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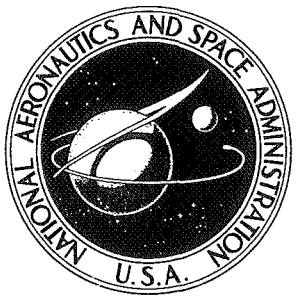

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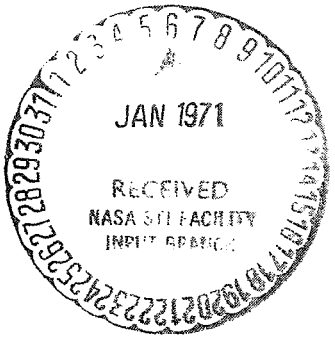

THERMAL ELECTROMOTIVE FORCE CHANGE FOR SOME NOBLE AND REFRACTORY-METAL THERMOCOUPLES AT 1600 K IN VACUUM, AIR, AND ARGON

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16. Abstract

Thermal electromotive force changes for 30 thermocouples using alumina insulators were determined in air, argon, and vacuum, at 1600 K for exposures up to 10 000 hours. Wire sizes ranged from 0.3 to 1.1 mm diameter with 0.5 mm being the most common size. An 87Pt13Rh/Pt pair exposed to air had a -5 K drift. In argon this and the 95W5Re/74W26Re thermocouple both drifted approximately -20 K. Most noble-metal thermocouples failed in a vacuum after a few thousand hours of use, while the refractory-metal thermocouples did not. Chemical and structural changes in the wires were determined by means of solids mass spectrometry, photomicrography, and hardness testing.

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SUMMARY

This experiment was undertaken to determine the thermal electromotive force changes of some commercially available thermocouple wires. Thirty pairs of noble- and refractory-metal thermocouple wires were tested, using high-purity alumina insulators and exposing the assemblies to air, argon, and vacuum environments at 1600 K for up to 10 000 hours. Thermocouple pairs of 87-platinum - 13-rhodium/platinum (87Pt13Rh/Pt) wires in air showed a maximum drift of -5 K.

Exposure in argon of 0.5-millimeter-diameter wires of 87Pt13Rh/Pt and 95-tungsten - 5-rhenium/74-tungsten - 26-rhenium (95W5Re/74W26Re) thermocouples produced drifts of approximately -20 K. The 70-platinum - 30-rhodium/94-platinum - 6-rhodium (70Pt30Rh/94Pt6Rh) thermocouple wires of the same size drifted about half as much.

Vacuum tests of the tungsten-rhenium (W-Re) alloy thermocouples were terminated by failures of tantalum test capsules; and the majority of the noble-metal thermocouple tests in vacuum were terminated by open-circuit failures.

Some smaller diameter (0.33 mm) noble-metal thermocouples behaved erratically in argon, with drifts of up to -72 K for the 10 000-hour test period.

Examination of the wires by means of solids mass spectrometry, photomicrography, and hardness testing was used to determine chemical and structural changes.

INTRODUCTION

There are several areas of aerospace-engineering research involving material studies, component testing, and complete systems operation that require the use of thermocouples over long periods of time in air, inert gas, or vacuum. One such example is a space-power system designed to operate continuously for 10 000 hours.

Under these conditions, thermoelectric stability becomes important because the investigator has to distinguish between actual temperature change and the thermal electromotive force (emf) change at constant temperature, commonly called thermocouple drift. This drift may be associated with change in the composition or structure of the thermocouple materials when exposed to a thermal gradient.

Chemical composition changes occur by exchange of material between the wires and also between the wires and the surrounding media. Some of the mechanisms involved are diffusion, chemical action, selective evaporation of an alloy constituent, or evaporation from one element and subsequent deposit and combination with the other.

Among the factors affecting drift are insulator and sheath materials, assembly geometry, fabrication method, gas environment, rate of thermal cycling, and nuclear radiation environment, if present.

Walker, Ewing, and Miller (ref. 1) indicated that the major cause of drift in noble-metal thermocouples using alumina insulators involved contamination of the wires by iron transferred from the insulator. The magnitudes of the changes were directly related to the amount of the impurity present in the various grades of insulators. One test in their series of experiments was performed on 87Pt13Rh and platinum thermocouple wires fired in various grades of alumina insulators in argon at 1650 K for 120 hours. The wires were then removed from the test furnace, and the thermal emf change for each wire was determined by recalibration in a separate calibration furnace. In this furnace the wires were subjected to a gradient extending from the junction at a temperature of 1130 K to room temperature. From the results, one can calculate that, for a low-purity insulator, the maximum change for an 87Pt13Rh/Pt thermocouple pair was -96 K, and, for a high-purity insulator, the change was a negligible -2 K. (A negative sign represents a drop in emf.)

Zysk (ref. 2) reports that silicon contamination, particularly in the pure platinum leg of a platinum-rhodium alloy/platinum thermocouple, causes both thermal emf change and mechanical failure. Mechanical failure is explained by the fact that, in pure metals, large grains will grow when the material is subjected to high temperature for long periods of time, resulting in structural weakening. In the case of platinum, when silicon is present, a platinum-silicon eutectic can form and enter the grain boundaries. This attack in the grain boundaries affects the output emf as well as accelerating structural failure. Zysk furthermore stated that some investigators observed erratic output signals prior to an open-circuit failure.

Metcalfe (ref. 3) postulated that the addition of rhodium to the pure platinum leg would make a thermocouple less susceptible to contamination, and he successfully developed and used an 87Pt13Rh/99Pt1Rh thermocouple. This approach eventually led to the introduction in Germany of commercially available 70Pt30Rh/94Pt6Rh thermocouples. At the National Bureau of Standards, Burns and Gallagher (ref. 4) did extensive work on

preparing calibration tables and qualifying the 70Pt30Rh/94Pt6Rh thermocouple for more general acceptance.

Hendricks and McElroy (ref. 5) tested 90Pt10Rh/Pt and 70Pt30Rh/94Pt6Rh thermocouples in high-purity alumina insulators at 4×10^{-8} torr and 1720 K for 1000 hours and found both thermocouple pairs to be stable to within ±10 K.

Szaniszlo (ref. 6) reports a test of 87Pt13Rh/Pt thermocouples in high-purity alumina insulators at 3×10^{-8} torr and 1530 K for 3700 hours. An electrostatic mass spectrometer was used to determine gas composition in the vacuum system, and chemical, electrical, and mechanical changes were examined through the use of emission spectroscopy, wire resistivity measurements, photomicrography, and hardness testing. The measured drift was approximately -3 K for the 3700-hour exposure.

Rudnitskii and Tyurin (ref. 7) report a drift test of two noble-metal thermocouple pairs, with alumina insulators, in air at 1820 K for 400 hours. The change in emf of the 90Pt10Rh/Pt thermocouple was -75 K, and the 70Pt30Rh/94Pt6Rh thermocouple drifted -38 K. This is a rather severe deviation for an air environment test; unfortunately the report gives no indication of the purity of the insulators. However, one may note that the drift of the 70Pt30Rh/94Pt6Rh thermocouple was approximately one half the drift of the 90Pt10Rh/Pt thermocouple.

When aerospace and nuclear technology advanced to the state of requiring measurements at temperatures and in environments not suitable for the use of noble-metal thermocouples, investigation of refractory-metal thermocouples was accelerated. This led to the development and commercial production of tungsten-rhenium alloy thermocouples. A great deal of investigation was done in this area (refs. 8 to 13), but, since much of it dealt with material studies and applications not specifically relevant to the scope of the present report, only that reported material that appears pertinent will be presented. Perhaps one of the most significant conclusions to be reached from the studies is that it takes a determined effort to control the purity and processing of the thermocouple assembly to achieve reliability and accuracy at the higher temperatures.

Fanciullo (ref. 14) measured the drift of several 95W5Re/74W26Re thermocouples using high-purity alumina insulation in a 99Cb1Zr sheath that was exposed to an inert-gas environment at 1370 K for 10 000 hours. The resultant drift averaged -10 K.

Hendricks and McElroy (ref. 5) tested 95W5Re/74W26Re thermocouples in a high-purity alumina insulator at 4×10^{-8} torr and 1720 K for 1000 hours and found them to be stable within ±10 K.

Hall and Spooner (ref. 15) report drift rates of -0.9 K per 1000 hours for 95W5Re/74W26Re thermocouples in argon at 1370 to 1870 K for periods of 1000 to 4000 hours. A summary of the results of the investigations just cited is presented in table I.

It becomes readily apparent from a review of work relating to drift studies that many variables are involved and any single investigation, being limited in scope, does

TABLE I. - SUMMARY OF RESULTS OF PREVIOUS INVESTIGATIONS

(a) Noble-metal thermocouples

Thermocouple	Temperature, K	Time, hr	Environment	Relative purity of alumina insulator	Drift, K	Reference number
87Pt13Rh/Pt 87Pt13Rh/Pt	1650	120	Argon	High Low	[a]-2 [a]-96	1
90Pt10Rh/Pt 70Pt30Rh/94Pt6Rh	1720	1 000	Vacuum	High	±10	5
87Pt13Rh/Pt	1530	3 700	Vacuum	High	-3	6
90Pt10Rh/Pt 70Pt30Rh/94Pt6Rh	1820	400	Air	Not stated	-75 -38	7

(b) Refractory-metal thermocouples

95W5Re/74W26Re	1370	10 000	Inert	High	-10	14
95W5Re/74W26Re	1720	1 000	Vacuum	High	±10	5
95W5Re/74W26Re	1370 to 1870	1000 to 4000	Argon	No insulator	-0.9/1000 hr	15

[a]Recalibrated at 1130 K.

not reveal a general solution, but merely supplies limited information usually relating to a particular application. Furthermore, failure to completely define the variables involved results in apparent contradictions and causes difficulty in correlating the results of several investigators.

The present investigation was intended not to study the effect of all possible operating conditions, but rather to establish the drift that might result when thermocouple-assembly materials, construction, and usage were selected, in advance, to minimize drift. Selection was based on the best judgment that could be exercised from results previously reported by others. To this end, for example, thermocouple materials were of the best grade commercially available. Construction and test installation were such that mechanical strain on the wires was minimized. Additional precautions taken will be described in the next section.

This report compares the relative merits of some commercially available thermocouple wires in high-purity alumina insulators exposed to air, argon, and vacuum at 1600 K for up to 10 000 hours. These tests were performed simultaneously in one test installation. The thermocouples tested were 87Pt13Rh/Pt, 70Pt30Rh/94Pt6Rh, and

95W5Re/74W26Re. These thermocouples were chosen because the first is a common type with a wide background of published information, the second should potentially have better drift characteristics than the first, and the third is commercially available and, although usually used at a temperature level higher than that of the present test, it appeared to be a likely candidate for long-term use at the lower temperature level.

