TABLE 6

CALIBRATION CHANGES IN PLATINUM-13% RHODIUM VERSUS PLATINUM THERMOCOUPLES MADE IN STIRRUP CONFIGURATION FROM THREE WIRE SIZES AND EXPOSED TO A TEMPERATURE GRADIENT OF 1475°C/cm

Total Heating Time at 1500°C (hours)	Equivalent Temperature Change* from Initial Calibration (°C)		
	Wire Diameter (mm)		
	0.81	0.51	0.25
0	0.0	0.0	0.0
1	- 0.2	-11.8	- 2.5
5	- 0.8	- 7.6	-10.4
10	- 1.8	- 6.0	- 6.0
15	- 3.6	- 8.4	-14.6
20	- 6.8	-12.4	-20.4
25	-11.3	-16.4	-22.8
30	- 8.6	-14.0	-----
34	-----	-----	-26.2
35	- 6.0	-13.5	-----
40	- 4.2	-12.4	-----
45	- 2.6	- 8.6	-----
50	- 2.2	-11.7	-----
55	- 1.8	-22.0	-----
60	- 0.6	-31.2	-----
65	+ 0.2	-----	-----
70	+ 1.4	-----	-----
80	+ 2.8	-----	-----
100	+ 2.4	-----	-----
115	+ 6.8	-----	-----
130	+ 5.6	-----	-----
150	+ 2.9	-----	-----
165	+ 3.3	-----	-----
180	0.0	-----	-----
190	+ 3.2	-----	-----
202	+ 2.8		

*+ indicates that thermocouple emf became greater than the initial calibration value at 1500°C; - indicates that thermocouple emf became less.

Note: A change in calibration of 30°C is 2.0% of the nominal junction temperature, 1500°C.

TABLE 7

RHODIUM CONCENTRATION IN A SECTION OF PLATINUM-13% RHODIUM THERMOCOUPLE COMPONENT AFTER EXPOSURE TO JUNCTION TEMPERATURE OF 1500°C AND TEMPERATURE GRADIENT OF 1475°C/cm FOR 60 HOURS*

Longitudinal Traverse		Radial Traverse	
Distance from Bead (μm)	Rhodium Concentration by Weight (%)	Distance from Wire Surface (μm)	Rhodium Concentration by Weight (%)
Next to bead	11.7	At wire surface	7.5
100	11.8	20	7.6
200	11.8	40	8.5
300	12.1	60	8.9
400	12.2	80	9.6
500	12.2	100	10.0
600	12.4	120	10.4
700	12.7	140	11.0
800	12.9	160	11.5
900	12.4	180	11.6
1000	12.9	Center of wire	11.8
1100	12.8	At opposite surface	9.5
2500	13.0		
Comparison specimen from untested thermocouple next to bead	12.6	Comparison specimen from untested thermocouple at wire surface	12.6

*The thermocouple was of stirrup configuration and fabricated from 0.51-mm-diameter wire. The thermoelectric results are given in table 6.

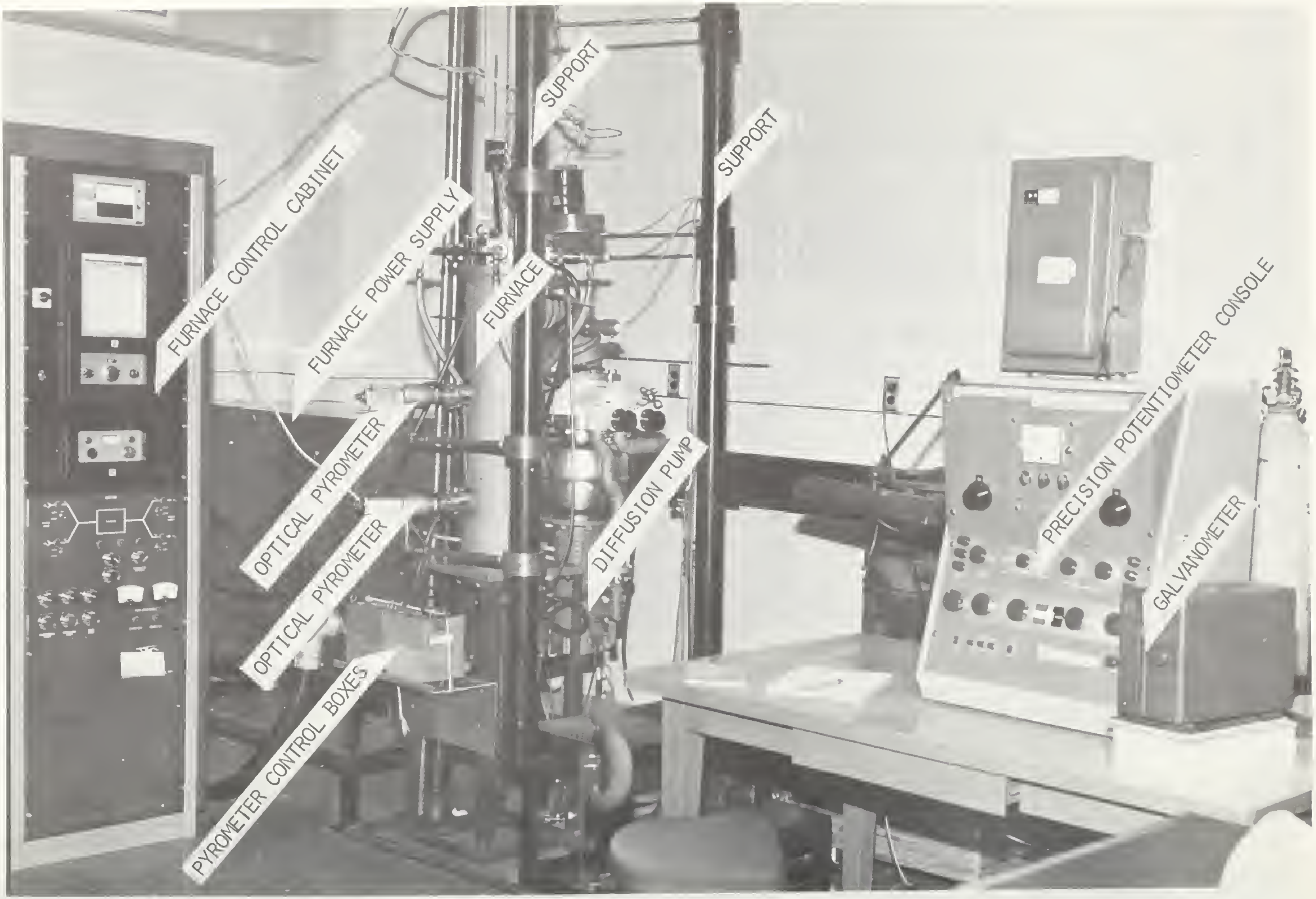


FIGURE 1: OVERALL VIEW OF THE STABILITY-TEST APPARATUS. THE APPARATUS IS DESCRIBED IN DETAIL IN THE TEXT, 2.3.

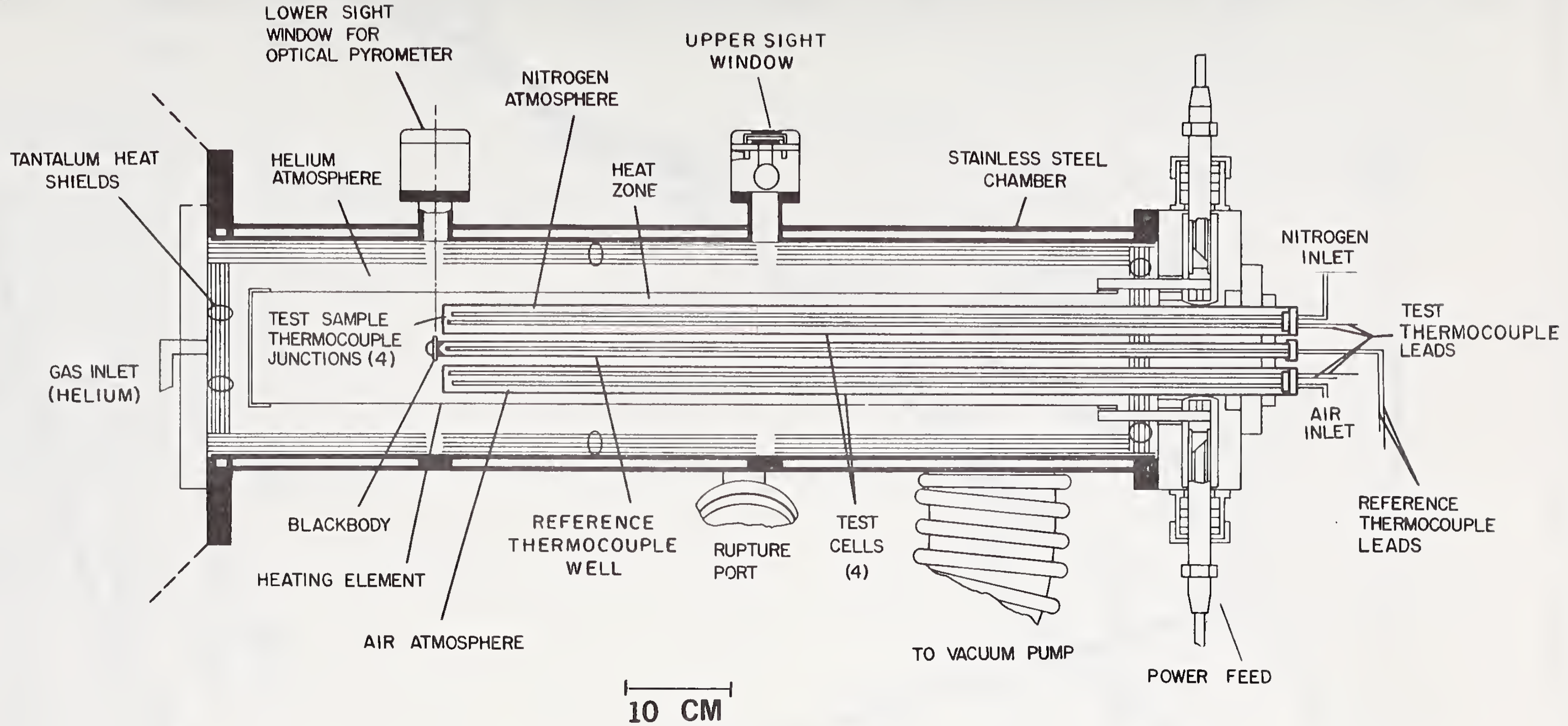


FIGURE 2: CROSS SECTION OF THE STABILITY-TEST FURNACE. THE FURNACE IS DESCRIBED IN DETAIL IN THE TEXT, 2.3.1.

