

# STUDIES OF THE PERFORMANCE OF W-RE TYPE THERMOCOUPLES

G. W. BURNS AND W. S. HURST

*National Bureau of Standards  
Washington, D.C.*

The effect of exposure of bare-wire and BeO-insulated commercial W-Re thermocouple materials to high temperatures in gaseous environments has been investigated. The temperature range of interest has been primarily 2000 to 2400 K, and the investigations have been confined to thermocouple wires of 0.25 mm diameter. With high temperature exposure of the bare thermoelements, an initial shift in the emf-temperature relationship of the exposed thermoelements versus an unexposed "as received" thermoelement was exhibited, and thereafter no discernible drift occurred with exposure in environments of Ar, He, H<sub>2</sub> or N<sub>2</sub> for periods up to 1000 hours. Aging studies were performed to determine the time-temperature parameters of the shift. Thermoelements were examined for metallurgical structural changes and chemical changes by conventional methods. In the temperature range of interest, grain growth was inhibited in the chemically doped W-3 percent Re alloy, and excellent room temperature ductility was retained subsequent to the exposure. The compatibility of high purity (in excess of 99.8 percent), sintered BeO insulators with the thermoelements differed, depending upon whether the BeO-insulated thermoelement assemblies were self-heated electrically or heated in a furnace; in tests in argon environments, highly reliable performance occurred when the assemblies were heated in a furnace. BeO-insulated W-3 percent Re vs W-25 percent Re thermocouples, constructed with degassed and aged materials, exhibited drifts equivalent to about 3 mK/h during 1000 hours of exposure at 2073 K in argon while in the presence of tantalum.

## INTRODUCTION

A program of research is in progress\* in which we have been investigating the material performance and thermoelectric behavior exhibited by W-Re type thermocouples at temperatures principally between 2000 and 2400 K. The research is directed towards improving the general reliability of metal-sheathed, ceramic-insulated, W-Re type thermocouple sensors during prolonged operation (for many thousands of hours) at temperatures above 1800 K. Useful criteria are being sought regarding the selection, preparation and performance of materials that might be applied in the design and construction of such sensors. Sensors that will function reliably for these periods of time are now being required in engineering research to develop the technology of nuclear power systems and energy conversion devices, as well as in other applications.

In this program the sensor components have been limited to W-Re type thermoelements of

nominally 0.25 mm diameter, high purity, sintered beryllium oxide (BeO) insulators, and Ta sheaths of nominally 1.6 mm outer diameter. The experimental approach has been to study the performance of each component of the sensor separately, then the performance of two components together, and finally the performance of all three components when assembled together in a completed sensor.

Studies were first performed with the bare (non-insulated) thermoelements to determine the changes in thermoelectric properties that resulted from exposure to high temperatures in various high purity gaseous environments and in vacuum. The thermoelements were also examined for changes in other properties, such as the metallurgical structure, the room temperature ductility, and the chemical composition. Studies were then performed with BeO-insulated thermoelements and thermocouples to characterize their material behavior with exposure in an argon environment. This paper presents some of the principal results obtained thus far. These results, together with a description of the general experimental procedures and apparatus employed, are given in more detail elsewhere.<sup>1,2,3</sup>

\*Work supported by NASA - Lewis Research Center.

## EXPERIMENTAL APPARATUS AND GENERAL PROCEDURES

### Chambers for Testing of Thermoelements

For testing of the bare thermoelements, stainless steel test chambers<sup>1,2</sup> were employed in which 90 to 100 cm long thermoelements could be uniformly exposed to high temperatures in high purity gaseous environments at a pressure of nominally  $1.0 \times 10^5 \text{ N} \cdot \text{m}^{-2}$  (1 atm)<sup>4</sup> or in a vacuum of less than  $1.3 \times 10^{-6} \text{ N} \cdot \text{m}^{-2}$  ( $1 \times 10^{-8}$  Torr).<sup>5</sup> During the high temperature exposure, the thermoelements were heated electrically with alternating current (60 Hz) and their temperature was determined and monitored with a calibrated visual optical pyrometer. After specific exposure times, the thermoelements were removed from the test chamber and the relative changes in the thermal emf-temperature relationship<sup>6</sup> due to exposure were determined: The thermal emf of the exposed thermoelement versus an "as received" unheated thermoelement from the same spool (lot) of wire was measured at 200 K intervals from 673 to 2073 K. For these measurements, the samples were heated in argon in a resistance heated calibration furnace.

For the thermoelements, the maximum uncertainty in the measurement of the relative changes resulting from exposure is estimated not to exceed  $\pm 30 \mu\text{V}$  (equivalent  $\Delta T$  of  $\pm 1.5 \text{ K}$ ) at 1273 K and  $\pm 50 \mu\text{V}$  (equivalent  $\Delta T$  of  $\pm 3.2 \text{ K}$ ) at 2073 K for all lots of wire tested.<sup>7</sup> The uncertainty results primarily from the thermoelectric non-uniformity of the particular lot of wire that was tested (the test and the unheated "as received" thermoelements were taken at random from the particular lot). The change in the thermal emf-temperature relationship of a composite thermocouple, in which both thermoelements have been exposed, may be obtained by combining the changes measured for the separately exposed thermoelements. For the composite thermocouple, the maximum uncertainty in the value of the change is assumed to be twice the uncertainty given above for the thermoelement.