During the testing, measurements were made of the thermocouple drift, the purity of the argon environment, and the gas composition in the vacuum environment. Post-test analyses were made to determine the compositional and structural changes in the thermocouple wires.

FACTORS AFFECTING THE STABILITY OF A THERMOCOUPLE

The selection of a thermocouple assembly that is to be stable over long periods of time involves considerations of the many factors that influence the magnitude of emf change. Some of these factors present choices in the design selection, and others are related to the operating conditions.

A general list of factors relating to thermoelectric drift may be grouped as follows:

(1) Design selection
- (a) Wire type
- (b) Wire diameter
- (c) Sheath material
- (d) Insulator
- (e) Assembly geometry
- (f) Fabrication method and its control

(2) Operating conditions
- (a) Temperature level
- (b) Time
- (c) Temperature gradient
- (d) Environmental gas
- (e) Pressure level
- (f) Thermal cycling
- (g) Nuclear radiation

The selection of the type of wire is usually made on the basis of the application temperature range and previous experience of the drift characteristics of the wire.

Wire diameter is often compromised by the size and geometry of the assembly necessary to fit the application. However, it is reasonable to conclude that if some impurity in the environment is available to cause degradation, then for the same conditions a smaller wire will be degraded more than a larger wire, the surface-to-volume ratio

being greater for the smaller wire. Walker, Ewing, and Miller (ref. 1) have shown such a size-stability relation for some environments.

If the thermocouple assembly includes a sheath, then the sheath must be compatible with the external environment as well as with the components it contains.

The type and purity of the insulator have been shown by many investigators to be of prime importance, as previously discussed in this paper.

Although the geometry of the thermocouple assembly is usually dictated by size and mechanical considerations, possible variations in insulator geometry, clearance between wire and insulator and between insulator and sheath, and metallic foil barriers (ref. 14) can be considered for preventing or decreasing contamination among the elements of the assembly.

Quality control during fabrication is necessary to prevent the introduction of contaminants into the assembly.

Exposure time and temperature level are both important factors contributing to the magnitude of drift for a particular system. The importance of the location of the thermal gradient in the application and in post-test evaluation for drift have been emphasized by Browning and Miller (ref. 17), and by Moffat (ref. 18).

The nature of the environmental gas, namely, whether it is oxidizing, neutral, or reducing, will govern the kinds and degree of compositional changes that occur. Even in the case of a vacuum application, possible backstreaming of hydrocarbons from the diffusion-pump system must be prevented by proper cold trapping, and the release of constituents in the system due to outgassing at high temperatures must be considered as part of the reactant environment.

The pressure level affects the rate of change in composition because of selective evaporation in alloy wires.

Villamayor (ref. 19) has reported an emf change related to thermal cycling rate for bare and insulated 95W5Re/74W26Re thermocouples.

The final consideration in the list of factors involves the effect of nuclear radiation on the wire composition. Compositional changes can occur by transmutation resulting from the production of a radioactive isotope, which decays into an isotope of a different element. The effect of this change in material on the drift is, however, dependent on the magnitude and location of the thermal gradient in the application (ref. 17).

The present investigation involves consideration of the aforementioned factors with the exception of the last two items, namely, thermal cycling and nuclear radiation.

APPARATUS

Figure 1 is a schematic of the overall test system, which is composed essentially

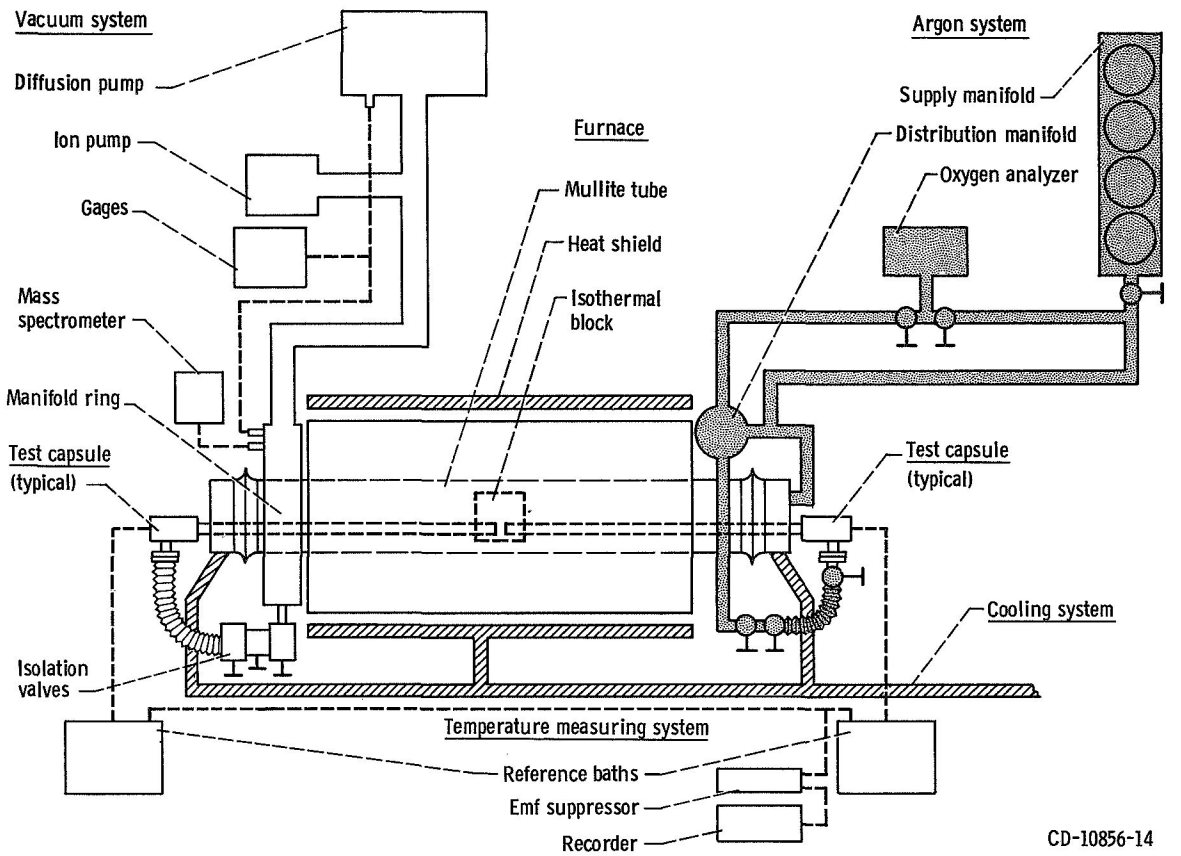


Figure 1. - Overall test system.

of the following subsystems and their instrumentation: (a) furnace, (b) test capsules, (c) vacuum system, (d) argon system, (e) cooling system, and (f) temperature measurement system.

Furnace

General description. - The test furnace was a muffle-type furnace using a vitreous refractory mullite tube, 20.3 centimeters in diameter, with a 0.95-centimeter wall, and 168 centimeters long. The internal configuration of the furnace tube and end-plate assembly detail are shown in figure 2. A 29-kilogram cylindrical molybdenum block was placed in the center of the furnace to provide a uniform temperature zone; the block had 18 holes (nine in each end) for insertion of thermocouple test capsules. Molybdenum guide tubes leading to the immersion holes in the block were free to expand because they were attached to a free-sliding internal end plate. There was a separate guide tube

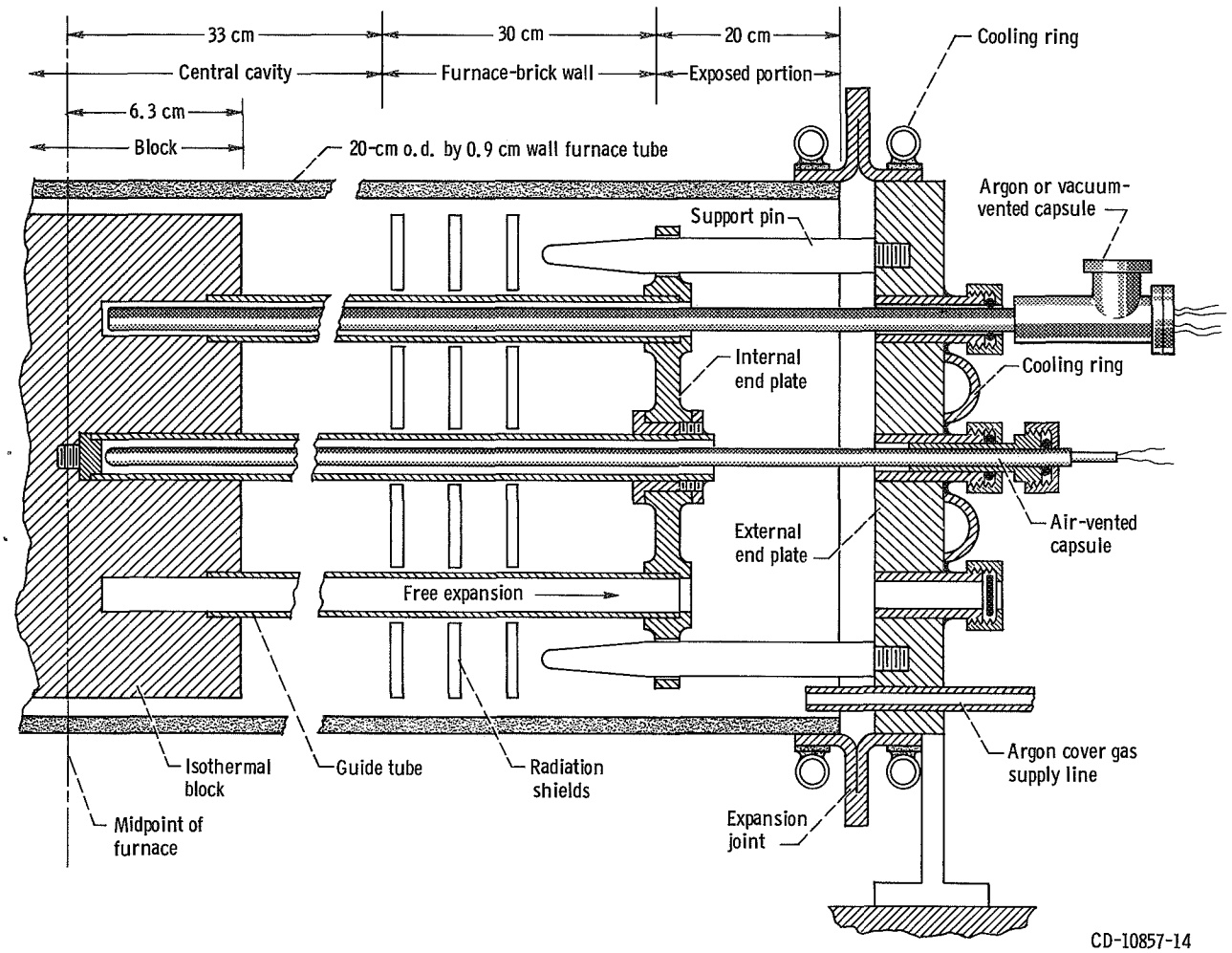


Figure 2. - Furnace tube assembly, with details of internal structure and external end plate.

for each test capsule. Radiation shields placed along the guide tubes decreased the radiant heat loss from the block to the water-cooled end plates. A flexible silicone-rubber joint with water-cooled clamping rings connected the furnace tube to anchored end plates and allowed the tube to expand freely in an axial direction. The external end plates contained compression fittings, coaxial with the guide tubes, to hold and seal individual test-capsule assemblies. After the internal assembly was completed, the mullite tube was sealed, evacuated, and backfilled with high-purity argon. An absolute pressure of 1.2×10^5 newtons per square meter (1.2 atm) was maintained in the system during the test period.