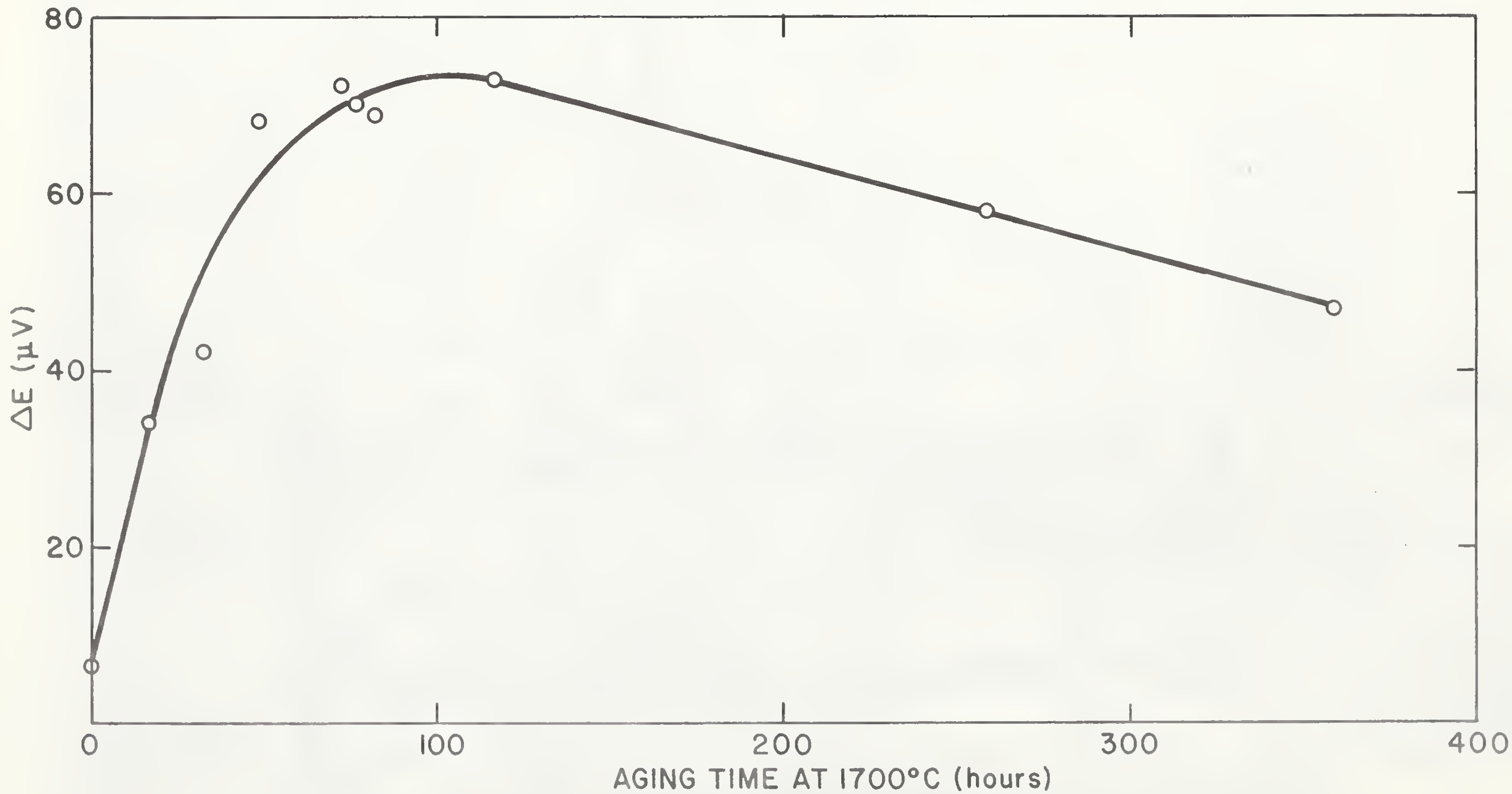


Figure 3: Relative change in thermal emf, ΔE, (μV), as a function of aging time (hours) at 1700°C. Test and reference thermocouples were iridium-40% rhodium versus iridium, of 0.81-mm-diameter wire. See text.

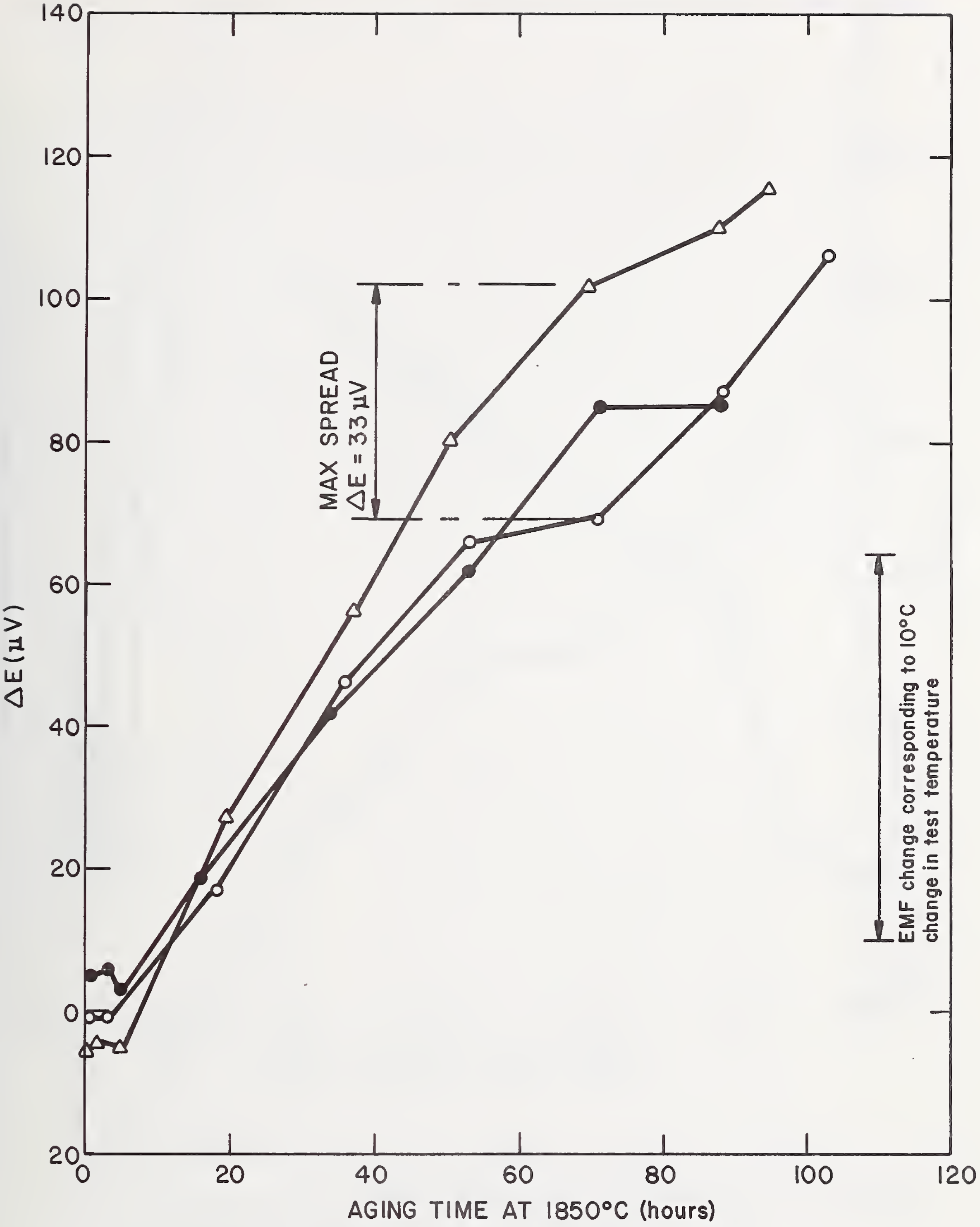


FIGURE 4: PLOTS OF RELATIVE CHANGE IN THERMAL EMF FOR THREE THERMOCOUPLES OF 0.81-MM-DIAMETER WIRE AS A FUNCTION OF AGING TIME AT 1850°C. THE PLOTS ARE FOR CALIBRATIONS AT 1850°C. RELATIVE CHANGE IN THERMAL EMF IS DEFINED AS THE DIFFERENCE BETWEEN THE THERMAL EMFS OF THE TEST THERMOCOUPLE IN AIR AND THE REFERENCE THERMOCOUPLE IN NITROGEN. THERMOCOUPLE SYSTEM: IRIDIUM-40% RHODIUM VERSUS IRIDIUM.

