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# THERMAL ELECTROMOTIVE FORCE CHANGE FOR 87Pt13Rh/Pt THERMOCOUPLES IN 1530 K, $10^{-8}$ TORR ENVIRONMENT FOR 3700 HOURS

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## ABSTRACT

The thermal-emf change for 87Pt13Rh/Pt thermocouples was determined by recalibrations in air after 3700 hours exposure to a low-impurity environment with a temperature of 1530 K and a nitrogen equivalent pressure of $3\times10^{-8}$ torr. Wire size was 0.05 cm (0.020 in.), with two-hole, high-purity alumina (99.5 percent) as the insulator. The range of the thermal-emf changes was -2.0 to -3.6 K (average value, -2.8 K). Wire-impurity concentration along the wire was determined by emission spectrographic analysis, which showed iron to have the highest concentration increase at the junction and the largest concentration gradient near the junction. The change in the ratio of resistance at 300 K to the resistance at 4.2 K was determined for samples of the platinum-wire leg, and test-induced grain-structure changes determined with photomicrographs.

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## SUMMARY

The average thermal electromotive force (emf) change for 87-percent platinum - 13-percent rhodium/platinum (87Pt13Rh/Pt) thermocouples was determined by recalibrations in air after 3700 hours exposure to a controlled, low-impurity environment with a mean temperature of 1530 K and a mean nitrogen equivalent pressure of $3\times10^{-8}$ torr. Wire size was 0.05 centimeter (0.020 in.) with two-hole, high-purity alumina (99.5 percent) as the insulator. The range of the thermal-emf changes was -2.0 to -3.6 K, with an average value of -2.8 K. Also, the change in wire-impurity concentration along the wire was determined by emission spectrographic analysis, which showed iron to have the highest concentration increase at the junction and the largest concentration gradient near the junction. Finally, the change in the ratio of resistance at 300 K to the resistance at 4.2 K was determined for samples of the platinum-wire leg, and test-induced grain-structure changes determined with photomicrographs.

## INTRODUCTION

Noble-metal thermocouples are commonly used as high-temperature sensors. They offer the features of high melting points, simple construction, remote sensing capability, and a stable value of thermoelectric power in an oxidizing atmosphere. Because of these features, platinum-rhodium thermocouples are used in space-power and nuclear research programs. These research programs can have test times lasting thousands of hours. However, some of these long-duration tests at elevated temperatures have revealed that thermocouple thermoelectric power can become variable (ref. 1).

There have been some investigations of the processes that may cause noble-metal thermoelectric-power change. This change may be produced by contamination of the thermocouple wire, by a change in the amount of lattice defects or by grain growth. Con-

tamination of the thermocouple wire may occur by the following basic processes: (1) diffusion of impurities into the wire and within the wire, (2) volatilization of a wire alloy constituent from one thermocouple leg and deposition onto the adjacent leg, and (3) chemical reaction between the platinum wire and the silicon-containing insulators, forming platinum silicide. A change in the amount of lattice defects can be produced by the processes of quenching and/or cold working (ref. 2). Reference 3 states that grain growth, resulting from continued exposure at high temperature, weakens the wire mechanically and renders it more susceptible to contamination. Deterioration of both thermoelectric and mechanical properties is hastened when grain growth is combined with the effects of silicon as an impurity. However, Walter, Ewing, and Miller (ref. 4) found that neither grain growth nor cold working changed the thermal electromotive force (emf) of platinum wire.

Vines (ref. 5) states that any impurity in platinum, other than gold, makes its thermal emf positive with respect to the National Bureau of Standards (NBS) platinum sample Pt 27. Zysk (ref. 3) suggests that contamination is perhaps the main reason for the change of calibration. The major contaminant found in his experiment was silicon, which came from the insulators and protection tubes. Silicon was also reported by Jewell (ref. 6) to attack platinum and 87Pt13Rh wires to form platinum silicide. The degree of contamination was greater for the platinum wire. Grube and Speidel (ref. 7) found that platinum showed a strong melting point lowering when placed in a silicate-containing ceramic tube at 1620 K through which hydrogen gas flowed. Chaussian (ref. 8) also found that platinum wire changes its thermoelectric power when heated at 1570 K in silica powder. Moreover, whatever the degree of wire contamination, the thermal-emf change induced varied linearly with calibration temperature and linearly with exposure time at a constant temperature. Additionally, Rudnitskii and Tyurin (ref. 9) measured a thermal-emf change of -32 K at 1356 K for a 90Pt10Rh/Pt thermocouple in a corundite tube that had been held at 1620 K in air for 588 hours.

Walker, Ewing, and Miller (ref. 4) state that contamination of noble-metal thermocouples by impurities from ceramic protection tubes is the principal cause of the thermal-emf changes. This was determined by exposing thermocouples at temperatures up to 2000 K with a maximum exposure time of 240 hours. The observed thermal-emf change for the 87Pt13Rh/Pt thermocouple in argon at 1650 K for a 120-hour exposure time was -10 K when calibrated at 1130 K. However, the thermal-emf change in air was only -1.4 K for the same time and temperature conditions. The active impurity found in the alumina was iron (rather than silicon, aluminum, or copper). Results slightly less than those reported for an argon environment are reported by the same authors (ref. 10) for noble-metal thermocouples exposed at a high temperature for 120 hours in a vacuum.

Freeman (ref. 11) tested thermocouples made with several platinum-rhodium alloys at high temperature in air. Maximum exposure time was 510 hours. As other investi-

gators had also discovered, the negative thermocouple leg (platinum) had the highest degree of altered homogeneity; when the thermocouple had a platinum-rhodium alloy sheath, the chief contaminant found in the platinum was rhodium.