Furnace temperature control. - The furnace used silicon carbide rods for resistance heating, was rated at a 30 kilovolt-ampere peak load, and used approximately 10 kilovolt-amperes at the test-operation temperature of 1600 K. In the event of failure of the electrical power supply to the furnace and its subsystems, an automatic transfer

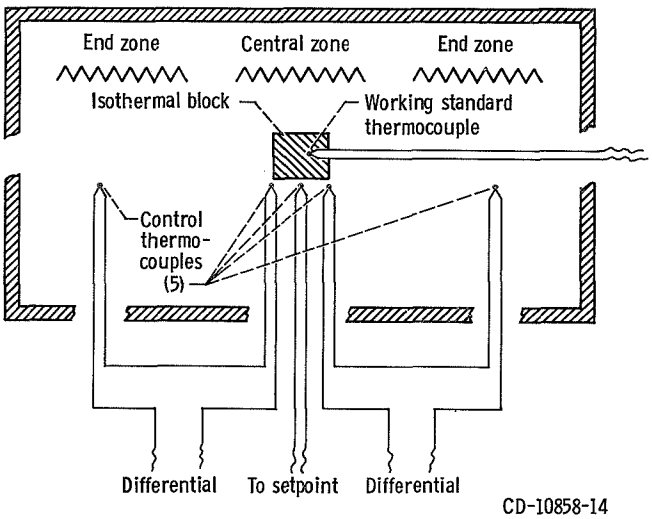


Figure 3. - Control thermocouple system with working standard thermocouple for set point adjustment.

switch would select an alternate power source to prevent accidental termination of the test. For purpose of control, the silicon carbide heating rods were distributed in the furnace cavity and electrically wired in such a manner as to form three heating zones. A schematic of the control system is shown in figure 3. Power to the central heating zone was controlled by an error signal between a set point selector and a furnace control thermocouple (87Pt13Rh/Pt), which monitored the temperature of the central zone. This error signal was fed to a direct-current null detector whose output in turn went to a current-adjusting controller with adjustable proportional band, reset, and rate compensation. The output from the controller went through a magnetic amplifier to saturable-core reactors that varied the power to the heating rods. The control of the two outer zones was similar to the control of the central zone except that the error signal was the emf generated by a differential control thermocouple system that sensed the temperature difference between the central zone and the respective outer zone. Functionally then, this control system is such that the central zone temperature is controlled around a selected set point and the two outer zone temperatures equal the central zone temperature. All of the control thermocouples were inserted into closed-end ceramic tubes vented to the atmosphere at the connector end. The thermocouple wire insulators and ceramic tubes were hard-fired, high-purity alumina.

Although it has been reported that platinum-rhodium thermocouples are very stable in an air environment, it was anticipated that the control thermocouples would be subject to a small degree of drift over the 10 000-hour exposure time and that a set-point adjustment would have to be made to correct for the central control-thermocouple drift.

To accomplish this, an air-exposed test thermocouple could be periodically removed (about once every 1000 hr) from the center of the molybdenum block and replaced by a

calibrated 87Pt13Rh/Pt working standard. This working standard would remain in the block just long enough (about 20 min) to insure accurate test-block temperature measurement; at other times it was carefully stored in a clean tube at room temperature. The furnace central-zone set point could then be adjusted whenever the working standard indicated a change in block temperature from the initial set point. This refinement of maintaining test-block temperature to within a few degrees was introduced because it was easy to do and it provided a check on the control system.

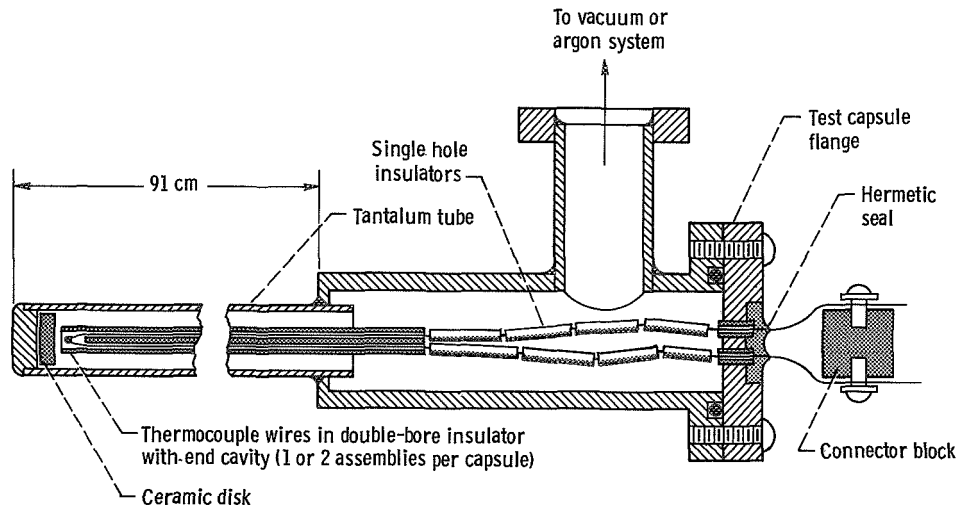
It will be noted later, however, that the drift measurements of the test thermocouples involved only temperature-difference measurements, so that the results would be independent of the exact block temperature level, provided the approximate temperature level were maintained.

Test Capsules

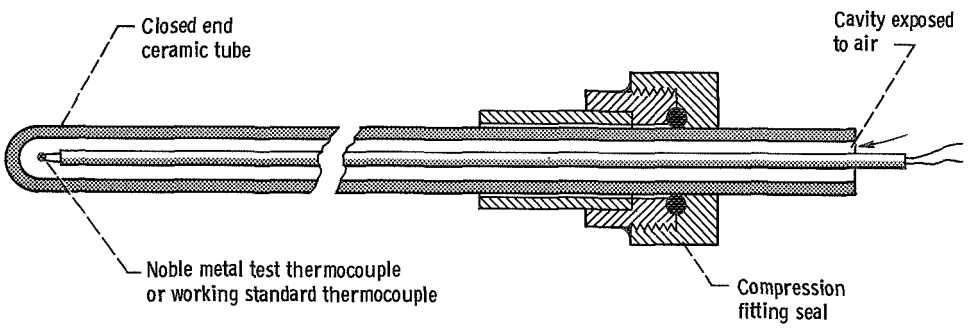
Two types of test capsules to contain the thermocouple assemblies were used to allow a choice in the gas environment surrounding the thermocouple assembly. A thermocouple assembly consists of a calibrated pair of thermocouple wires in a two-hole insulator. One type of capsule (fig. 4(a)), which exposed a tantalum-tube plenum in the hot zone, was used to contain either a vacuum or argon environment. Each of this type of capsule contained one or two thermocouple assemblies. The other type of capsule (fig. 4(b)) used a high-purity-alumina closed-end tube and was vented to the atmosphere, to afford an air environment for its thermocouple assembly. Each of this type of capsule contained one thermocouple assembly. With this arrangement, assemblies exposed to air, argon, and vacuum environments could all share the same isothermal block. All ceramic exposed to the test environments was recrystallized alumina of not less than 99.5 percent purity. In the test capsules that contained two thermocouple assemblies, care was taken to use random lengths of ceramic so chosen that the interface between two pieces of ceramic of a particular thermocouple assembly did not lie adjacent to the interface of the other thermocouple assembly sharing the capsule. This was done to prevent possible line-of-sight exchange of wire material from one thermocouple assembly to the other.

Thermocouple junctions were formed by arc welding in an inert-gas atmosphere. Copper chill blocks were used to hold the tungsten-rhenium alloy thermocouples during welding to reduce the length of the embrittled heat-affected zone, as suggested by reference 15.

Tantalum tubing used in capsule plenum construction was degreased in trichloroethylene vapor, pickled in an aqueous solution of nitric and hydrochloric acid, flushed with distilled water, and dried with hot air. During fabrication and assembly, thermo-



(a) Test capsule for argon and vacuum environments.



(b) Test capsule for air environment.

Figure 4. - Test capsules containing thermocouple assemblies.

couple wires, insulators, and refractory-metal components subjected to the test environments were handled with clean-room-type nylon gloves and were stored in polyethylene bags.

Table II lists the wire diameter and number of each type of the 30 thermocouples tested in air, argon, and vacuum environments. All types included pairs of 0.51-millimeter-diameter wires, so that a common size could be used for intercomparison of results in the various environments.

Vacuum System

The primary vacuum pumping system equipment was a 10-centimeter oil diffusion

TABLE II. - THERMOCOUPLE WIRE PAIRS TESTED

Thermocouple pair	Wire diameter		Number of thermocouples tested		
	B. & S. gage	mm	In air	In vacuum	In argon
87Pt13Rh/Pt	28	0.33	-	3	3
	24	.51	1	3	3
	20	.81	1	-	-
	17	1.12	1	-	-
70Pt30Rh/94Pt6Rh	24	0.51	-	3	3
95W5Re/74W26Re	24	0.51	-	5	4

pump using silicone oil with a freon-refrigerated cold trap held at 250 K. The pump had an effective pumping speed at the system inlet port of 300 liters (0.3 m^3) per second at a pressure of 100 microtorr, with an ultimate pressure in the mid 10^{-7}-torr range. A secondary 140 liters (0.14 m^3) per second ion pump operated in parallel with the primary diffusion pumping system. The main purpose of the ion pump was to hold system pressure in the event of nonelectrical failure of the primary system. If such an event occurred during testing, a pneumatically operated valve was arranged to automatically isolate the primary pump from the rest of the vacuum system. The vacuum pumping stations were connected to a manifold ring positioned around the external portion of the furnace tube by 10-centimeter-diameter stainless-steel piping. Three thermocouple-type thermal conductivity gages were used in the pumping system to measure pressures during initial phases of system pump down, and three Bayard-Alpert ionization gages were used during testing. One ionization gage was positioned at the throat of the primary pump and two (one for redundancy) were positioned in the vacuum-system manifold ring (fig. 5). An electrostatic mass spectrometer tube was also fitted into the manifold to monitor gas composition in the ring. Individual test capsules were connected to the manifold by flexible metal tubing with appropriate isolation valving (fig. 5). All the test capsules connected to the vacuum system were inserted at one end of the furnace tube, while all of the argon environment capsules were at the opposite end. Capsules vented to the air were inserted in both end plates. A portable helium leak detector was available on site to locate any vacuum system leaks occurring during test operation.