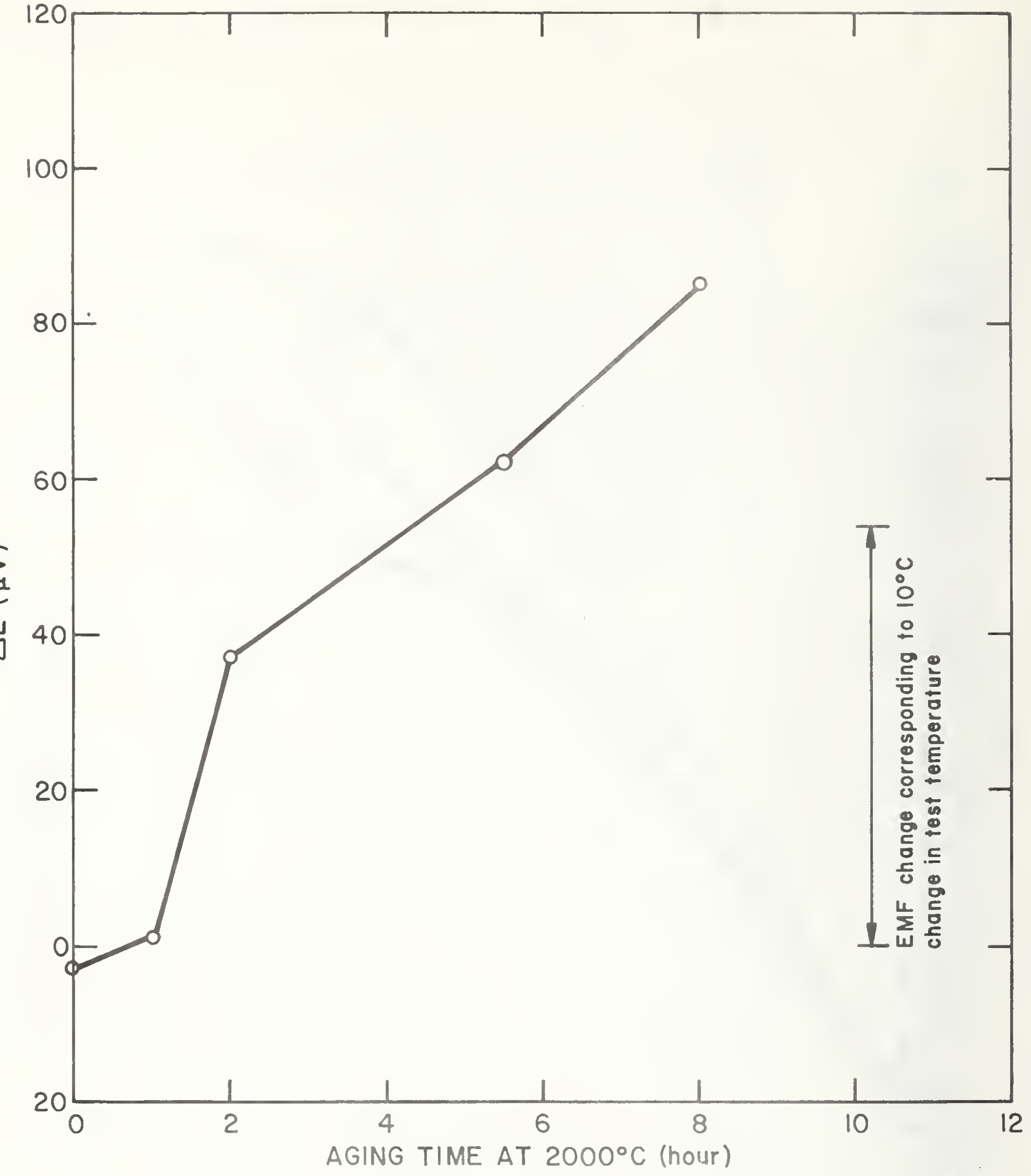


FIGURE 5: PLOT OF RELATIVE CHANGE IN THERMAL EMF OF A SINGLE THERMOCOUPLE OF 0.51-MM-DIAMETER WIRE AS A FUNCTION OF AGING TIME AT 2000°C. THE PLOT IS OF FIVE CALIBRATIONS MADE AT 2000°C. RELATIVE CHANGE IN THERMAL EMF IS DEFINED AS THE DIFFERENCE BETWEEN THE THERMAL EMFS OF THE TEST THERMOCOUPLE IN AIR AND THE TEST-REFERENCE THERMOCOUPLE IN NITROGEN. THERMOCOUPLE SYSTEM IRIDIUM-40% RHODIUM VERSUS IRIDIUM.

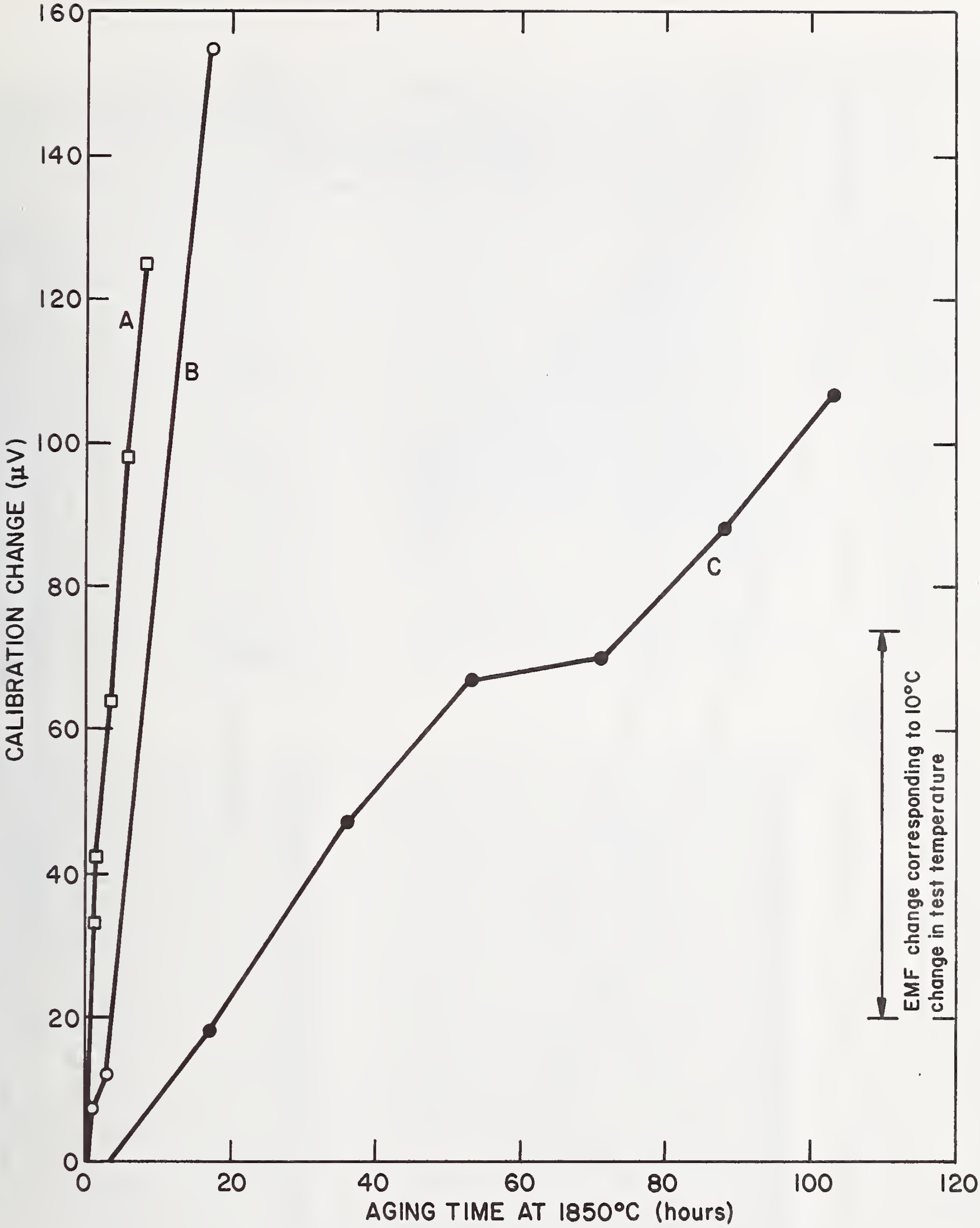


FIGURE 6: PLOTS OF CHANGES IN CALIBRATION (THERMAL EMF) OF THREE THERMOCOUPLES OF WIRE SIZES (A) 0.25, (B) 0.51, AND (C) 0.81 MM AS A FUNCTION OF AGING TIME AT 1850°C. THE CALIBRATION TEMPERATURE WAS ALSO 1850°C. THERMOCOUPLE SYSTEM: IRIDIUM-40% RHODIUM VERSUS IRIDIUM.