Thermoelectric-power change is also affected by interdiffusion at the hot junction (ref. 12). References 9 and 13 state that use of rhodium-based alloys in each thermocouple leg improves thermal-emf stability in both oxidizing and neutral atmospheres. They further show that the 80Pt20Rh/Rh thermocouple is 20 times more stable than the 90Pt10Rh/Pt thermocouple.

Metcalfe (ref. 14) reports that the thermal emf of the 87Pt13Rh/Pt thermocouple decreases after prolonged exposure in an 1870 K high-vacuum environment. This emf decrease in a vacuum is attributed to the vapor transfer of rhodium to the pure platinum.

Hendricks and McElroy (ref. 15) tested platinum-rhodium thermocouples in alumina insulators. Exposure time was 352 hours at 1575 K and at $2\times10^{-7}$ torr. The 90Pt10Rh/Pt and 70Pt30Rh/Pt6Rh thermocouples were stable within ±10 K. Wire size and alloy content did not change the thermal emf. Reference 4 reports contamination to be independent of wire size for an air environment. However, contamination was dependent on wire size for argon and vacuum (refs. 4 and 10).

The determination of the thermal-emf change after a long exposure for 87Pt13Rh/Pt thermocouples in pure alumina insulators was the purpose of the investigation reported herein. In the experiment, the thermocouple design and the thermocouple environment were chosen, within the bounds of practical limitations on available materials, to create conditions most favorable to a stable thermal emf. A controlled low-impurity-level, high-vacuum environment was used. This environment was maintained for nearly 4000 hours at 1530 K. Any change in thermal emf of these thermocouples was determined by recalibrations in air using a National Bureau of Standards (NBS) secondary standard thermocouple as a reference. The resistances $R_{300\,K}$ at 300 K and $R_{4.2\,K}$ at 4.2 K were also determined for samples from the platinum leg of two thermocouples exposed to high temperature and for samples from the unexposed platinum lead wire. Ratios of resistance $R_{300\,K}/R_{4.2\,K}$ for each sample were then compared. The resistance ratio is known to be sensitive to a change in wire purity and/or to a change in the amount of lattice defects present; the thermal emf is sensitive to a similar change (refs. 2, 5, 16, and 17). The resistance-ratio change, therefore, was used to help confirm the direction of the thermal-emf change measured. An emission spectrographic analysis was also used to establish that contamination of the thermocouple wires exposed to the high temperature did occur. Finally, grain-size changes in the wire were determined by photomicrographs.

# APPARATUS

## Pumping System and Test Chamber

The test stand used in this investigation is shown in figure 1. A 15-centimeter (6-in.) stainless-steel cross is directly connected to the top of the ion pump. All flange seals are copper gaskets, and all flanges are water cooled. Pressures below $10^{-4}$ torr

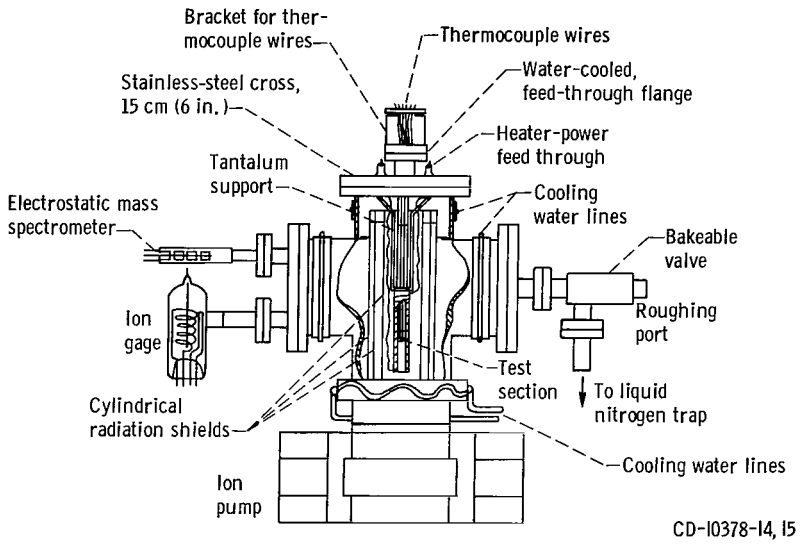



Figure 1. - Thermocouple test stand with cutaway showing test section.

are monitored by the ion gage. Gas composition is determined with the electrostatic mass spectrometer. A gold-seal bakeable vacuum valve is used to seal the system off from the roughing pump-down equipment. All roughing is done through the liquid-nitrogen cold trap, which minimizes back-streaming. Dry nitrogen gas is used to backfill the system to atmospheric pressure. Heater power enters the system through water-cooled feed-throughs mounted on the top flange. Centered on and spaced above the top flange of the cross is a small water-cooled flange. Passing through the center of this small flange, a 30 centimeter long by 0.4 centimeter inside diameter, closed-end platinum tube, gold-nickel welded to the flange, permits insertion or removal of a reference thermocouple while the test is in progress. The upper end of this thermocouple well is open to room atmosphere which is, as previously stated, a stabilizing environment for the reference thermocouple.