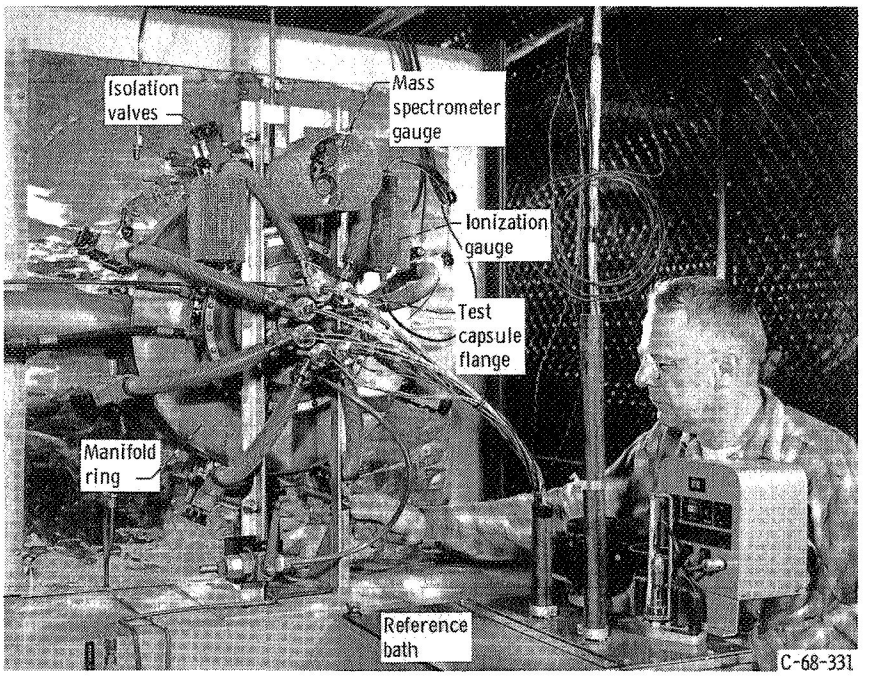


Figure 5. - Vacuum system manifold ring.

Argon System

Several bottles of argon containing less than 2 ppm of oxygen and less than 5 ppm of water were connected to a standard high-pressure manifold (fig. 1). A metal-diaphragm pressure regulator reduced the manifold pressure to a system pressure of 1.2×10^5 newtons per square meter (1.2 atm). The main branch of the argon system was connected to two cylindrical manifolds located adjacent to the external portion of the furnace tube. These manifolds, through flexible tubing and appropriate valving, fed the individual test capsules containing an argon environment. The argon was essentially dead ended in the test capsules, the only circulation being due to free convection. A second supply line branched off from the main line to supply an argon cover-gas inside the muffle-furnace tube. Two sampling lines, one originating near the supply-manifold pressure regulator, and the other coming from the capsule distribution manifold, were connected to a galvanic-cell oxygen analyzer for on-the-line monitoring of oxygen content in the argon system. The analyzer had a range of 0 to 10 ppm with an inaccuracy of ±5 percent of full scale.

Cooling System

A water cooling system was necessary to supply the diffusion pump, furnace end

plates, and expansion joint clamps and for two cooling coil heat shields hung adjacent to the sides of the furnace to absorb heat that would have normally been rejected to the room (figs. 1 and 5).

Temperature Measurement System

Thermocouple wire was run from the test-capsule connector blocks to stirred constant-reference-temperature oil baths (figs. 1 and 5). These connecting wires were from the same lots or spools as the test-capsule wire to which they were attached. The wires were joined directly to each other at the connector block; the block itself was of insulating material and merely furnished mechanical support. Thus, the thermocouple circuit extending from the junction to the reference bath was composed entirely of calibrated pairs of thermocouple-grade wire. Shielded copper wiring was then brought out of the baths, through an emf-suppression system and into two 24-point, 2-millivolt span, strip-chart recorders. The emf recording system contained calibration circuits whereby, through appropriate switching, emf's could be periodically introduced into the circuit with a calibrated precision potentiometer at a circuit location equivalent to a capsule electrical connector, to check zero setting, linearity, and stability of the electrical recording system.

APPARATUS PERFORMANCE

Furnace and Reference Temperature

The furnace was brought to the test point temperature at a rate not exceeding 20 K per hour. This heating rate was necessary to prevent thermal shock rupture of the large ceramic furnace tube.

The set-point controller established an initial operating temperature of 1593 K, as determined by the working-standard thermocouple, and this temperature level was maintained to within ±2 K during the 10 000-hour test, by the method previously described in the section Furnace temperature control. It was necessary to adjust the control set point only about three times during this period to correct for the drift of the control thermocouple.

Thermocouple drift was determined by the indicated change in temperature difference between the reference block and each test thermocouple as a function of time. This method eliminated the need of keeping the block at one fixed temperature. About 300 data points were taken for each test thermocouple that completed the 10 000-hour test period.

The reference-block temperature existing at the time a set of data (30 points) was recorded was taken to be the corrected temperature of one of the 87Pt13Rh/Pt, air-exposed test thermocouples, which was used as a reference. This reference thermocouple was subject to a systematic drift amounting to -4.8 K at the 10 000-hour end point; however, its drift was determined directly by periodically comparing its output with the output of the calibrated 87Pt13Rh/Pt working standard that was placed in the test capsule just long enough to measure true block temperature. Thus, after completing all the tests, a drift curve was generated for the reference thermocouple; then this curve was used as a correction curve to establish block temperature at any previous time.

Figure 6 shows one side of the furnace centerline axial temperature profile from the

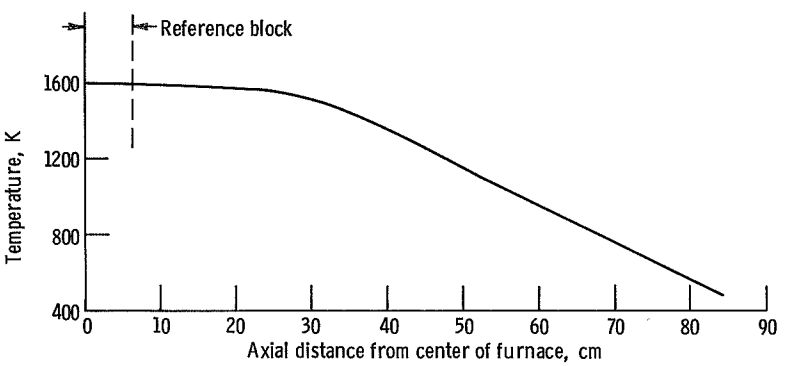


Figure 6. - Furnace axial centerline temperature profile.

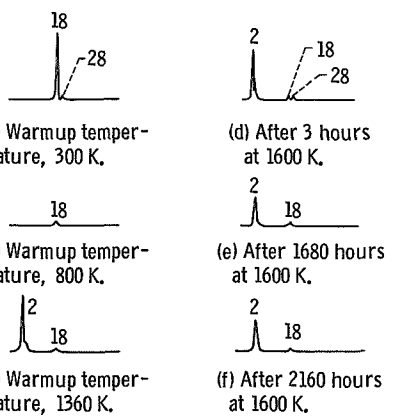
center of the block to one end of the furnace tube. A survey of the other side indicated symmetry in both directions.

Vacuum Level and Composition

The mean nitrogen-equivalent pressure of the vacuum manifold ring was monitored with the ionization gage during the tests. After initial vacuum-system pump down and furnace warmup to the test temperature, the pressure in the manifold ranged between 3×10^{-6} and 5×10^{-6} torr. At about 3100 hours test time, the pressure in the manifold was observed to be slowly rising with time. A systems check indicated that one of the tantalum plenums of a test capsule was leaking. This individual capsule had to be isolated (see isolation valves, figs. 1 and 5) from the pumping system after 3480 hours; subsequently, as other tantalum plenums failed, they also were valved off, with the final vacuum capsule shut down at 4080 hours. The capsules were always isolated before vacuum manifold pressure exceeded 8×10^{-6} torr.

Failure and subsequent shut down of the vacuum system prematurely ended the vacuum-exposed refractory-metal thermocouple test. However, the vacuum-system failure did not essentially affect the noble-metal thermocouples exposed to the vacuum environment because the majority of this type failed physically, prior to vacuum-system failure. The thermocouples undergoing tests in the air and argon environments were not affected by vacuum-system shutdown and continued performing to 10 000 hours or to their failure point, whichever came first.

Gas composition in the vacuum ring was periodically monitored by the electrostatic mass spectrometer system. Gas composition after initial pump down and during warmup at furnace temperatures of 300, 800, and 1360 K, are shown in figures 7(a) to (c). Rel-



(a) Warmup temperature, 300 K.

(b) Warmup temperature, 800 K.

(c) Warmup temperature, 1360 K.

(d) After 3 hours at 1600 K.

(e) After 1680 hours at 1600 K.

(f) After 2160 hours at 1600 K.

Figure 7. - Gas composition in vacuum manifold ring during furnace warmup and at test temperature. Peaks are labeled with the molecular weight.

ative amplitudes indicate relative gas concentrations if equal ionization efficiencies are assumed for all gases indicated. Molecular weights of 18 and 28 appeared at the low-temperature levels with 2 appearing and being the main constituent at 1360 K. When the furnace reached its operating temperature of 1600 K, a molecular weight of 2 was still predominant, with small amounts of 18 and 28 appearing (fig. 7(d)). The compositional changes from this point on essentially amounted to small traces of molecular weight 44 appearing periodically, the disappearance of the 28 indication, and a slow diminishing of the amount of molecular weight 2. The background finally stabilized into a fixed quantity of molecular weight of 2 and 18 as shown by figures 7(e) and (f), which are from records taken 480 hours apart.

When the vacuum system pressure began to rise because of individual tantalum-plenum leaks, allowing argon to be drawn into the vacuum system from the mullite furnace-tube interior, a molecular weight of 40 was indicated on the mass spectrometer.

It should be noted that the gas-composition gage and vacuum-system gages were mounted in the vacuum ring, since the gages could not be subjected to internal furnace conditions. The actual pressure in the vacuum test capsules therefore would be higher than that indicated by the measuring system. Likewise, the gas composition in the higher temperature region of the test capsule could be different from that indicated in the colder manifold. Furthermore, the fact that the vacuum manifold ring was not baked out would account for the continued presence of water vapor, as indicated by a molecular weight of 18. This constituent is commonly found in vacuum systems which have not been baked out.