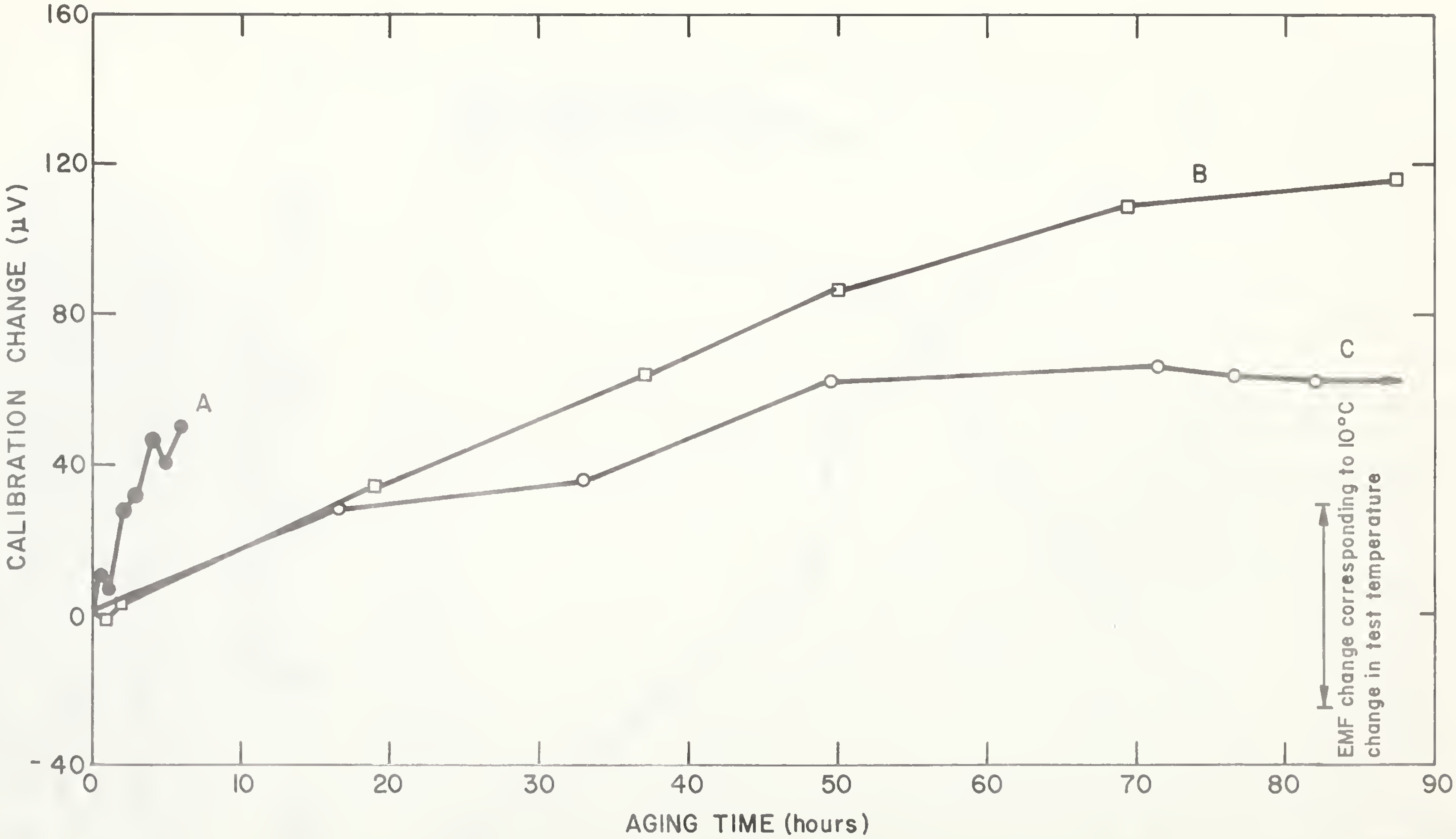


FIGURE 7:- PLOTS OF CHANGES IN CALIBRATION (THERMAL EMF) OF THREE THERMOCOUPLES OF 0.81-MM-DIAMETER WIRE AS A FUNCTION OF AGING TIME AT 2000°C (A), 1850°C (B), AND 1700°C. EACH THERMOCOUPLE WAS CALIBRATED AT ITS AGING TEMPERATURE. THERMOCOUPLE C FAILED AT 359 HOURS. THERMOCOUPLE SYSTEM: IRIDIUM-40% RHODIUM VERSUS IRIDIUM.

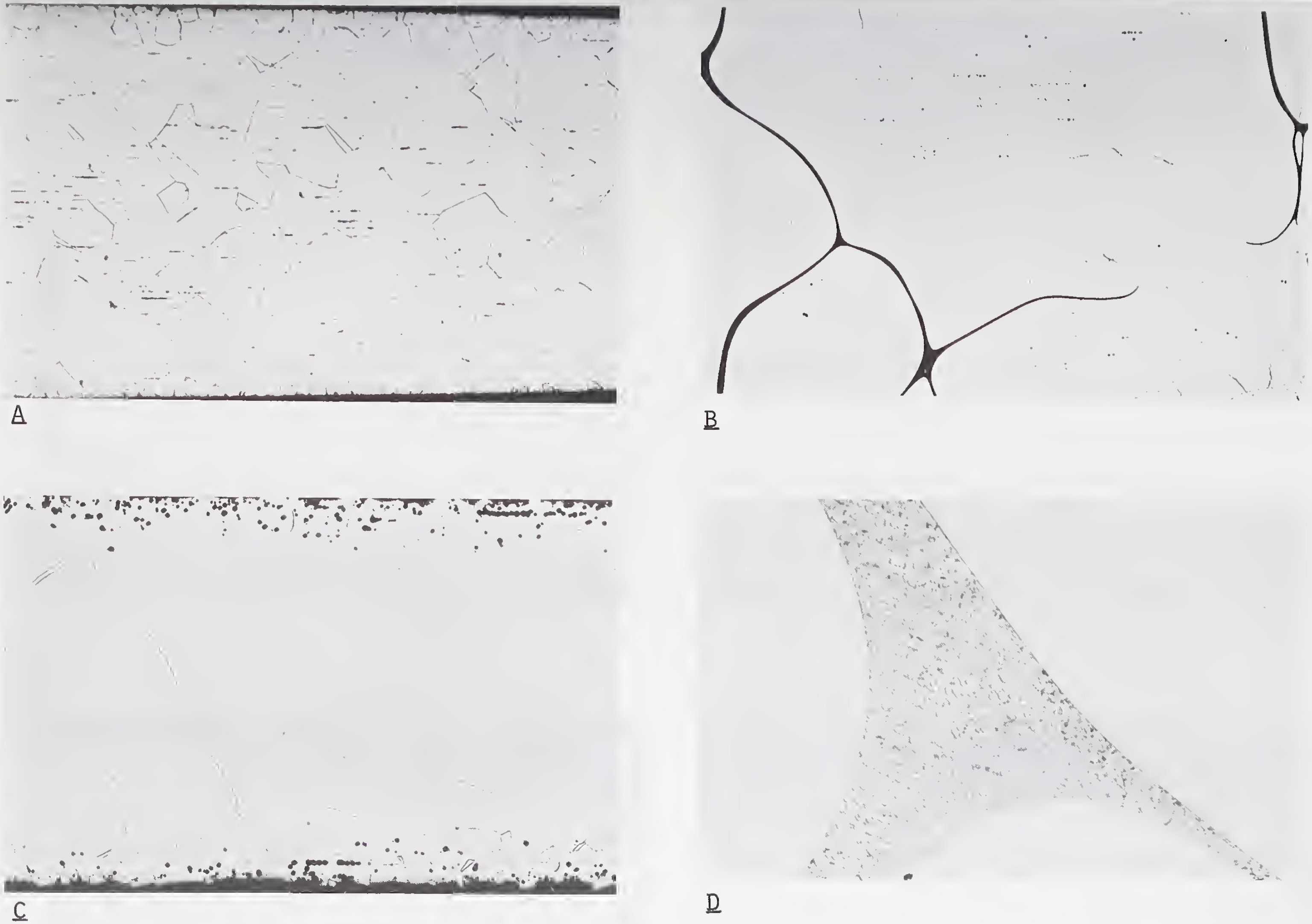
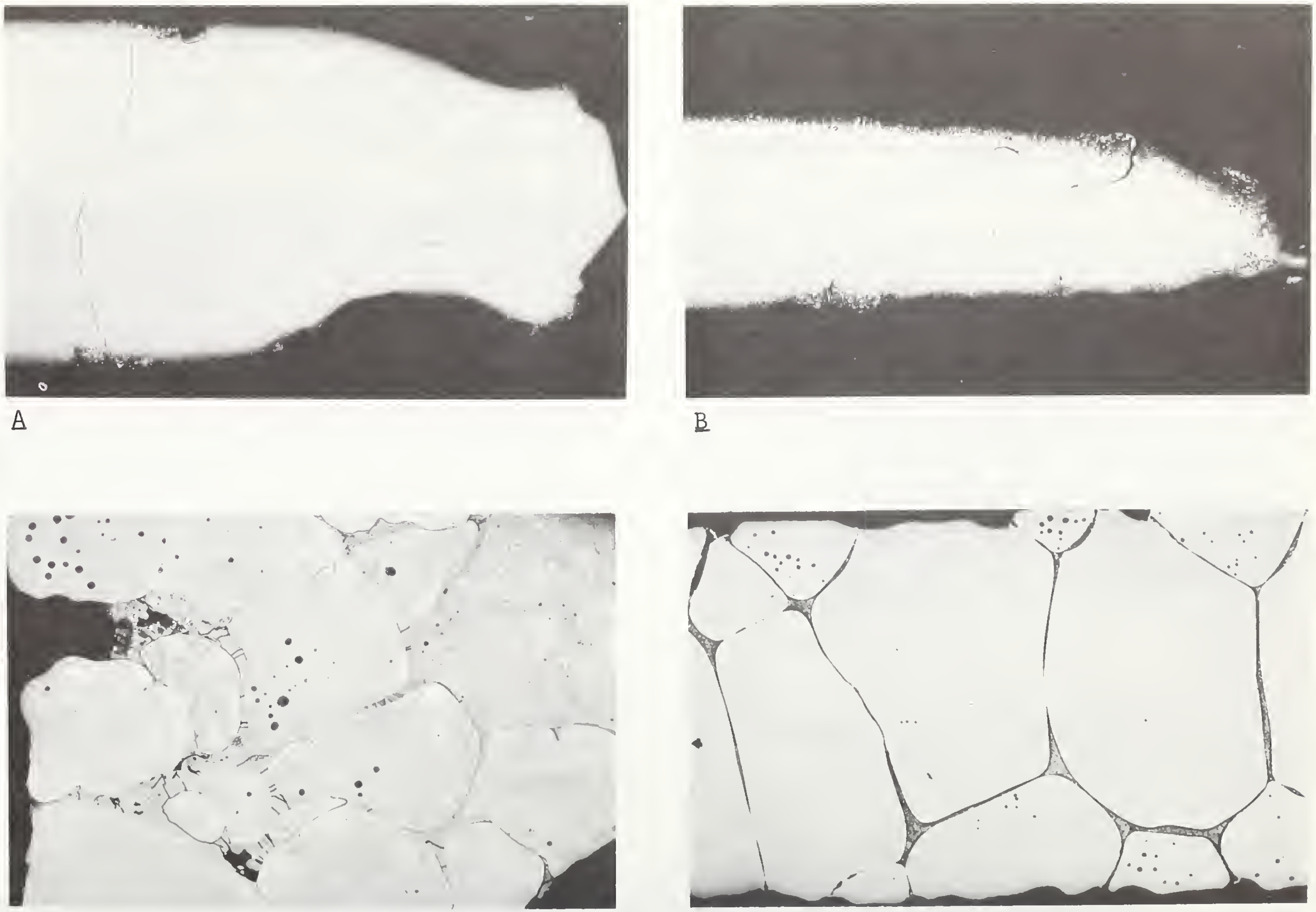