Sixteen 0.05-centimeter (0.020-in.) diameter wires of the eight test thermocouples pass directly through the small water-cooled flange. Each test-thermocouple wire is insulated from the flange with alumina tubes, the wire-alumina tube combination being

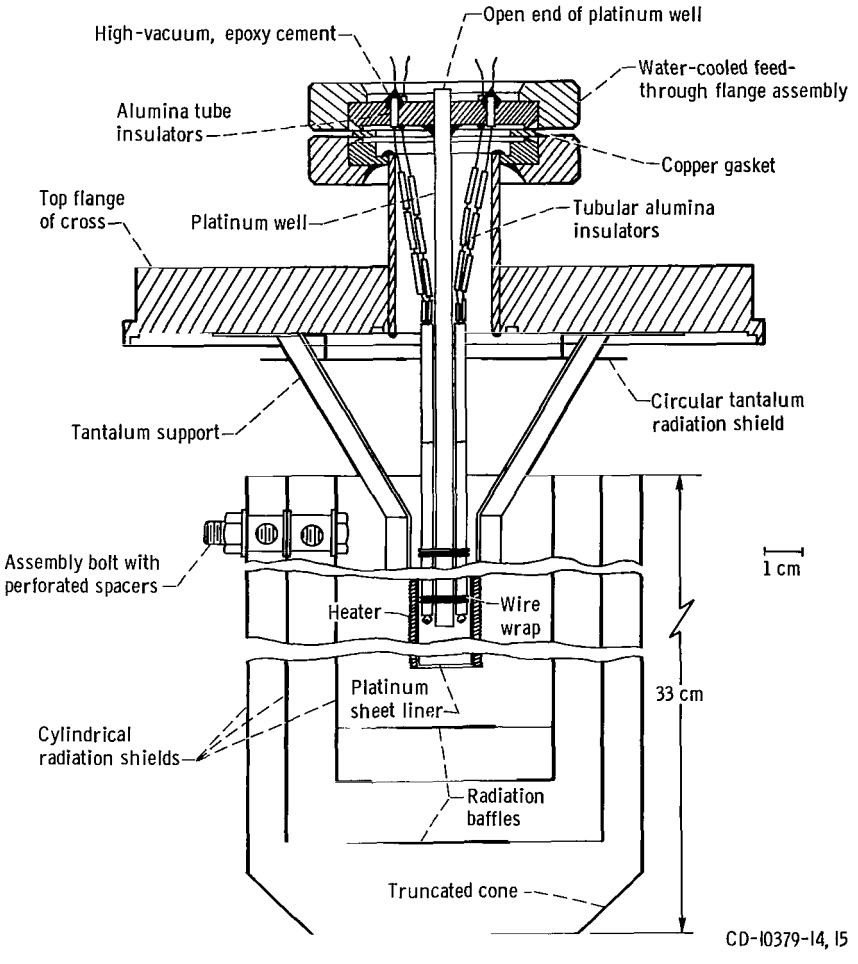



Figure 2. - Test chamber details showing only two of eight thermocouples tested.

vacuum sealed in place with high-vacuum epoxy cement. All test-thermocouple wires are terminated on a thermally insulated, multiple-point switch. All emf measurements were made with a manually balanced null potentiometer.

Details of the test chamber are shown in figure 2. Three cylindrical radiation shields are mounted inside the cross. The inner two shields are made of tantalum. The outer shield is stainless steel. A truncated cone acting as a reflector is attached to the bottom of the outer shield. Heater end losses are also minimized by optically tight radiation baffles held by the inner two cylindrical shields. The tantalum baffle is inside the truncated cone. The cone and baffle addition resulted in a noticeably reduced heater input power. Minimum baffle spacing is about 2 centimeters. This spacing prevents a low gas conductance for the radiation shield assembly. Also, four tantalum supports suspend the heater test section from the top flange. These tantalum supports are made from 0.025-centimeter (0.010-in.) sheet and are longitudinally bent $90^{\circ}$ for rigidity.

## Heater Test Section

The temperature of the heater test section is kept within selected limits by a temperature controller and recorder. Temperature level is sensed by the controller from the average signal of two test thermocouples. The mean reference-thermocouple temperature obtained is 1530 K with practically all the data points within ±30 K about the mean. A cross section of the heater test section is given in figure 3. The externally threaded,

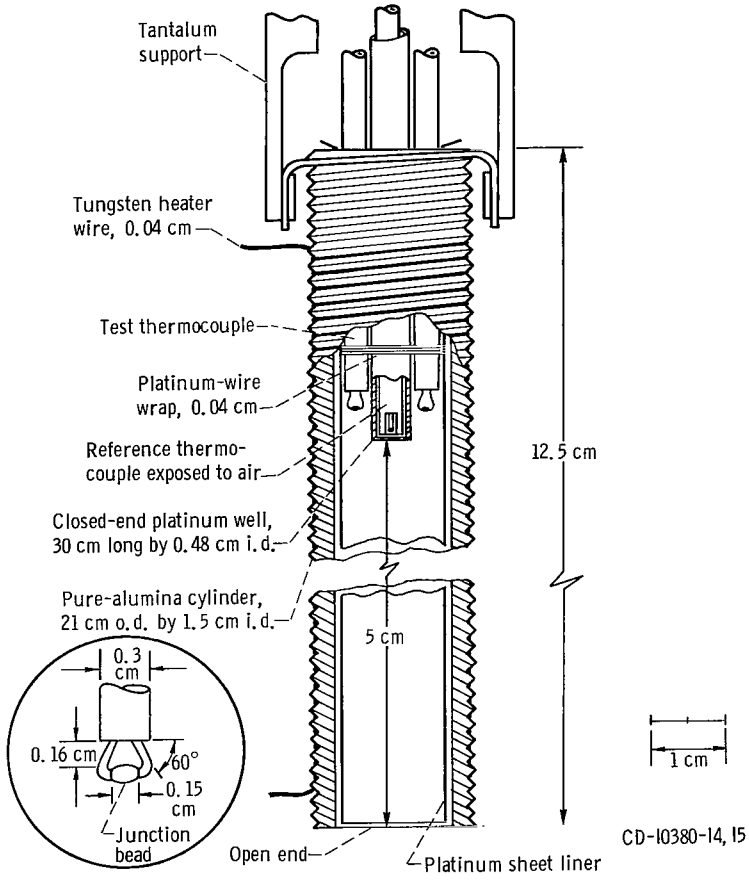



Figure 3. - Heater test section showing only two of eight thermocouples tested.