An explanation for the presence of a constituent of molecular weight of 2 can be related to the tantalum test-capsule tubes. Hydrogen is used in the metallurgical processing of refractory metals. In the case of tantalum the solubility of hydrogen increases with decreasing temperatures; thus hydrogen can be absorbed during a cooling cycle. Conversely, the absorbed hydrogen can be released by heating in a vacuum. Reference 20 relates that the release will occur by heating above 870 K in a 10^{-6} torr vacuum. These conditions, of course, were reached in the present tests, so that it is quite likely that the constituent of mass 2 is hydrogen being released from the tantalum.

Argon Purity

During the 10 000-hour test period, measurements with the oxygen analyzer indicated from 0.2 to 0.9 ppm of oxygen at the argon-system-regulator sampling station and 0.5 to 1 ppm of oxygen at the argon-capsule distribution manifold.

Accuracy in Drift Determination

One method of calibrating immersion temperature sensors at a given temperature is to place the devices in holes located in a high-heat-capacity isothermal block and compare their output with a reference device placed in another hole in the block. If the block is not truly isothermal this will introduce an error in the calibration.

If the test system is used to determine test-sensor drift over a long period of time at a given temperature level, it is not essential that the test block be absolutely isothermal nor must the test-block temperature level remain at an absolute fixed value. It is only essential to accurately determine for each set of data (taken at a given time) the temperature of the reference hole and the change in the initial difference between this reference-hole temperature and the temperature indicated by each test device. The added provision is that the block temperature distribution remain constant with time and temperature

level. These considerations, along with the long-term stability of the recording system, are involved in determining the accuracy of the experiment.

Applying these factors to the present tests, the specific considerations are the long-term stability of the temperature distribution in the high-temperature isothermal block, the constancy of the temperature in the cold-junction reference bath, the voltage stability of the emf-suppression device, and the readability and reproducibility of the recorders.

The test thermocouples were equally spaced on a 5 centimeter radius circle centered about the reference thermocouple in the isothermal block. At the starting time of the experiment, the difference in temperature between the center hole and the circumferential test holes varied between 0.4 and 0.3 K. A final check of temperature difference between one test hole and the center reference hole after 10 000 hours was within 0.1 K of the difference at zero hour. These two tests thus showed that the initial spatial variation of temperature within the isothermal block was negligibly small and also indicated a negligible change after 10 000 hours. The junction reference bath temperature was held constant to within ±0.1 K.

The voltage stability of the emf-suppression device was checked periodically during the experiment. The suppression values remained constant to within ±3 microvolt or about ±0.2 K.

The recorders were basically used as indicators in that the zero, mid-, and full-scale values were checked before each readout, and adjustments were made when required. So the error introduced by the recorders was due to readability and reproducibility, which was about ±5 microvolts or ±0.4 K.

The square root of the sum of the squares of the above errors is ±0.5 K. This estimate of error includes both random scatter of the experimental data and uncertainty in the knowledge of systematic factors that appear in the experiment.

TEST RESULTS

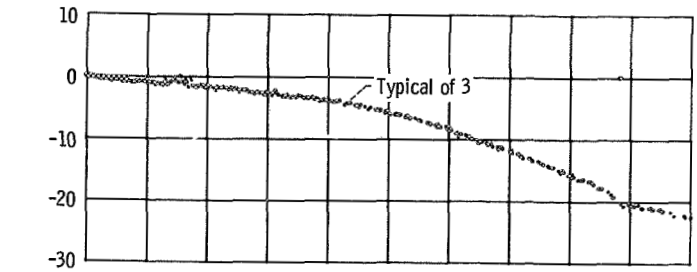
Table III presents a summary of the drift-test results, indicating the period of time each thermocouple was tested, the reason for test termination, and the magnitude of drift at test termination time.

Figures 8 to 12 are plots of drift for various selected pairs, arranged to facilitate comparison of results. The curves presented in these figures are data from a single test thermocouple that has been selected as typical for the several thermocouples of each type tested. The data points plotted show the typical variation in the rate of change of drift with time for each case. The data points forming the curves of figures 8 to 12 were machine plotted as part of the computer program used in data reduction.

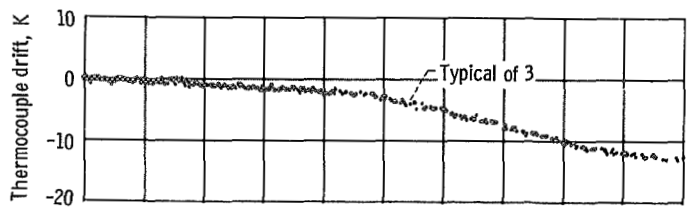
TABLE III. - SUMMARY OF DRIFT TEST RESULTS

Thermocouple pair	Environment	Wire diameter, mm	Time tested, hr	Final drift, K	Cause of termination
87Pt13Rh/Pt	Argon	0.51	10 000	-18.8	Test completed
				-22.6	Test completed
				-27.6	Test completed
		0.33	5 660	-19.2	Open circuit
			10 000	-58.8	Test completed[a]
			10 000	-71.8	Test completed[a]
	Vacuum	0.51	1 610	-1.5	Open circuit
			1 760	-2.6	Open circuit
			1 970	-4.7	Open circuit
		0.33	3 170	-6.8	Open circuit
			3 430	-8.0	Open circuit
			4 080	-8.5	Capsule failure
	Air	1.12	10 000	2.9	Test completed
		.81	10 000	-.1	Test completed
		.51	10 000	-4.9	Test completed
70Pt30Rh/94Pt6Rh	Argon	0.51	10 000	-7.2	Test completed
				-12.7	Test completed
				-18.1	Test completed
	Vacuum	0.51	2 780	-3.2	Open circuit
			2 950	-4.0	Open circuit
			4 110	-4.7	Capsule failure
95W5Re/74W26Re	Argon	0.51	10 000	-21.1	Test completed
				-21.6	Test completed
				-22.2	Test completed
				-22.5	Test completed
	Vacuum	0.51	3 480	-14.3	Capsule failure
			3 480	-15.3	Capsule failure
			3 700	-15.9	Capsule failure
			3 860	-15.4	Capsule failure
			3 860	-15.7	Capsule failure

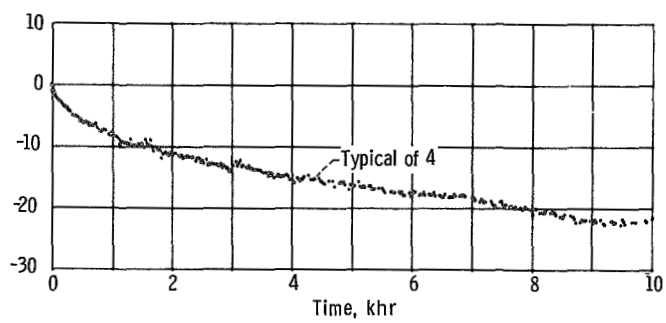
[a]Erratic signals during test.



(a) Thermocouple, 87Pt 13Rh/Pt.



(b) Thermocouple, 70Pt 30Rh/94Pt 6Rh.



(c) Thermocouple, 95W 5Re/74W 26Re.

Figure 8. - Drift of 0.51-millimeter-diameter thermocouples in argon at 1600 K for 10 000 hours.

Drift in Argon

Figure 8 shows the typical drift for 0.51-millimeter-diameter wire of the three types of thermocouples tested in argon. It is interesting to note the similarities and differences in the shapes of the curves generated over the 10 000-hour period. The drift of the two noble-metal thermocouples can be described as approximately linear for the first 4000 hours and nonlinear thereafter. The converse is true for the 95W5Re/74W26Re thermocouple, which responded in a nonlinear manner for the first 4000 hours but was approximately linear the remaining 6000 hours.

The average magnitude of the drift for both the 95W5Re/74W26Re and the 87Pt13Rh/Pt was about the same (averaging -22 K) at the end of 10 000 hours. However, the consistency of the drift was higher for the refractory-metal thermocouples than for

the noble-metal thermocouples. Table III shows that the four 95W5Re/74W26Re test thermocouples were at this time in closer agreement (1.4 K spread) with each other than were the three 87Pt13Rh/Pt thermocouples (8.8 K spread).

The drift (-13 K) of the typical 70Pt30Rh/94Pt6Rh thermocouple in argon (fig. 8(b)), was about one half the drift for the other two types. It should be noted, however, by again referring to table III, that the spread (10.9 K) among the three 70Pt30Rh/94Pt6Rh thermocouples in argon was close to the spread among the three 87Pt13Rh/Pt thermocouples in argon.

Drift in Vacuum

Figure 9 shows the drift for the same size of wire and the same thermocouple types as shown in figure 8, but for the case of a vacuum environment. The tests of the noble-metal types were essentially ended by open-circuit failure. Up to the time of failure, the 87Pt13Rh/Pt thermocouple in vacuum performed similarly to the same size and type in argon, but the 70Pt30Rh/94Pt6Rh thermocouple had a drift in vacuum approximately twice that of its like kind in argon.

The testing of the 95W5Re/74W26Re thermocouples in vacuum was terminated between 3480 and 3860 hours by test-capsule failures. However, the drift curve generated

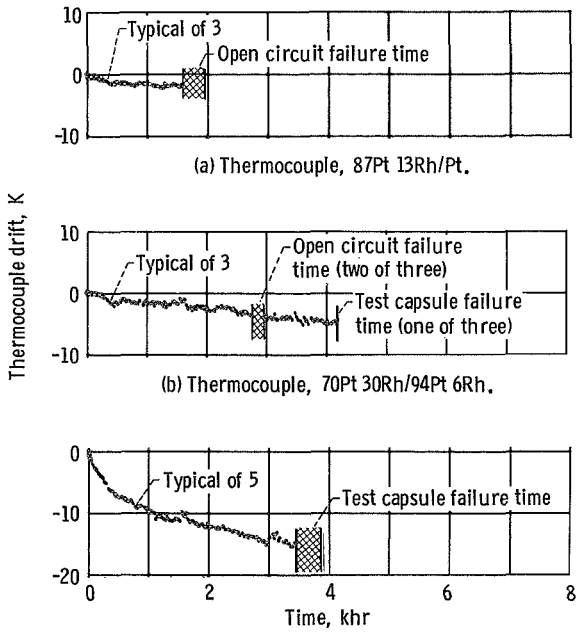


Figure 9. - Drift of 0.51-millimeter-diameter thermocouples in 10^{-6} torr vacuum at 1600 K.