Figure 8: Micrographs of sectioned iridium-40% rhodium component of a test thermocouple aged at 1700°C for 359 hours. Photographs A, B, and C were taken with a magnification of 100X: D, an enlargement of a grain-boundary phase from B, at 1200X. Further description is in the text, 2.7.2. Thermocouple system: iridium-40% rhodium versus iridium.



A B C D

Figure 9: Micrographs of sectioned components of test (B, iridium and D alloy) and reference (A, iridium and C, alloy) thermocouples aged at 1850°C for 28 hours. The magnification was 80X. Further description is in the text, 2.7.2. Thermocouple system: iridium-40% rhodium versus iridium.

Figure 10: Micrographs of sectioned components of test thermocouples unheated (A, alloy and C, iridium) and aged at 2000°C for 8 hours (B, alloy and D, iridium). The magnification was 80X. Further description is in the text, 2.7.2. Thermocouple system: iridium-40% rhodium versus iridium.

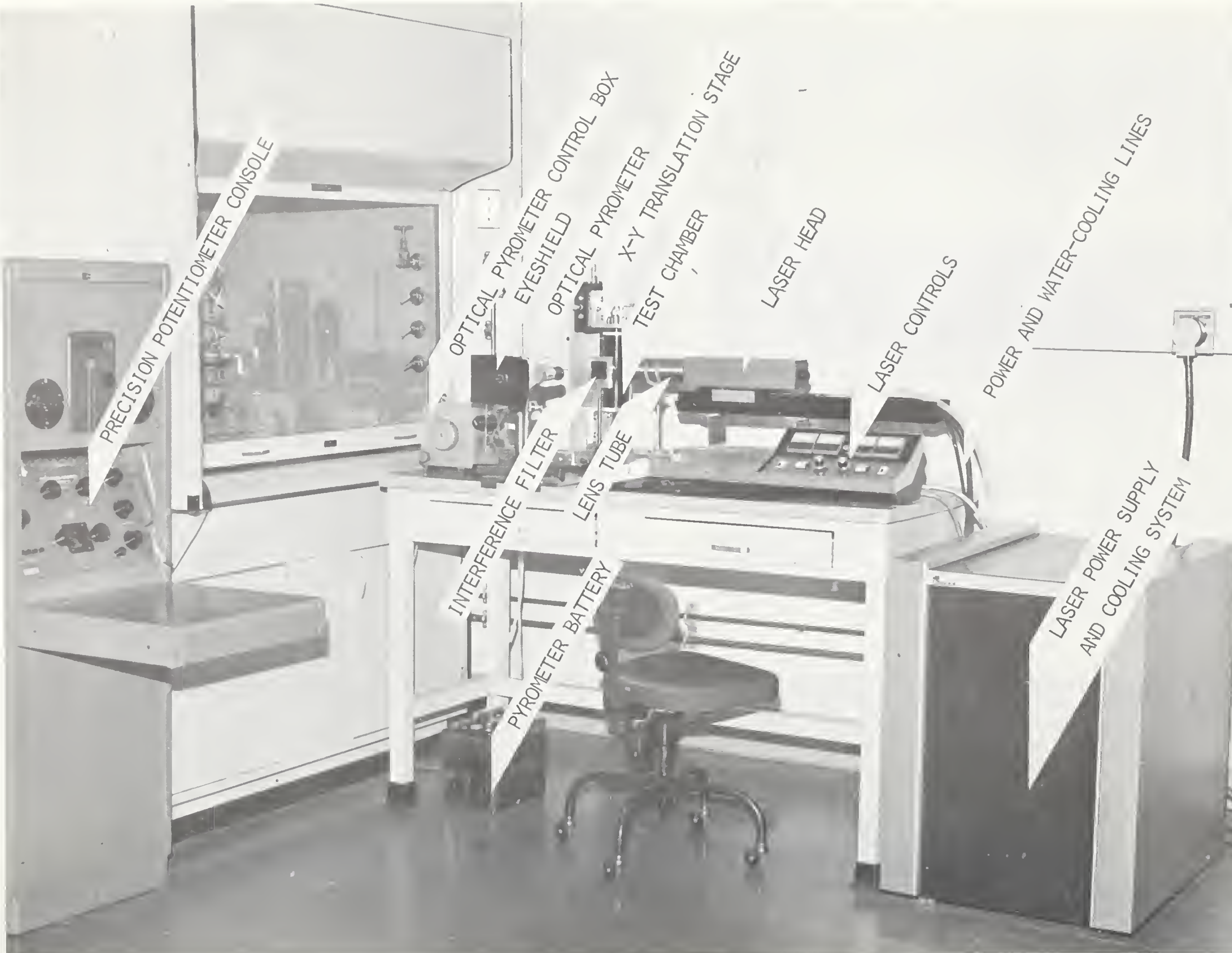


Figure 11: Overall view of the gradient-test apparatus. The apparatus is described in detail in the text, 3.3.