99.5-percent-pure alumina tube is wound with cleaned tungsten wire to form the heater. A platinum cylindrical liner is centered inside the heater along its length to minimize any direct contamination of the test thermocouples by vapors emitted from the alumina. The fact that the heater is open at the end permits the ion gage indicated pressure to represent the pressure at the junction region more accurately. A platinum well is axisymmetrically

placed within the heater. Platinum wire firmly secures the test-thermocouple alumina insulators parallel to and circumferentially around the platinum well. Such support of the insulators reduces the stress on the thermocouple wires and maintains intimate thermal contact between the insulators and the platinum well. This tends to keep all the insulators at the same temperature.

### Test Thermocouples

Test thermocouples were fabricated from commercially available 0.05-centimeter (24 gage) platinum and 87Pt13Rh wire. This wire pair conforms to the Instrument Society of America recommended practice by having deviations from the standard tables no greater than ±0.2 percent from 810 to 1760 K (ref. 18). A more detailed description of the wire pair used is given by the results of the emission spectrographic analysis and the values of the resistance ratios $R_{300K}/R_{4.2K}$ reported herein.

The insert in figure 3 shows the geometry of the test-thermocouple junctions. The heli-arced junction bead is bare and is not in contact with any insulators. The two-hole ceramic insulators extend to within 1 centimeter of the underside of the small flange (fig. 2). All ceramic insulators are alumina of 99.5 percent purity.

## TEST PROCEDURE

### Basic Operations

The test procedure consisted of the following basic operations:

(1) Samples of test-thermocouple-wire pairs were initially calibrated in air against a NBS calibrated 87Pt13Rh/Pt thermocouple.

(2) The empty test section was evacuated and cleaned, through baking, before the test thermocouples were installed. The test section was backfilled with dry nitrogen after it had cooled.

(3) Test thermocouples were installed and held in the vacuum at the test temperature.

(4) A reference thermocouple was inserted periodically in the central hole, which was always exposed to air, to check the average test-thermocouple temperature. This measurement was considered to provide a more reliable mean-temperature measurement, in the event that the test thermocouples were to drift excessively.

(5) At the conclusion of the test. test thermocouples were cooled, removed from the test apparatus, and recalibrated in the same calibration furnace as used for item (1). Details of each of these operations are given in the next sections.

## Initial Thermocouple Wire Calibration

Samples of test-thermocouple-wire pairs were initially calibrated in air against an NBS calibrated thermocouple at 530, 810, 1360, and 1735 K. A smooth curve fit of the data gave an initial deviation at 1530 K less than 0.3 K. This deviation will be corrected for in determining the net thermal-emf change for this test.

## Heater System Bakeout

The heater was baked out in the vacuum test stand twice before the test thermocouples were installed. The purpose of these high-temperature bakeouts was to clean the heater and adjacent structures in the vacuum system by removing volatile contaminants. Both bakeouts were done without having the platinum well in place. Heat for the bakeouts was supplied by the tungsten heater wire. The first bakeout was at a heater temperature above 480 K for 23 hours. This bakeout was followed, without opening the vacuum system, by a second bakeout at 800 K for 170 hours, after which the temperature was raised to 1400 K and held for an additional 23 hours. The pressure near the end of the bakeout was $6\times10^{-7}$ torr. After cooling, the test section was backfilled with dry nitrogen to 1-atmosphere ($1\times10^{5}$ N/m$^{2}$) pressure.

## Test-Thermocouple Handling

Eight 87Pt13Rh/Pt thermocouples were installed after the initial bakeouts. Installation time, during which the test section was exposed to room atmosphere, was about 15 minutes. Next, the temperature of the test section was slowly increased, while a pressure below $5\times10^{-6}$ torr was maintained. This slow increase in temperature was intended to prevent the presence of large concentrations of volatile contaminants by removing contaminants as fast as they were generated. Also, during this warmup period the test-thermocouple wires become annealed. The thermocouple temperature reached 1570 K after 190 hours of warmup.

## Measurement Operations

After 3700 hours of test-thermocouple exposure to an environment with a mean temperature of 1530 K and a pressure of $10^{-8}$ torr, the test was terminated because of a heater power supply failure. All eight thermocouples were then removed. The thermal-

emf change data were then obtained by a recalibration in the separate calibration furnace, against a NBS secondary standard thermocouple. These calibrations were performed in air. Next, the value of $R_{300K}/R_{4.2K}$ was determined for the test-thermocouple wires and the lead wires. Spectrographic analyses were then made to identify any changes in chemical composition in the vicinity of the junction. Finally, photomicrographs were made to identify grain size changes.