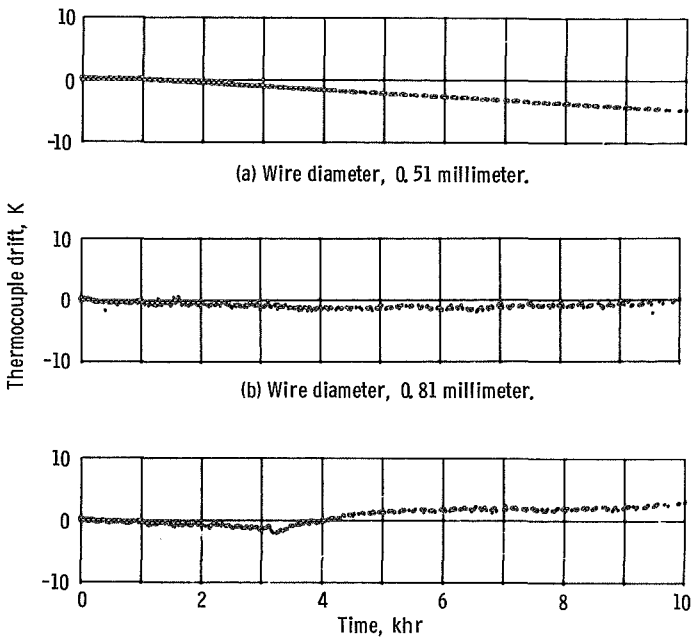


Figure 10. - Drift of 0.51-, 0.81-, and 1.12-millimeter-diameter 87Pt 13Rh/Pt thermocouples in air at 1600 K for 10 000 hours.

in vacuum up to the time of failure was practically identical in magnitude and shape to the drift curve for exposure to argon. Therefore, although the tests were terminated prematurely, a first approximation for predicted drift at 10 000 hours would be equal to the value (-22 K) for the typical example in argon (fig. 8(c)).

Drift of Noble-Metal Thermocouples in Air

Figure 10 shows the drift of the 0.51-, 0.81-, and 1.12-millimeter-diameter 87Pt13Rh/Pt thermocouples exposed to air for 10 000 hours. These results show negligible drift for all three sizes, with the average drift being less than 1/4 percent limit of error calibration tolerance specified for commercially available special-grade wire of this type. Figure 10 indicates a systematic wire size effect for the air-atmosphere tests, with the two larger sizes of wire actually reversing their initial trend at about 3000 hours and, in fact, showing a slight emf gain over the original output for the largest diameter wire.

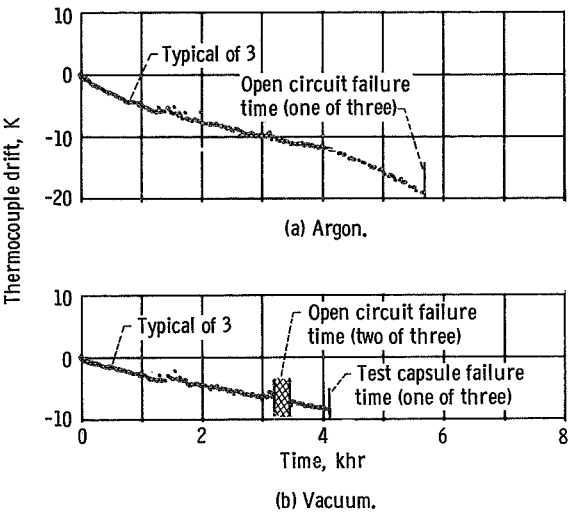


Figure 11. - Drift of 0.33-millimeter-diameter 87Pt 13Rh/Pt thermocouples in argon and in 10^{-6} torr vacuum at 1600 K.

Drift of Smaller-Size Wire

Figure 11 shows the drift of some of the 0.33-millimeter-diameter 87Pt13Rh/Pt wires in argon and vacuum environments. One of the thermocouples shown for the argon case failed after 5660 hours. The tests in vacuum ended between 3170 and 4080 hours. In both of these cases, the drift rates to the point of failure were about twice that for the 0.51-millimeter-diameter wires of like type (figs. 8(a) and 9(a)).

Figure 12 shows the drift of one of two other 0.33-millimeter-diameter, 87Pt13Rh/Pt thermocouples in argon, each of which acted erratically for a period of time during the 10 000-hour test. Zysk (ref. 2) has reported possible erratic behavior of noble-metal thermocouples just prior to failure. It is noted, however, in the present case, that after about 4000 hours of erratic behavior, the output returned to a systematic trend, although the final drift rate was much greater than that displayed before the erratic behavior period. Zysk contended that the erratic behavior is a possible result of a low-melting-point eutectic that forms a film across the interfaces in the grain boundaries. If we apply this explanation to these tests, it appears that for the period of time that the film of eutectic is spreading through the grain boundaries, unstable, erratic behavior results. However, as this process continues, it appears possible that enough eutectic is formed finally to complete a stable circuit. The final emf produced, however, is strongly affected by the eutectic film, as indicated by the large departure from the original calibration (fig. 12 and table III).

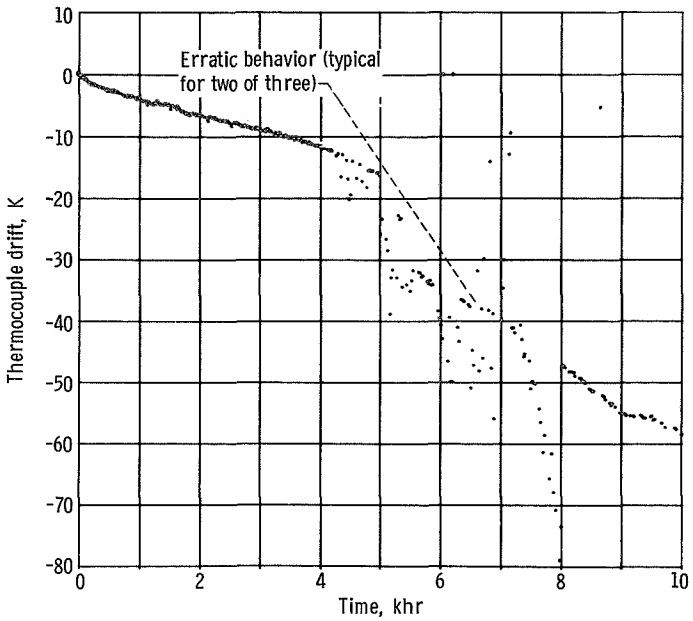


Figure 12. - Drift of 0.33-millimeter-diameter 87Pt 13Rh/Pt thermocouple in argon at 1600 K for 10 000 hours.

TABLE IV. - SUMMARY OF EXPECTED DRIFT

Thermocouple pair	Wire diameter		Expected drift per 10 000 hr, K		
	B. & S. gage	mm	In air	In vacuum	In argon
87Pt13Rh/Pt	28	0.33	----	[a]-65	[b]-65
	24	.51	-5	[a]-23	-23
	20	.81	-0.5	----	----
	17	1.12	3	----	----
70Pt30Rh/94Pt6Rh	24	0.51	----	[a]-26	-13
95W5Re/74W26Re	24	0.51	----	-22	-22

[a]Open-circuit failure expected after 2000 to 4000 hr. The values shown assume the same shape curve as in argon.

[b]Erratic behavior expected after 4000 hr.

Summary of Expected Drift

Table IV summarizes the results by indicating the drift rates to be expected in various environments for the thermocouple combinations tested. Qualifying annotations for some of the entries are indicated in the table. Extrapolated values are used for the tests in which the thermocouple or test apparatus failed before the 10 000 hours of operation were reached.

Material Analysis

Post-test examinations involving photomicrographs, hardness testing, and mass spectrography were performed on the thermocouple assemblies exposed to the air and argon environments. Assemblies exposed to the vacuum environment were not included, since tantalum plenum failures terminated the tests, thereby exposing the assemblies to an argon environment.

Photomicrographs. - Figures 13 to 16 are photomicrographs of longitudinal sections of some of the 0.51-millimeter-diameter test wires, showing the typical grain structure before exposure and the change after exposure to argon and air environments for 10 000 hours. The photomicrographs also display Knoop-test indentation marks, with their associated hardness values. The wire samples were taken from three sources:

(1) As received

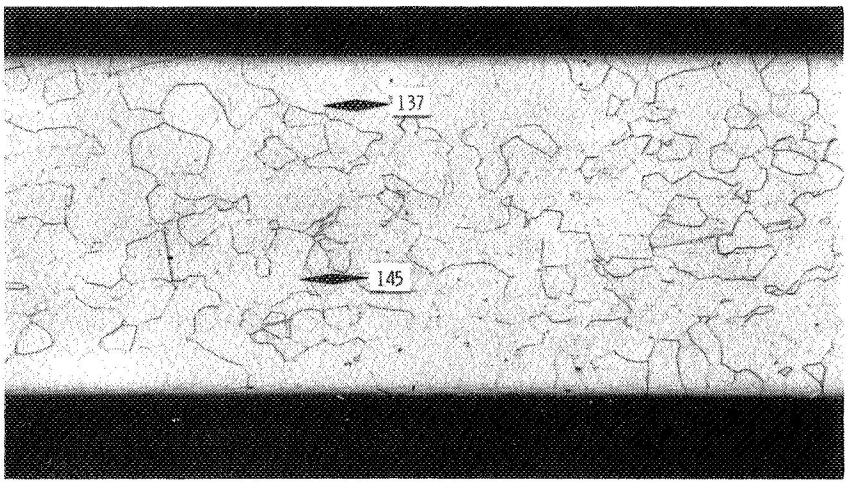
(2) A section of wire which was located in the test furnace at a point 46 centimeters from the junction, where the wire was at 1250 K (see fig. 6)

(3) A section of wire, 1.3 centimeters from the junction, in the 1600 K zone.

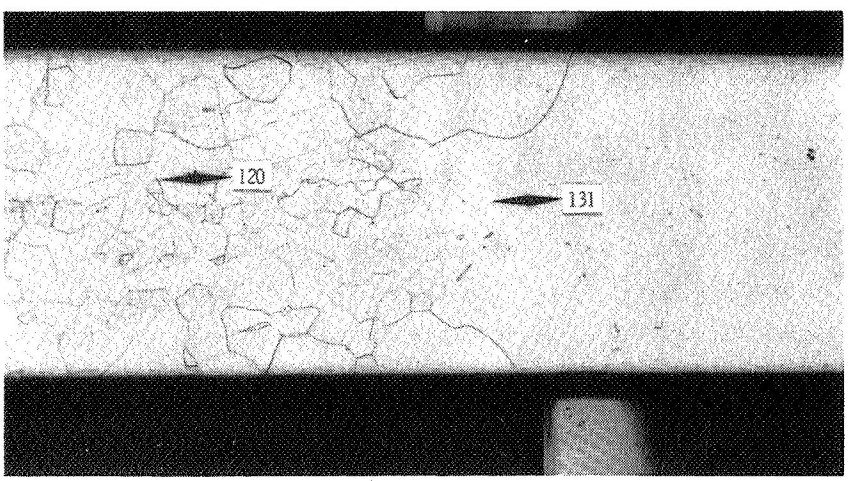
Figure 13 shows the grain growth and change in Knoop hardness ratings of 87Pt13Rh wires subject to two elevated temperature levels in argon for 10 000 hours. Figure 13(b), which is for a section of wire that was in a temperature gradient at about 1250 K, shows a rather abrupt transition of grain structure from that similar to the as-received (fig. 13(a)) structure to a larger grain structure. Figure 13(c) shows large crystal structure with one grain completely crossing the diameter of the wire. There was no gross change in hardness for these three samples.