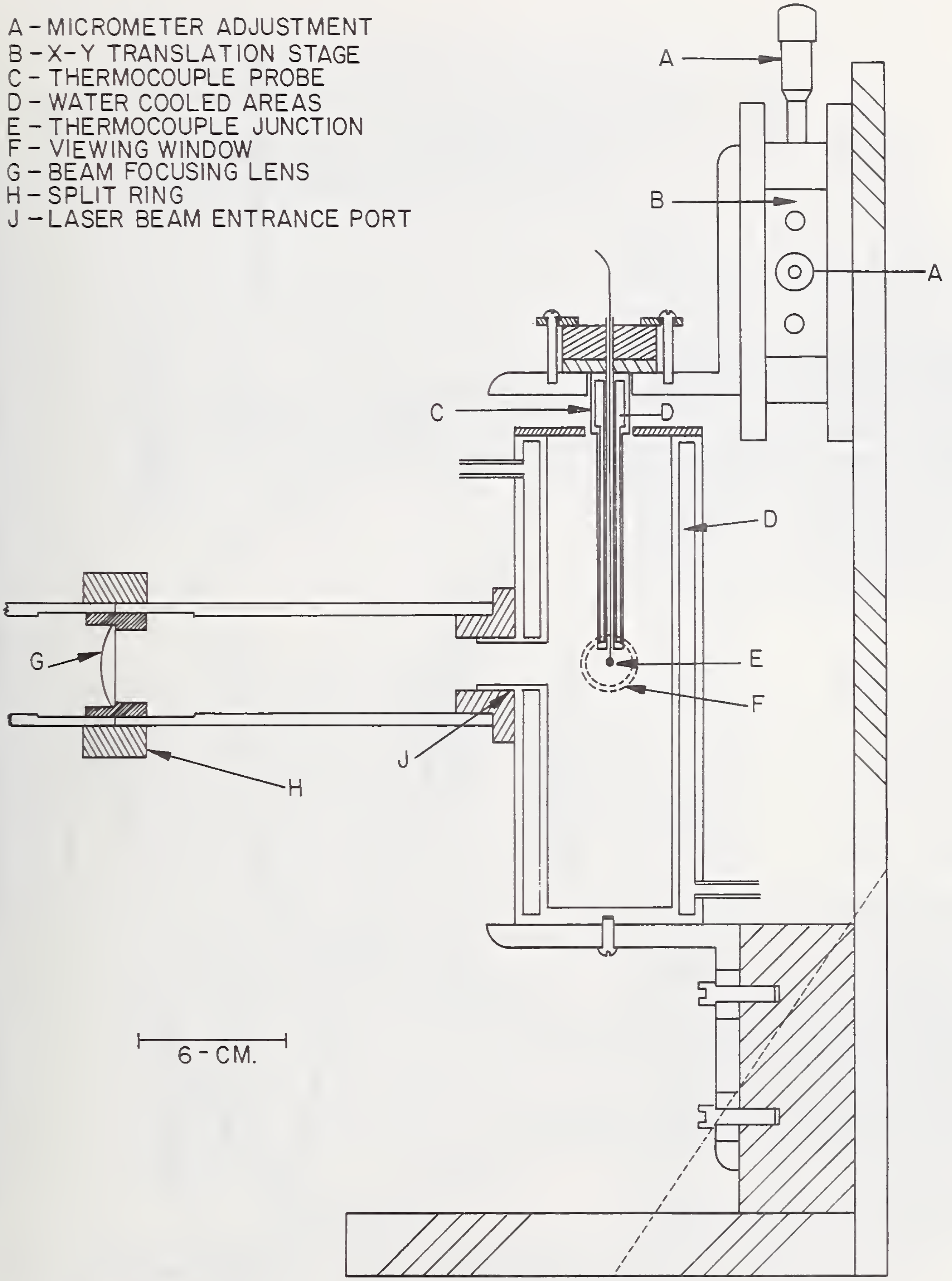


FIGURE 12: CROSS SECTION OF TEST CHAMBER USED IN GRADIENT STUDIES. THE CHAMBER IS DESCRIBED IN DETAIL IN THE TEXT, 3.3.1.

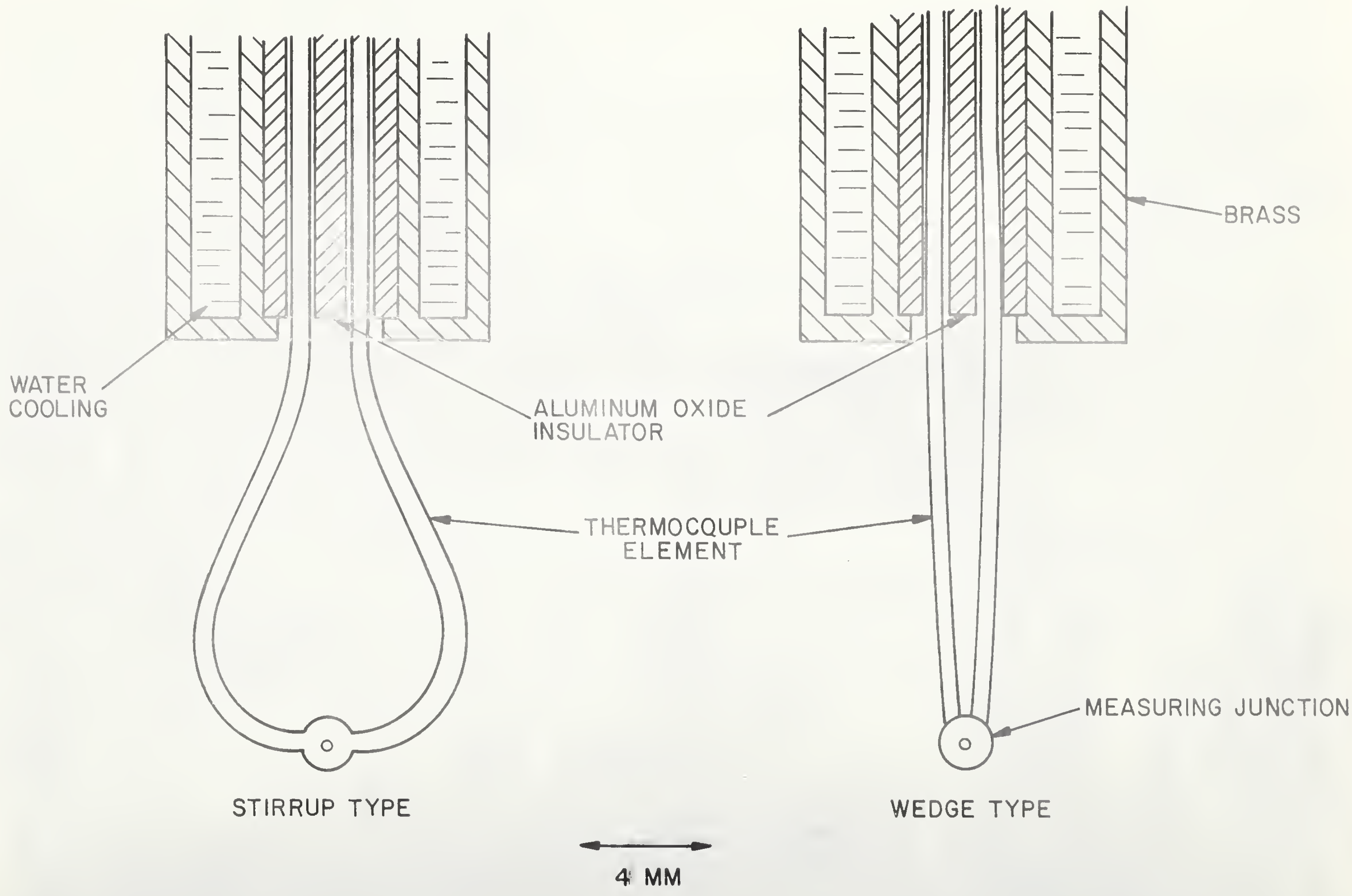


FIGURE 13: TEST THERMOCOUPLE CONFIGURATIONS, STIRRUP (LEFT) AND WEDGE (RIGHT). THE LOWER END OF THE MOUNT IS SHOWN IN CROSS SECTION AT THE TOP OF EACH DRAWING.

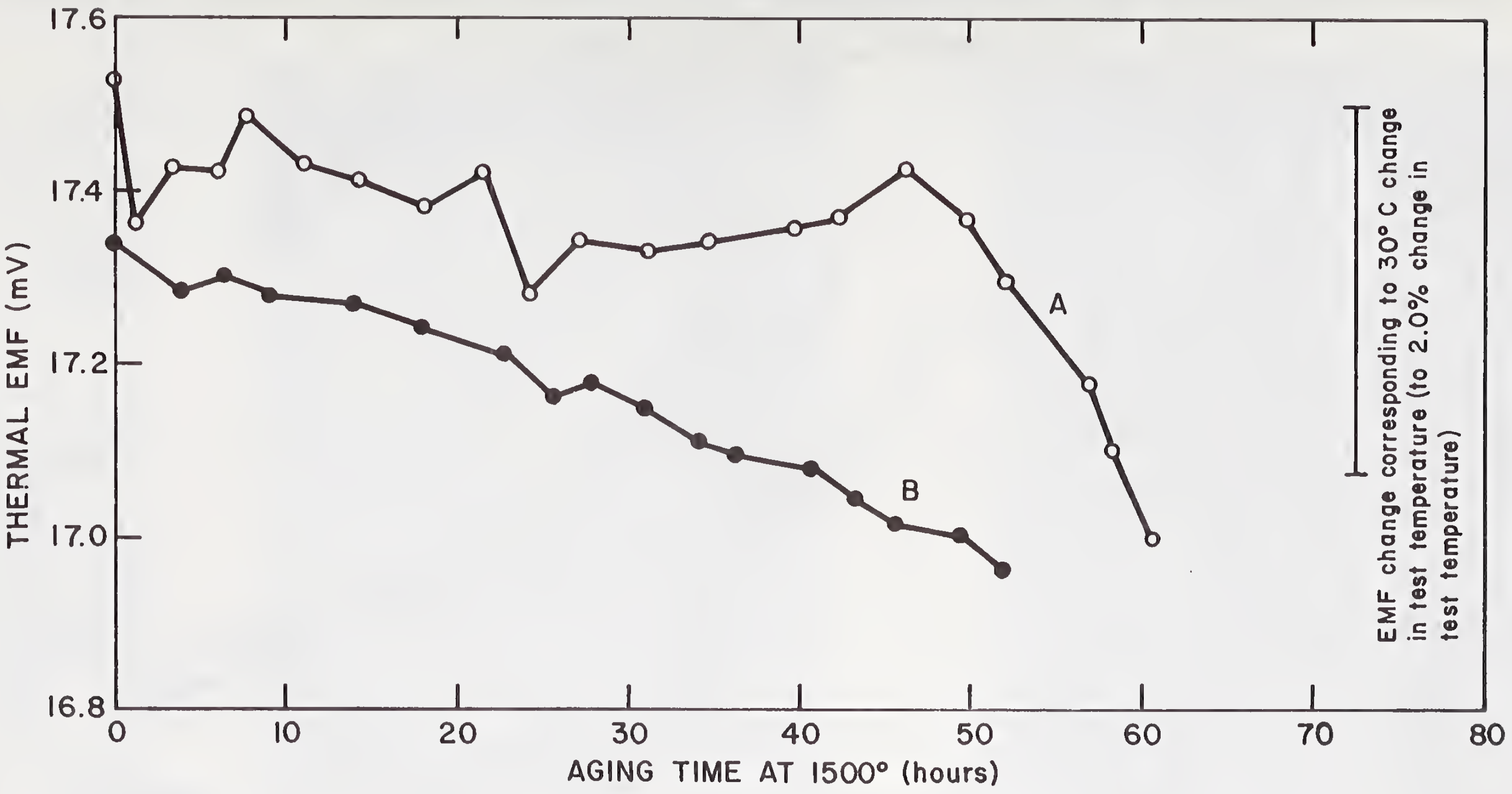


FIGURE 14: COMPARISON OF THERMAL EMFS OF STIRRUP-CONFIGURATION THERMOCOUPLE (A) AND WEDGE-CONFIGURATION THERMOCOUPLE (B). THE TEST CONDITIONS WERE A JUNCTION TEMPERATURE OF 1500°C AND A GRADIENT OF 1475°C/CM; WIRE SIZE WAS 0.51 MM. THERMOCOUPLE SYSTEM: PLATINUM-13% RHODIUM VERSUS PLATINUM.