## RESULTS AND DISCUSSION

### Heater Test-Section Performance

The pure alumina heater wrapped with tungsten wire as the heating element was kept at a 1530 K temperature level for the entire test duration. After over 4000 hours of use, it had not failed. However, the heater did not produce a completely isothermal region. Figure 4 shows the circumferential temperature profile inside the heater. The maximum

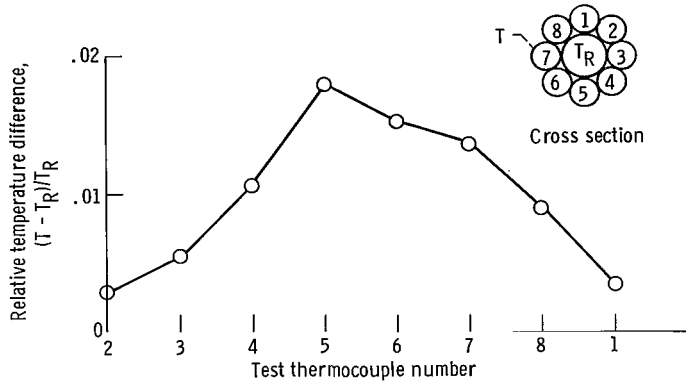



Figure 4. - Typical test-section circumferential temperature profile ($T_R$, reference temperature, 1535 K).

relative temperature difference is less than 2 percent. The physical cause of the non-isothermal distribution was the displacement of the thin platinum liner, which fused to the platinum wire wrap near test thermocouple 5. This fact was discovered during disassembly.

The axial temperature gradient established during the test is shown by figure 5. This temperature distribution was determined by slowly withdrawing the reference thermocouple from the closed-end platinum tube. Figure 5 also shows the axial temperature profile in the muffle furnace used for the calibrations in air. For every different tem-

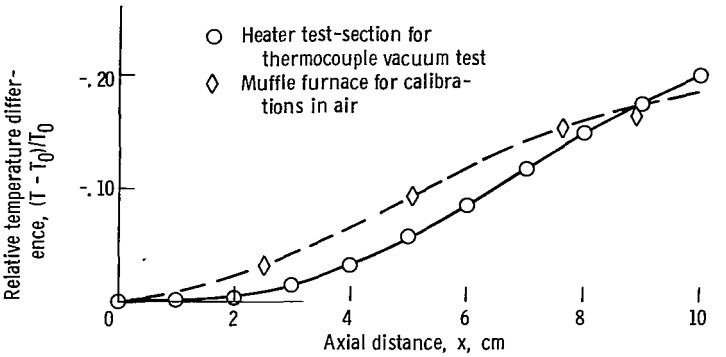
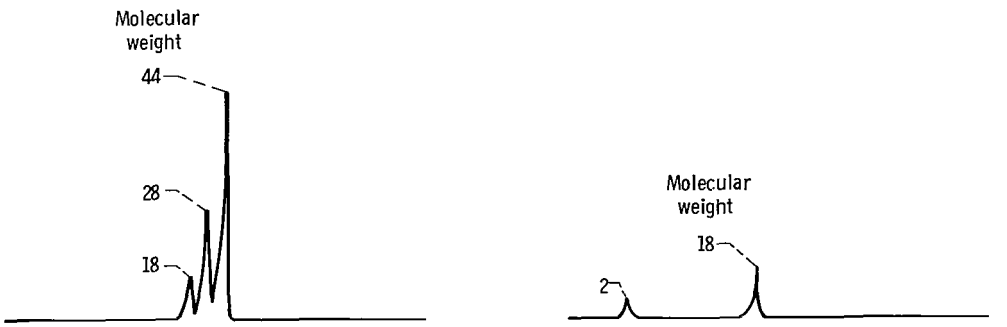



Figure 5. - Axial temperature profiles at 1500 K ($T_0$ = temperature at x = 0).

perature gradient at a given exposure time, there occurs a different amount of physical and chemical change at any particular location along a thermocouple wire. If a thermocouple is placed in a temperature gradient that differs from the temperature gradient it had been exposed to for a long period of time, the portions of the wire with the induced changes are now at different temperatures and become sources of different thermal emf's. Hence, the net effect obtained by placing the thermocouple in a different temperature gradient but with an unchanged junction temperature is a changed or new thermal-emf value for the same junction temperature. Consequently, the close similarity of temperature distribution curves shown by figure 5 minimizes the error in measuring the thermal-emf change by recalibrating in a separate furnace. Calibration times were less than 30 minutes.

The pressure at the start of the tests was $3\times10^{-6}$ torr, and decreased monotonically to an equilibrium value of $2\times10^{-8}$ torr at 1000 hours. Gas composition during the preparatory second bakeout is shown by figure 6(a). Relative amplitudes indicate relative




(a) Gas composition after 23 hours of heater bakeout at 1400 K. Vacuum system nitrogen equivalent pressure $6\times10^{-7}$ torr. Test thermocouples were not in vacuum system.

(b) Gas composition near 1000-hour thermocouple test point. Heater temperature, 1533 K; vacuum system nitrogen equivalent pressure, $2\times10^{-8}$ torr.

Figure 6. - Gas compositions indicated by electrostatic mass spectrometer.

gas concentrations if equal ionization efficiencies are assumed for all the gases indicated. Near the 1000-hour point, the gas consisted principally of water and hydrogen as determined by the electrostatic mass spectrometer (fig. 6(b)). Comparison of figure 6(b) with the gas composition shown in figure 6(a) indicates that for the majority of the test time outgassing was minimal. The pressure data, the gas composition data, and the post-test pressure of $3\times10^{-10}$ torr indicate that the environment provided for the test thermocouples was low in chemically active molecules.

## Test-Thermocouple Performance

Thermal-emf change. - The thermal-emf difference between the test-thermocouple after 3700 hours exposure to a high-temperature vacuum environment and an unexposed thermocouple wire pair from the same spools is shown in the second column of table I, where changes are expressed as the equivalent temperature error. All the thermal-emf changes indicate a decrease in thermoelectric power. Two different air calibrations are represented. One calibration of four thermocouples is at 1550 K. The second calibration is of two thermocouples at 1620 K. The mean of all six differences is -2.8 K with a spread of 1.6 K neglecting any effects of the small difference in the absolute calibration temperatures. The values in table I, therefore, show that after several thousand hours the average thermal-emf change of the 87Pt13Rh/Pt wire is less than 0.2 percent of 1530 K. This change represents the minimum change obtainable at 1530 K with present day knowledge applied to practical thermocouple designs. For most engineering applications, so small a change can be neglected.