It was previously mentioned in the INTRODUCTION that large grains will result when the pure platinum leg is subjected to high temperature for long periods of time. The progressive growth into a larger crystal, however, should not result in an increase in hardness, and, in fact, usually a decrease in hardness will be noted. If grain growth is accompanied by an increase in hardness, one may suspect other activity such as the introduction of new constituents.

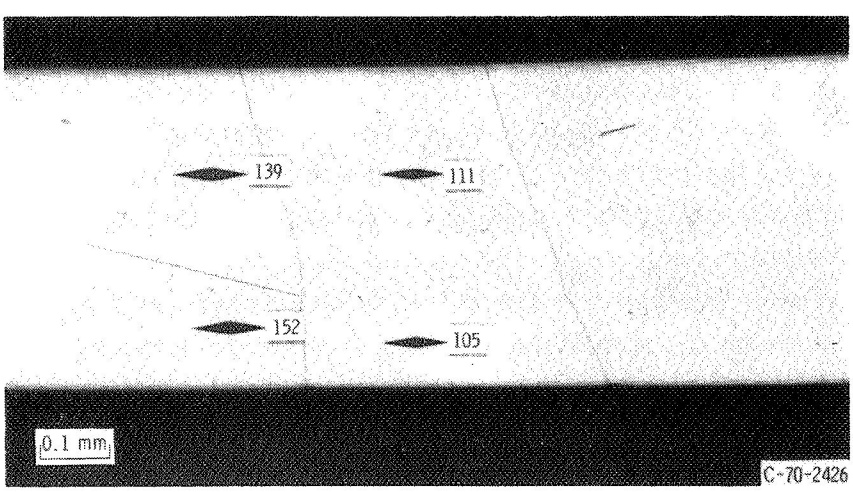
Figure 14 presents the same sampling as shown for figure 13 except that these



(a) As-received.

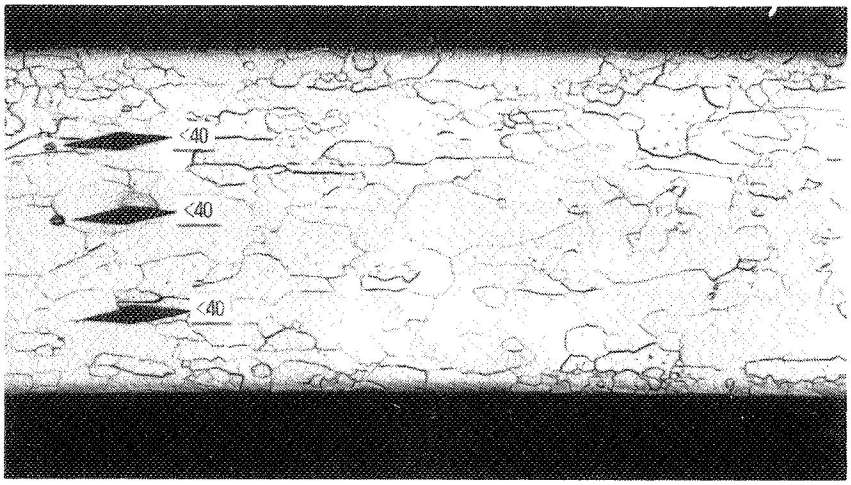


(b) After 10 000 hours in argon at 1250 K.

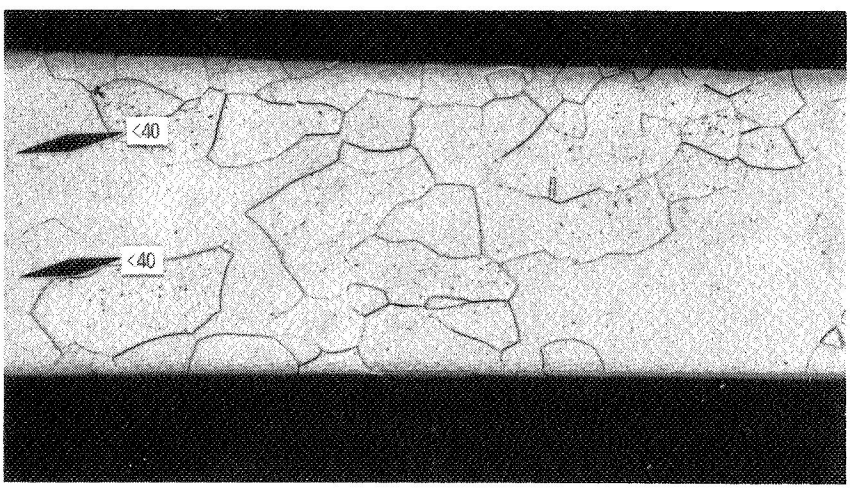


(c) After 10 000 hours in argon at 1600 K.

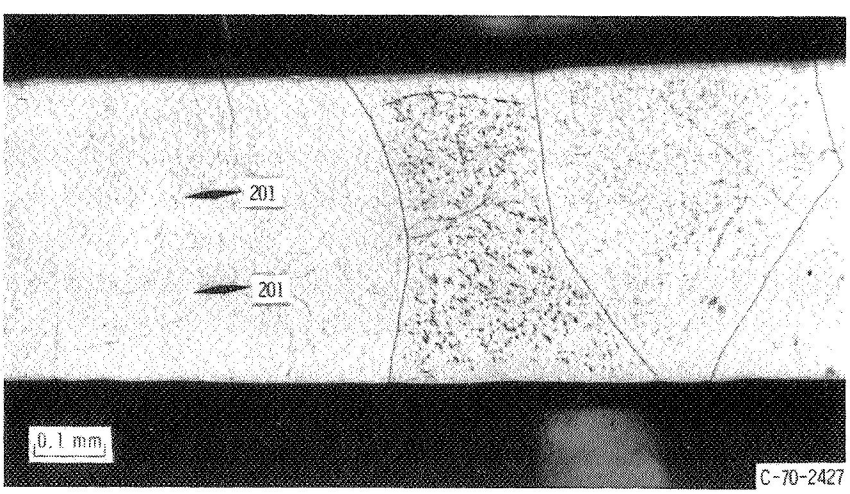
Figure 13. - Photomicrographs of longitudinal sections of 87Pt 13Rh thermocouple wire with Knoop hardness values.



(a) As-received.

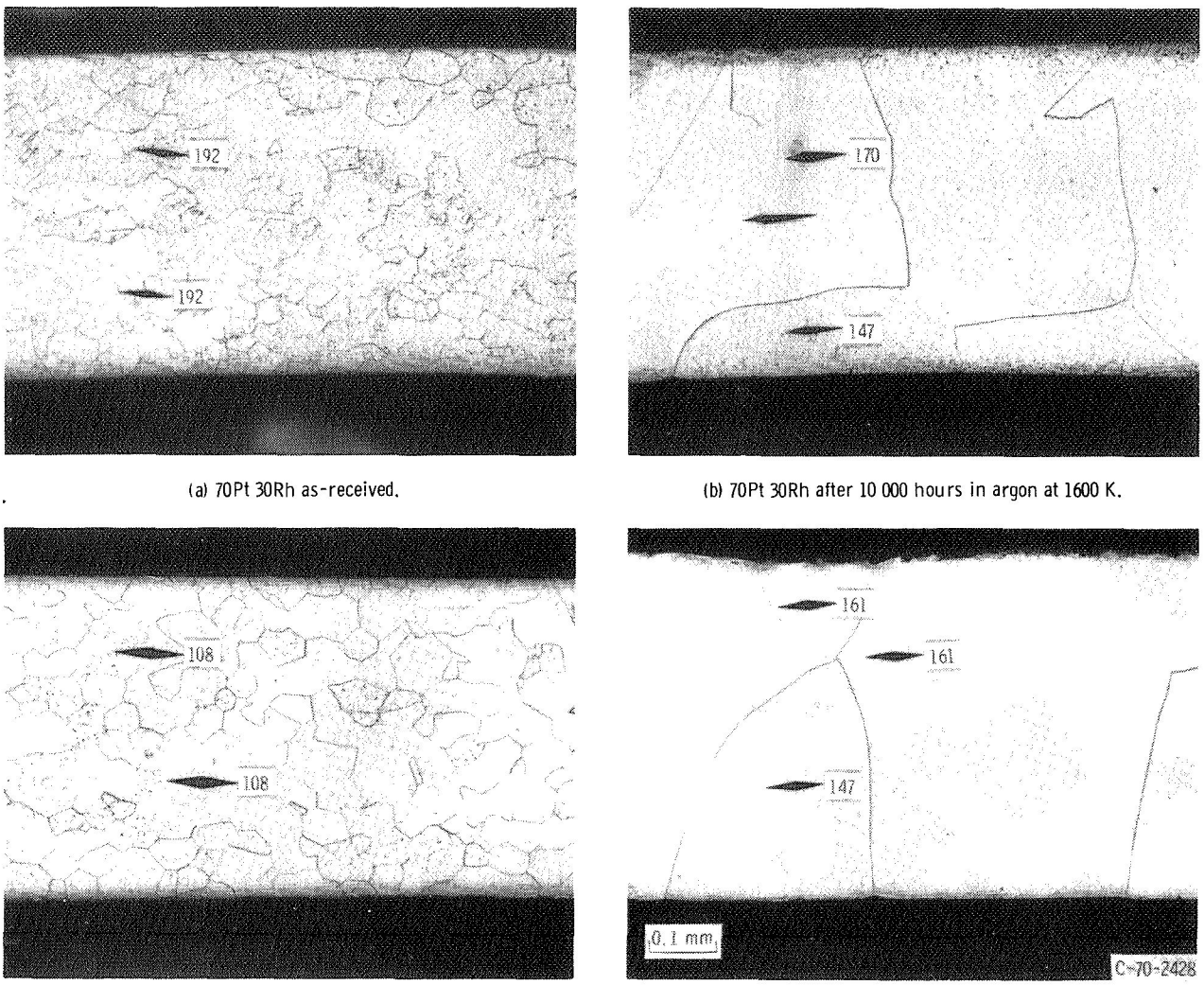


(b) After 10 000 hours in argon at 1250 K.