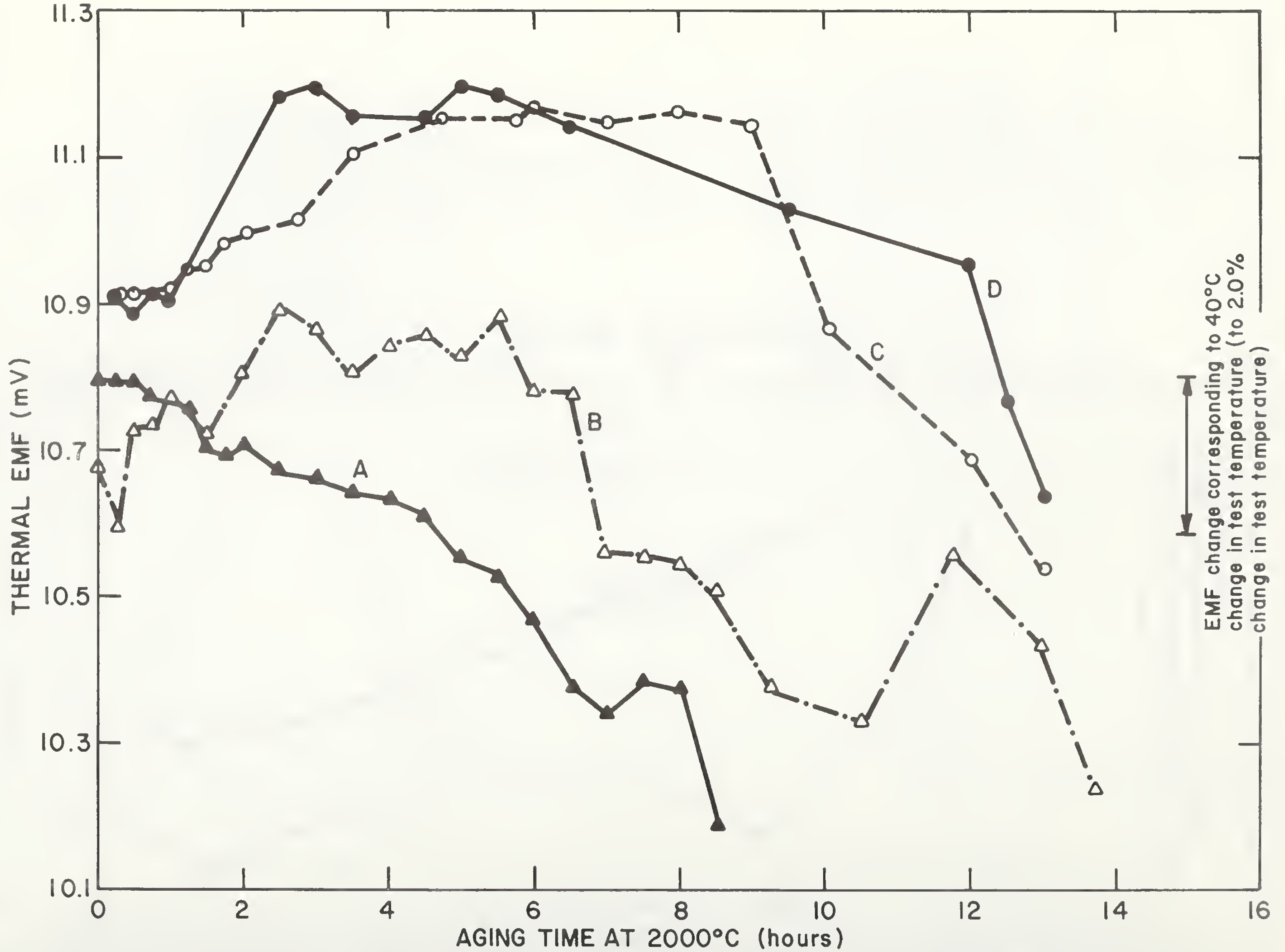
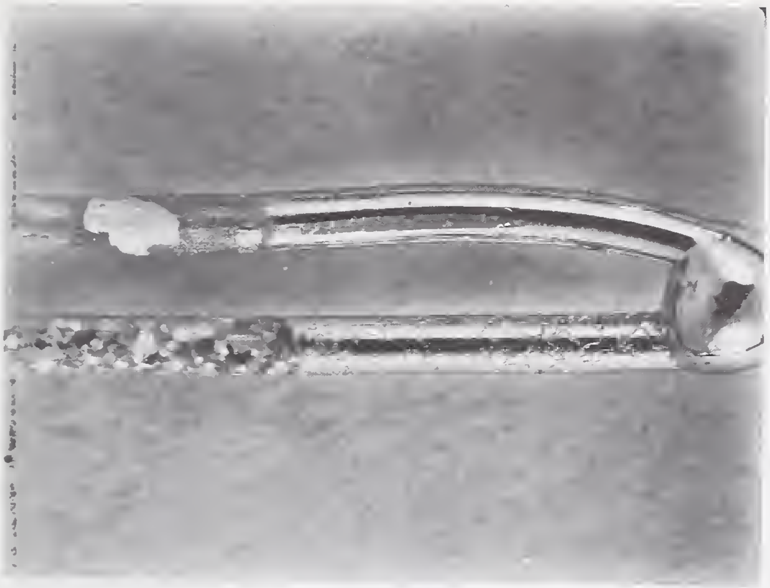


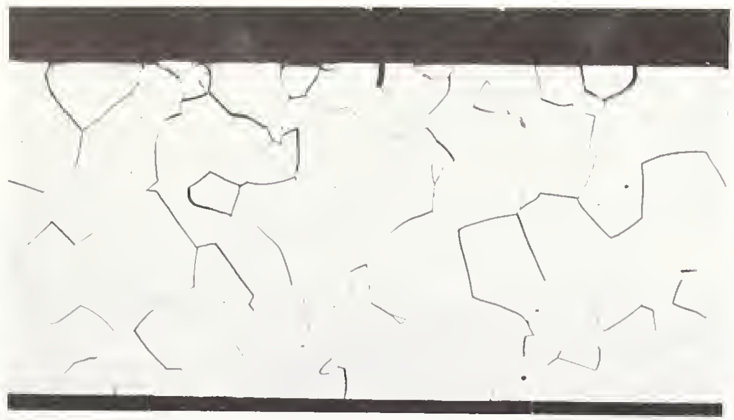
FIGURE 15: PLOTS OF THERMAL EMFS OF FOUR THERMOCOUPLES FABRICATED FROM 0.51-MM-DIAMETER WIRE AND EXPOSED TO A JUNCTION TEMPERATURE OF 2000°C AND TO GRADIENTS OF 700°C/CM (A AND B), 1500°C/CM (C), AND 1975°C/CM (D). THESE PLOTS ARE DESCRIBED IN THE TEXT, 3.7.1. THERMOCOUPLE SYSTEM: IRIDIUM-40% RHODIUM VERSUS IRIDIUM.



A

B

FIGURE 16: PHOTOGRAPHS AT MAGNIFICATION OF 15X OF WEDGE-CONFIGURATION (A) AND STIRRUP-CONFIGURATION (B) THERMOCOUPLES USED AT 1500°C AND AT A GRADIENT OF 1475°C/CM. THE PHOTOGRAPHS ARE DISCUSSED IN THE TEXT, 3.7.2. THERMOCOUPLE SYSTEM: PLATINUM-13% RHODIUM VERSUS PLATINUM.