Resistance ratio comparisons. - Two of the test thermocouples were not calibrated so that low-temperature resistance measurements could be made without subjecting them again to a high temperature. The total resistivity of a pure nonmagnetic metallic element can be represented to a good first-order approximation by the sum of two resistivity terms, only one of which is temperature dependent (Matthiessen's rule). Subtraction of the temperature-dependent term from the total resistivity yields the residual resistivity, which is due to the impurities and strains in the metal (ref. 19). At 4.2 K, the total resistivity of platinum represents the residual resistivity. The residual resistance $R_{4.2\,K}$ at 4.2 K was determined for each of the several test samples of platinum, as well as the total resistance $R_{300\,K}$ at 300 K. The $R_{300\,K}/R_{4.2\,K}$ ratios are shown in table I. The smaller the resistance ratio $R_{300\,K}/R_{4.2\,K}$, the larger the residual resistivity. The resistance ratios $R_{300\,K}/R_{4.2\,K}$ for the 12.5-centimeter-long samples are smaller than those for the 26-centimeter-long samples. The ratio for the 26-centimeter-long samples are still smaller than the resistance ratios for the as-received wires. Hence, the platinum wire near the junction appears to possess a higher degree of contamination and/or strain than the as-received wire. Furthermore, these resistance-ratio

TABLE I. - SUMMARY OF DATA FOR TESTED

87Pt13Rh/Pt THERMOCOUPLES

[Exposure, 1530 K at nitrogen equivalent pressure of $3\times10^{-8}$ torr for 3700 hr.]

| Test thermocouple | Thermocouple temperature indication error, K | Platinum wire leg resistance ratio, $R_{300K}/R_{4.2K}$ | | |
|---|---|---|---|---|
| | | Distance from junction[a], cm | | As-received wire[b] |
| | | 12.5 | 26 | |
| 1 | [c]-2.0 | --- | --- | --- |
| 2 | ----- | 276 | 389 | 455 |
| 3 | [c]-3.6 | --- | --- | --- |
| 4 | [d]-2.4 | --- | --- | --- |
| 5 | [c]-3.4 | --- | --- | --- |
| 6 | ----- | 291 | 431 | 471 |
| 7 | [d]-2.1 | --- | --- | --- |
| 8 | [c]-3.1 | --- | --- | --- |

[a]Average resistance ratio over length from junction to distance indicated.

[b]Portion of test wire not exposed to high-temperature, vacuum environment.

[c]Calibration temperature in air, 1550 K.

[d]Calibration temperature in air, 1620 K.

TABLE II. - IMPURITY ELEMENTS FOUND BY

EMISSION SPECTROGRAPHIC ANALYSIS

WITH A CONCENTRATION GRADIENT

[Test thermocouple 5; exposure, 1530 K at nitrogen equivalent pressure of $3\times10^{-8}$ torr for 3700 hr.]

| Element | Platinum-wire leg | | | 87Pt13Rh wire leg | | | |
|---|---|---|---|---|---|---|---|
| | Distance from junction, cm | | | | | | |
| | [a]91 | 15 | 2.5 | 0 | 2.5 | 15 | [a]91 |
| | Concentration[b], percent | | | | | | |
| Au | FT | ---- | ---- | ---- | ---- | T | T |
| Cu | T | T | FT | <0.1 | T | T | FT |
| Fe | FT | T | <0.1 | 1 | >0.1 | <0.1 | T |
| Ni | FT | FT | T | <0.1 | <0.1 | T | T |
| Rh | <0.1 | <0.1 | <0.1 | >5 | ---- | ---- | --- |
| Si | FT | FT | ---- | FT | FT | <0.1 | FT |
| Ti | ---- | ---- | ---- | ---- | ---- | ---- | FT |
| Zn | FT | ---- | ---- | ---- | ---- | ---- | ---- |
| Zr | FT | FT | ---- | ---- | ---- | ---- | T |

[a]Test wire as-received.

[b]Trace (T) of element in range of hundreds of ppm by weight; faint trace (FT) in range of several to tens of ppm by weight.

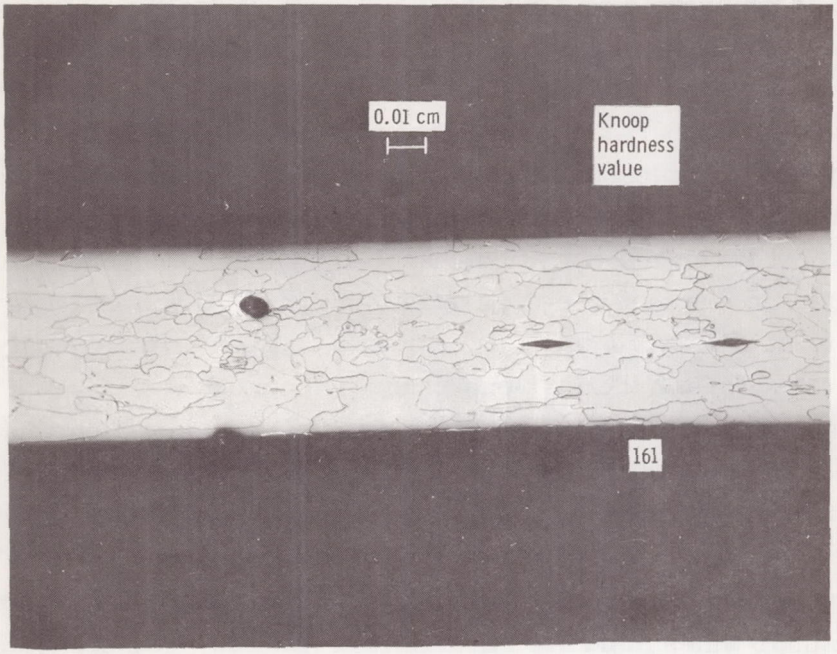
comparisons show that the direction of the resistance-ratio change matches the direction of the thermal-emf change.