(c) After 10 000 hours in argon at 1600 K.

Figure 14. - Photomicrographs of longitudinal sections of platinum thermocouple wire with Knoop hardness values.



(a) 70Pt 30Rh as-received.

(b) 70Pt 30Rh after 10 000 hours in argon at 1600 K.

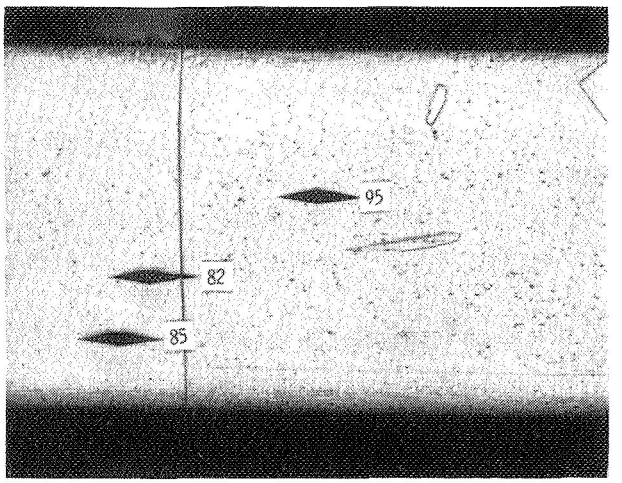
(c) 94Pt 6Rh as-received.

(d) 94Pt 6Rh after 10 000 hours in argon at 1600 K.

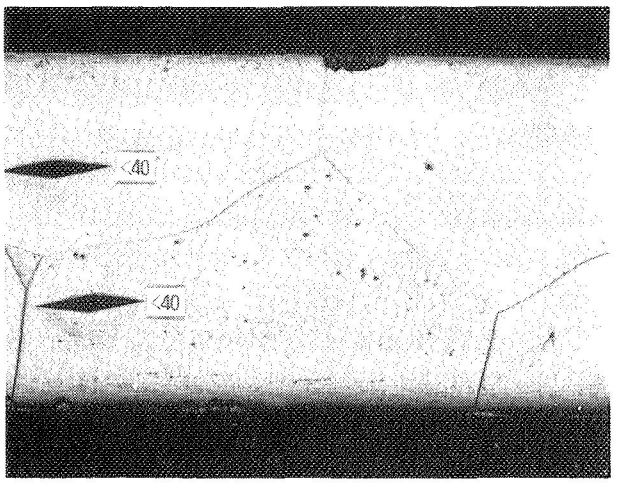
Figure 15. - Photomicrographs of longitudinal sections of 70Pt 30Rh and 94Pt 6Rh thermocouple wires with Knoop hardness values.

samples are of the adjacent platinum leg, for the same three conditions as in figure 13. Again, we can see the progressive growth of the grains as the temperature increases. However, figure 14(c) shows a significant increase in hardness over both the as-received sample (fig. 14(a)) and the 1250 K sample (fig. 14(b)). This increase in hardness may be accounted for by the display of small flecks which appear in the grain structure, indicating the presence of impurities. Reference 3 indicated that the platinum leg of a platinum-rhodium alloy/platinum thermocouple pair would be the most likely to take up impurities, and reference 1 showed it to be the leg most likely to change calibration.

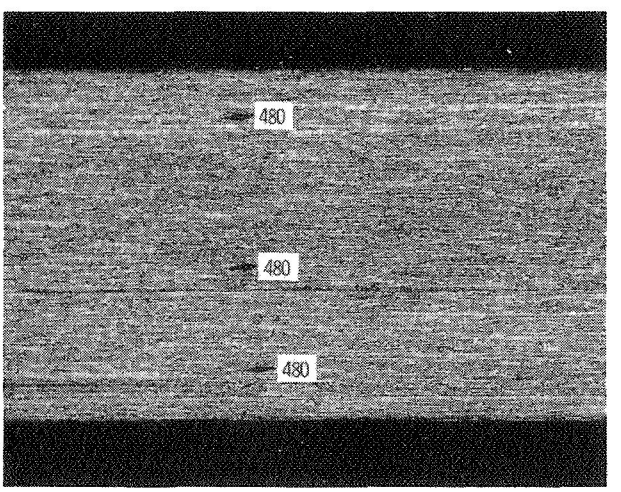
Figure 15 shows the changes in the 70Pt30Rh and 94Pt6Rh wires after exposure for 10 000 hours at 1600 K in argon. Again, we see large grain growth, with some reduc-



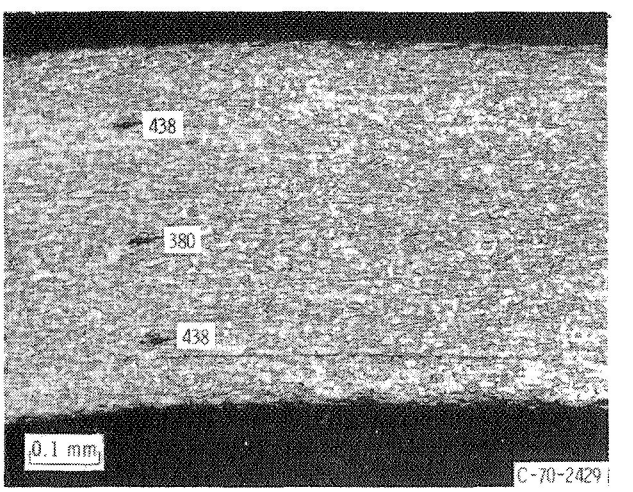
(a) 87Pt 13Rh after 10 000 hours in air at 1600 K.



(b) Platinum after 10 000 hours in air at 1600 K.



(c) 95W 5Re as-received.



(d) 95W 5Re after 10 000 hours in argon at 1600 K.

Figure 16. - Photomicrographs of longitudinal sections of 87Pt 13Rh, Pt, and 95W 5Re thermocouple wires with Knoop hardness values.

tion in hardness of the 70Pt30Rh wire but with an increase in hardness of the 94Pt6Rh wire.

Figures 16(a) and (b), which are for 87Pt13Rh and platinum wires exposed to air at 1600 K for 10 000 hours, can be compared with figures 13(c) and 14(c), respectively. Note that the platinum (fig. 16(b)) remained ductile and did not show the impurity flecks appearing in figure 14(c). Retention of ductility, clear grain structure (as shown in fig. 16(b)), and negligible drift of the 87Pt13Rh/Pt in air are in mutual agreement.

Figures 16(c) and (d) show the grain structure and hardness comparisons between as-received and exposed 95W5Re wire. There is only negligible change in the grain structure, along with some reduction in hardness. Photomicrographs for the 74W26Re

leg are not presented, but also show only slight structural change, and no change in hardness.

Mass spectrographic examination. - Mass spectrographic analysis was made of samples of the alumina insulators and thermocouple wires.

Alumina: The specifications on the alumina insulators stipulated a purity of not less than 99.5 percent (5000 ppm impurities). Examination verified this purity and, in fact, indicated a purity of 99.8 percent with the major impurities, in order of quantity present, being magnesium, silicon, sodium, and iron.

Thermocouple wire: Samples of thermocouple wires were examined before and after the 10 000-hour exposure in the air and argon environments. In order of quantities measured, the noble-metal wires showed an increase in aluminum, iron, silicon, and magnesium, and the refractory-metal wire impurities increased primarily in iron and silicon. The noble-metal wires were found to be fused to the ceramic insulators in the length of ceramic extending from the junction area (1600 K) as far back as the 1300 K area. These wires were so firmly bonded to the insulators in the 1600 K region that the insulators had to be broken away from the wires so that wire samples could be examined. This procedure left particles of alumina embedded in the wire samples and probably accounted for aluminum being the primary foreign constituent. The refractory-metal wires, unlike the noble-metal wires, did not bond to the ceramic and were easily removed from their insulators. Also, unlike their noble-metal counterparts, the post examination indicated no increase in aluminum content.

The iron and silicon impurities were the main impurities commonly picked up by both the noble and refractory wires and appeared in like quantities, ranging from 200 to 2000 ppm.

CONCLUDING REMARKS

This report has presented the drift characteristics and post-exposure material analysis of some thermocouple assemblies. These assemblies consisted of commercially available thermocouple wires in high-purity alumina insulators, which were exposed to air, argon, and vacuum environments at 1600 K for up to 10 000 hours. The thermocouple wire pairs tested were 87Pt13Rh/Pt, 70Pt30Rh/94Pt6Rh, and 95W5Re/74W26Re in wire size ranging from 0.33 to 1.12 millimeters. The findings include the following:

1. In argon, the 0.5-millimeter-diameter noble-metal thermocouples drifted very little in the first few thousand hours, but the drift rate increased subsequently. After 10 000 hours, the average drift was -22 K for the 87Pt13Rh/Pt pair and -13 K for the 70Pt30Rh/94Pt6Rh pair.

The refractory-metal-thermocouple drift, on the contrary was more rapid initially,

resembling a decaying exponential. After 10 000 hours, the average drift was -22 K.

2. Although the drifts for both the 95W5Re/74W26Re and the 87Pt13Rh/Pt in argon were about the same (-22 K) at the end of 10 000 hours, the several 95W5Re/74W26Re test thermocouples were in closer final agreement with each other (1.4 K total spread) than the several 87Pt13Rh/Pt thermocouples (8.8 K spread).

3. Because of the shape of the noble-metal drift curve, it would be difficult to predict the long-term drift of the noble-metal thermocouple on the basis of short-term results.

4. A comparison of the behavior of the 0.33-millimeter wire with the 0.5-millimeter-diameter noble-metal wire in argon and vacuum shows about twice the drift for the smaller wire. This reinforces the belief that the drift is caused by insulator impurities that contaminate the wire, since the surface-to-volume ratio is 1.7 times greater for the smaller wire. In air, these impurities are converted to harmless oxides.

5. The 87Pt13Rh/Pt thermocouple in vacuum performed like that of the same size and type in argon, up to the time of failure (1600 to 3400 hr). The 70Pt30Rh/94Pt6Rh thermocouple had a drift in vacuum (up to the time of failure) of about twice that of its like kind in argon.

Vacuum tests of the tungsten-rhenium alloy thermocouples were terminated by failure of the tantalum tubing test capsules. However, the drift curve of the tungsten-rhenium thermocouple up to the time of capsule failure (≈3500 hr) was identical to the drift curve for argon exposure, so that it appears safe to predict that the similarity would have been maintained to 10 000 hours, resulting in a drift of approximately -22 K.

6. Thermocouple pairs of 87Pt13Rh/Pt wires in air showed a maximum drift of -5 K.

7. There was negligible grain growth of the tungsten-rhenium wire in argon after the 10 000-hour exposure; whereas the noble-metal wire exhibited large grain growth upon exposure to argon or air.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 27, 1970,
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