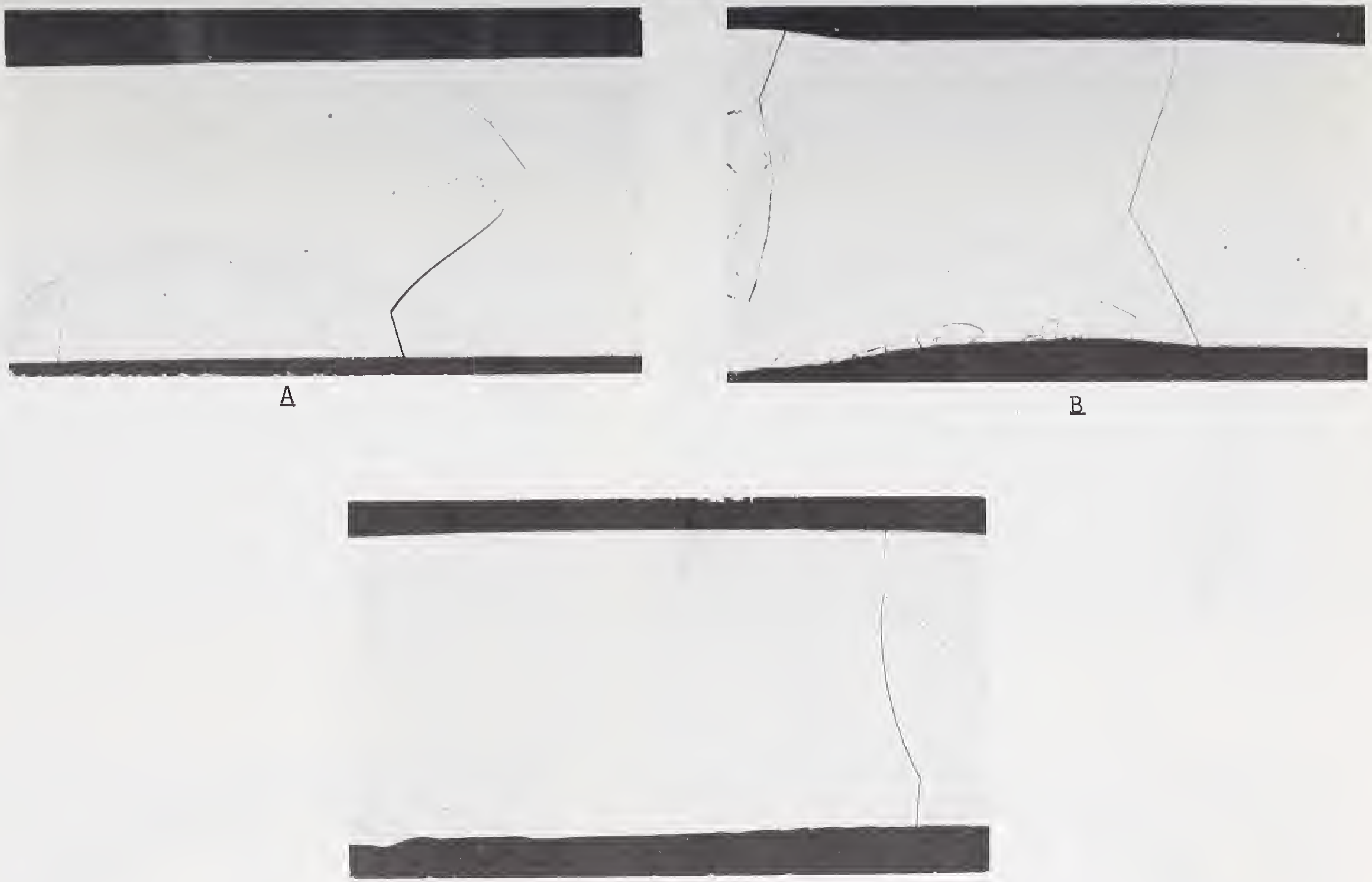


A

B

C

FIGURE 17: MICROGRAPHS OF SECTIONED ALLOY COMPONENT OF A TEST THERMOCOUPLE AGED AT 1500°C AND AT A GRADIENT OF 1475°C/CM FOR 60 HOURS. WIRE DIAMETER WAS 0.51 MM; THE MAGNIFICATION WAS 90X. PHOTOGRAPH A SHOWS A SECTION TAKEN 1.0 CM FROM THE JUNCTION; B, 0.5 CM FROM THE JUNCTION; AND C, 0.05 CM FROM THE JUNCTION. FURTHER DESCRIPTION IS IN THE TEXT, 3.7.2. THERMOCOUPLE SYSTEM: PLATINUM-13% RHODIUM VERSUS PLATINUM.



A B C

FIGURE 18: MICROGRAPHS OF SECTIONED PLATINUM COMPONENT OF A TEST THERMOCOUPLE AGED AT 1500°C AND AT A GRADIENT OF 1475°C/CM FOR 60 HOURS. WIRE DIAMETER WAS 0.51 MM; THE MAGNIFICATION WAS 90X. PHOTOGRAPH A SHOWS A SECTION TAKEN 1.0 CM FROM THE JUNCTION; B, 0.5 CM FROM THE JUNCTION; AND C, 0.05 CM FROM THE JUNCTION. FURTHER DESCRIPTION IS IN THE TEXT, 3.7.2. THERMOCOUPLE SYSTEM: PLATINUM-13% RHODIUM VERSUS PLATINUM.

Figure 19: Photographs at a magnification of 12X of components of two thermocouples aged at 2000°C and at gradients of 1975°C/cm (A and B) and 700°C/cm (C and D). The lengths of wire shown are approximately 2.5 cm in A and B and 3 cm in C and D. The wire size was 0.51 mm. Further description is in the text, 3.7.2. Thermocouple system: iridium-40%- rhodium versus iridium.

Report Distribution List
for
Contract No. C-67546-B*

Allison Division (1)
General Motors Corp.
Attn: W.J. O'Brien
P.O. Box 894
Indianapolis, IN 46202

ASTM Committee E-20 on (9)
Temperature Measurement
1916 Race Street
Philadelphia, PA 19103

Defence Standards Laboratories (1)
Metallurgy Division
Attn: Dr. Noel A. Burley
P.O. Box 50, Ascot Vale
Victoria 3032, Australia

Department of the Air Force (1)
AF Aero Propulsion Laboratory
Components Branch
Turbine Engine Division
Attn: Lt. L. Small
Wright-Patterson AFB, OH 45433

Engelhard Mineral-Chemical Corp. (1)
Attn: Mr. P. Bass
850 Passaic Avenue
Newark, NJ 07104

Engelhard Mineral-Chemical Corp. (1)
Attn: Mr. E.D. Zysk
497 Delancy Street
Newark, NJ 07105

Fiberglas Canada Limited (1)
Control System Technologist
Attn: Mr. G.A. Vincent
P.O. Box 3005
Sarnia, Ontario, Canada

General Electric Company (1)
Instrument Department
Attn: Mr. R.B. Clark
40 Federal Street
W. Lynn, MA 01905

General Electric Company (1)
Attn: Mr. C.M. Stanforth
Mail Drop H 78
Evendale, OH 45215

Harco Labs. Inc. (1)
Attn: Mr. M.A. Porto
186 Cedar Street
Branford, CT 06405

Howell Instruments, Inc. (1)
Attn: Mr. A.J. Droge
108 S. Franklin Avenue
Valley Stream, L.I., NY 11580

Information Center on High- (1)
Temperature Processes
Department of Fuel Science
Attn: Dr. L. Barker
The University, Leeds
LS2 9JT, England

Jet Propulsion Laboratory (1)
Attn: Library
4800 Oak Grove Drive
Pasadena, CA 91103

NASA-Ames Research Center (1)
Attn: Library
Moffett Field, CA 94035

NASA Flight Research Center (1)
Attn: Library
P.O. Box 273
Edwards, CA 93523

NASA-Goddard Space Flight Center (1)
Attn: Library
Greenbelt, MD 20771

National Aeronautics and Space (1)
Administration
Attn: A.J. Evans
NASA Headquarters
Program Office R.A.P.
Washington, DC 20546

National Aeronautics and Space (1)
Administration
Attn: N.F. Rekos
NASA Headquarters
Program Office R.A.P.
Washington, DC 20546

Nasa-Langley Research Center (1)
Langley Station Attn: Library
Hampton VA 23365

*The number of copies required by each addressee is given in parentheses.

NASA-Langley Research Center (1)
Langley Station
Attn: Mr. E. Germaine
Hampton, VA 23365

NASA-Lewis Research Center (20)
Attn: George Glawe
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (1)
Attn: F.O. O'Hallaron (M.S. 500-312)
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (1)
Attn: N.T. Musial (M.S. 500-113)
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (3)
Attn: I. Warshawsky (M.S. 77-1)
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (2)
Attn: Library (M.S. 60-3)
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (2)
Attn: Report Control Office
21000 Brookpark Road
Cleveland, OH 44135

NASA-Lewis Research Center (1)
Attn: Office of Reliability and
Quality Assurance
21000 Brookpark Road
Cleveland, OH 44135

NASA-Johnson Space Center (1)
Attn: Library
Houston, TX 77001

NASA-Marshall Space Flight Center (1)
Attn: Library
Huntsville, AL 35812

NASA Scientific and Technical Information Facility (40)
Attn: Accessioning Department
P.O. Box 8757
Balt/Wash International Airport
MD 21240

National Bureau of Standards (10)
Production Section 153.03
Washington DC 20234

National Bureau of Standards (12)
Advisory Panel for Electronic
Technology Division
Electronic Technology Division 425.00
Washington DC 20234

National Bureau of Standards (3)
Electronic Technology Division 425.00
Washington DC 20234

National Bureau of Standards (200)
Electronic Technology Division
Components and Applications Section 425.03
Washington DC 20234

National Bureau of Standards (2)
Institute for Applied Technology
Washington DC 20234

National Bureau of Standards (3)
Heat Division
Temperature Section 221.11
Attn: Mr. G. Burns
Washington DC 20234

Old Dominion University (1)
Thermal Engineering Department
Attn: Dr. R.L. Ash
Norfolk, VA 23508

Rosemont Engineering Company (1)
Attn: Mrs. R.A. Moen, Librarian
P.O. Box 35129
Minneapolis, MN 55435

Stanford University (1)
Mechanical Engineering Department
Attn: Dr. R. Moffatt
Stanford, CA 94305

U.S. Naval Research Laboratory (1)
Inorganic and Nuclear Chemistry Branch
Chemistry Division
Attn: Mr. C.T. Ewing
Washington DC 20390

USCOMM-NBS-DC