Emission spectrographic analysis. - Table II shows the results of the spectrographic analysis for test thermocouple 5. Only those elements whose concentration changed with distance from the thermocouple junction are listed. Silver is the only impurity uniformly distributed as a faint trace in the entire test-thermocouple length. Gold, titanium, and zirconium are listed as impurities for the lead wire in table II, but are not listed for the five different platinum samples analyzed in reference 17. The impurity with the largest concentration change is iron. At the junction, iron is the major impurity. Nickel and copper show the next lower concentration change along the wire. And, even though silicon is a known impurity in platinum and in pure alumina, table II shows a nearly constant concentration of silicon. Hence, in these experiments, silicon as an impurity is not assumed to be the prime cause for the thermal-emf changes reported.

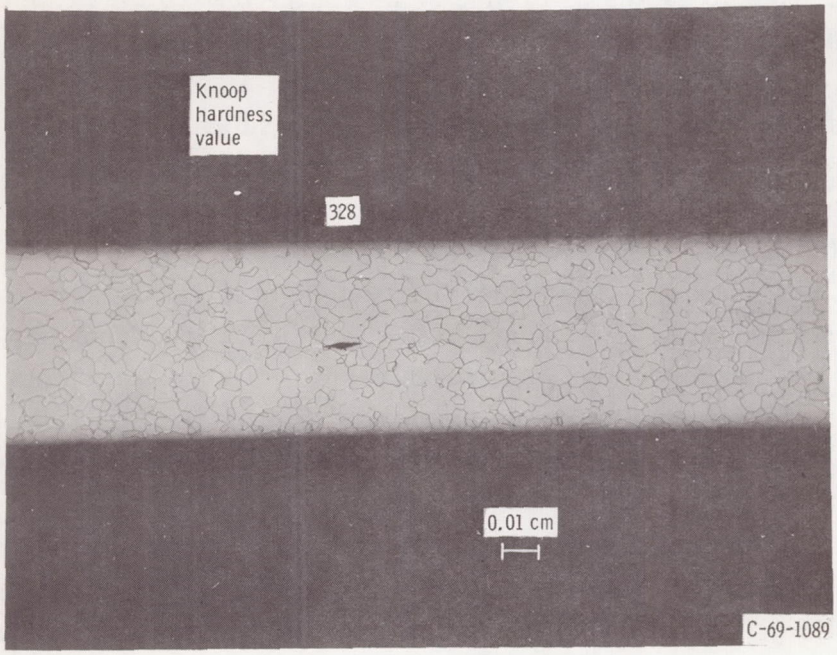
Note from table II that iron not only has the highest concentration, but also has the largest concentration gradient. Also, iron contamination in the 87Pt13Rh wire is greater than in the platinum wire. Other than the thermoelectric metals themselves, the alumina insulators inside the heater test section represent sources of iron. Iron as an oxide in alumina has been reported by several investigators (refs. 20 to 22). Even sapphire is reported to contain 10 times more iron than silicon (ref. 23). Reference 5 quotes reference 24 and reference 16 quotes reference 25 as stating that at 1470 K the thermal-emf change produced by 1-percent iron in platinum is about five times greater than the change produced by a 1-percent rhodium addition to platinum. Also, iron as the active impurity affecting noble-metal thermocouple emf is reported in reference 10. The preceding analysis, therefore, indicates that the reported thermal-emf changes are from an impurity concentration change in the wire. The alumina insulators are the most probable sources of the iron impurity.

Grain structure change. - The physical structure of a test thermocouple is represented in figures 7 and 8(a). Also shown in the figures are the Knoop hardness indentations along with the measured Knoop hardness values. Figure 7(a) shows the size and axial orientation of the grains in the platinum wire prior to testing. The grains shown by figure 7(b) have no preferential orientation and have no apparent size change from an unheated wire.

The post-test structure of the thermocouple junction and the connecting 87Pt13Rh wire is shown by figure 8(a). In comparison with figure 7(b), the large change in grain size is very distinct. These large grains occur not only at the junction, but also along the length of the adjacent wire. Similar observations hold for the platinum wire (not shown). The Knoop hardness values indicate the distribution of platinum and/or the presence of residual strain along the wire. Note that many of the grain boundaries form fairly direct paths across the diameter of the wire. Under these conditions, the prob-

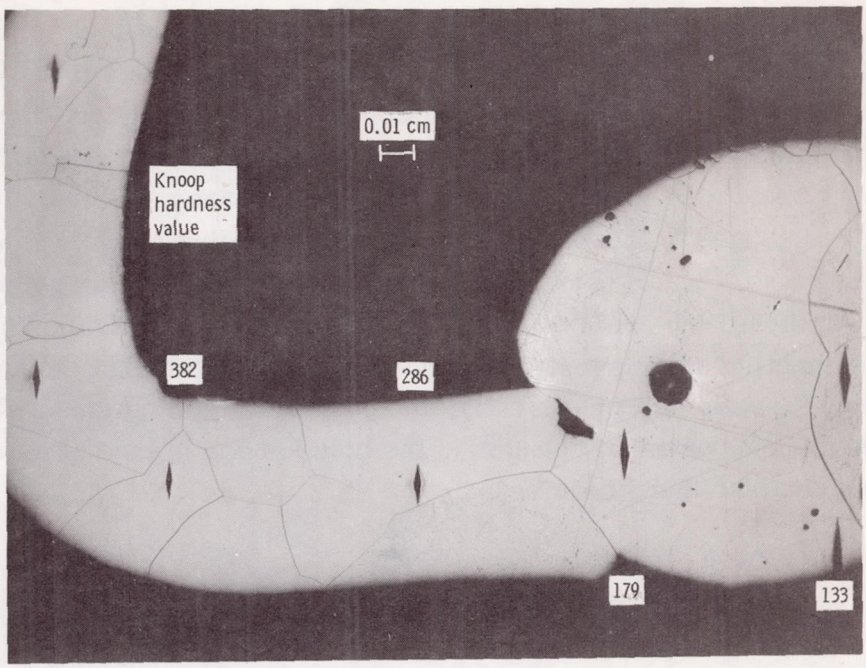



(a) As-received platinum wire.

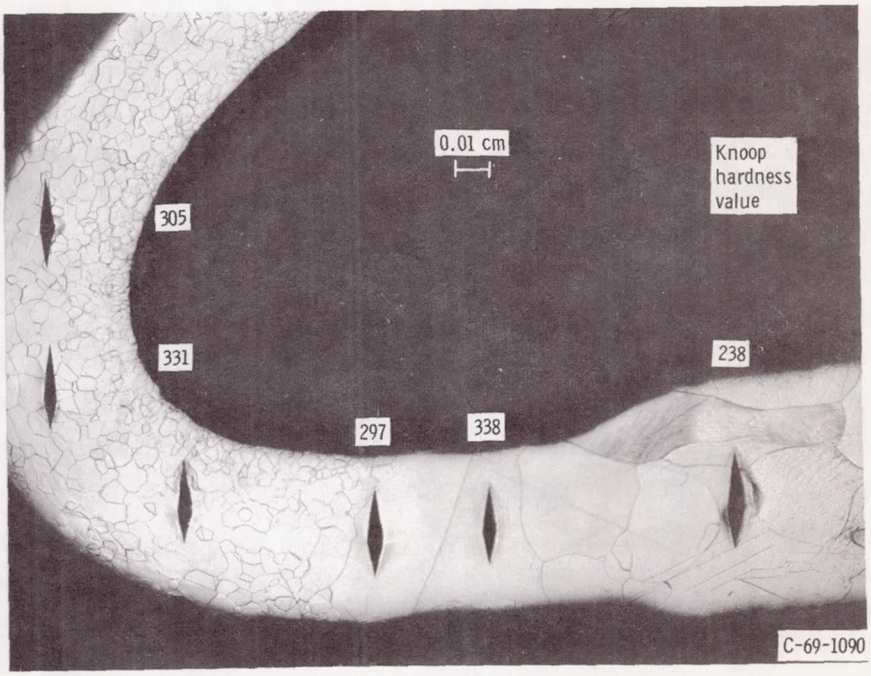



(b) 87Pt13Rh wire sample 15 centimeters from junction after testing. (Same as as-received wire.)

Figure 7. - Photomicrographs of test thermocouple.




(a) Thermocouple after test.




(b) Untested thermocouple fabricated from wire as-received.

Figure 8. - Comparison between 87Pt13Rh/Pt junction regions of tested thermocouple and untested thermocouple.

ability of mechanical failure of the thermocouple wire is increased when the wire is stressed. Hence, methods of reducing wire stresses should be an important design consideration for long-duration use of noble-metal thermocouples at high temperatures.

In order to establish the proportion of grain growth that is test induced, comparison was made with an untested thermocouple junction fabricated from test-thermocouple lead wires. This untested thermocouple is shown in figure 8(b). Note that large grains exist only in a region close to the junction bead. These grains are smaller than those in figure 8(a). The boundaries of these grains do traverse the diameter of the wire as they do in the test thermocouple. However, the wire away from the junction reveals no distinctive grain growth; here, the grain size matches the grain size in figure 7(b). The Knoop hardness at the junction of an untested thermocouple is greater than the hardness of the test-thermocouple junction. Consequently, the post-test examinations and comparisons reveal that test-induced physical changes in the junction and in the wires adjacent to the junction exist in the test thermocouple.

## SUMMARY OF RESULTS

The average thermal-emf change for the 87Pt13Rh/Pt thermocouple was determined by high-temperature recalibrations in air after 3700 hours exposure to a controlled, low-impurity environment with a mean temperature of 1530 K and a mean nitrogen equivalent pressure of $3\times10^{-8}$ torr. Wire size was 0.05 centimeter (0.020 in.) with two-hole high-purity alumina (99.5 percent) as the insulator. Also, the change in the ratio of resistance at 300 K to the resistance at 4.2 K was determined for samples of the platinum-wire leg. The change in wire-impurity concentration along the wire was determined by emission spectrographic analysis. Test-induced grain-structure change was determined with photomicrographs. The results of this study are as follows:

1. The average value of the thermal-emf change is -2.8 K, which is less than 0.2 percent of 1530 K. The spread in the data for the thermal-emf change is 1.6 K. These changes represent the minimum changes obtainable at 1530 K with present day knowledge applied to practical thermocouple designs; for most engineering applications, such changes can be neglected.

2. Resistance-ratio intercomparisons show that the direction of the resistance-ratio change matches the direction of the thermal-emf change.

3. The concentration of impurities in the wire did change, with iron having the highest concentration increase at the junction and the largest concentration gradient near the junction.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 27, 1969,
120-27-02-04-22.

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