It is convenient to express the change in thermal emf of the thermoelements and the thermocouples at a given temperature in terms

of an equivalent temperature change  $\Delta T$ . We shall use the following convention: For the composite thermocouple,  $\Delta T$  is obtained by dividing the change in the thermal emf of the thermocouple at a given temperature by the thermoelectric power ( $dE/dT$ ) of the thermocouple at the same temperature;  $\Delta T$  for the separate thermoelements is obtained similarly, except that for the W-25 percent Re thermoelement (negative element of thermocouple), a negative value for the thermoelectric power of the thermocouple is used, so that a positive change in emf results in a negative  $\Delta T$ . In this manner, changes occurring in the separate thermoelements are expressed in terms of their individual effects upon the composite thermocouple, and the algebraic sum of the  $\Delta T$ 's for each of the thermoelements equals the  $\Delta T$  for the thermocouple. Although the change,  $\Delta T$ , was determined at 200 K intervals from 673 to 2073 K, in most instances the  $\Delta T$  at 2073 K is a reliable measure of the changes experienced by the thermoelements.

### Furnace for Testing Assemblies

Studies of the performance of BeO-insulated thermoelements and thermocouples were performed in an ultra-high vacuum (UHV), high temperature furnace system.<sup>2,3</sup> The furnace has a tungsten wire-mesh heating element (6.4 cm in diameter by 30.5 cm long), which is surrounded by tungsten radiation shields. These are enclosed by a water-cooled, copper cold-wall that is mounted in a water-cooled, stainless steel vacuum chamber. The high vacuum pumping system consists of a 400 liter/s sputter ion pump and an accessory (three-filament cartridge type) titanium sublimation pump. With the furnace at ambient temperature (no power to the furnace) pressures of less than  $5 \times 10^{-11}$  Torr have been achieved within 10 hours after a 10 hour bake-out of the chamber and pumping system at about 525 K. The furnace is designed to produce hot-zone temperatures to 3000 K while maintaining the pressure in the  $10^{-8}$  Torr range.

The tests of material performance and compatibility in this study have been conducted with the furnace chamber filled with high purity argon ( $< 10 \text{ ppmv}$  total impurities) at a pressure of about 1 atm. For evaluating the long-term performance (drift) of BeO-insulated

W-Re thermocouples, a hollow cylindrical tantalum blackbody enclosure<sup>2,3</sup> with a 1 mm diameter blackbody opening was suspended in the hot-zone of the furnace. The enclosure was about 2.5 cm in diameter by 8 cm long, and was supported from above by a thin-wall tantalum tube of 0.56 cm inner diameter. Thermocouples for test were inserted through the tantalum supporting tube so that their measuring junctions were within the blackbody enclosure. The upper portions of the thermocouple wires were led out of the furnace chamber to ambient surroundings through metal-glass feed-throughs (the wires were sealed with a solvent-free epoxy resin), and the reference junctions were maintained at 273.15 K in an ice bath. The temperature of the enclosure was determined with both a calibrated visual optical pyrometer and an automatic photoelectric pyrometer.<sup>8</sup> Corrections were applied for the transmittance of the furnace window, which remained shuttered except for relatively short periods when the temperature measurements were made.

## MATERIALS TESTED

### Thermoelements

Thermocouple materials for the studies consisted of 0.25 mm diameter W, W-3 percent Re, W-5 percent Re and W-25 percent Re thermoelements that were obtained (except where noted) as "matched lots" from two major commercial thermocouple wire suppliers.<sup>9</sup> Emphasis has been placed upon the thermoelements of W-3 percent Re and W-25 percent Re; the investigations with these thermoelements have included bare-wire studies in environments of argon, helium, hydrogen, nitrogen and high vacuum ( $< 1 \times 10^{-8}$  Torr), studies of BeO-thermoelement compatibility, and studies of the long-term performance of BeO-insulated W-3 percent Re vs. W-25 percent Re thermocouples. Studies with the other commercially available thermoelements have been limited to the effects of bare-wire exposure in argon only.

The W-3 percent Re thermoelement is an alloy which has been "doped" by adding small amounts of potassium, silicon and aluminum compounds to the tungsten oxide prior to its reduction to a metal. The residual doping

elements which remain after the wire forming process modify the metallurgical structural changes that occur in the wire when it is exposed to high temperatures and result in improvements in the mechanical properties.<sup>10</sup> The W and one class of W-5 percent Re thermoelements are also "doped." The other class of W-5 percent Re thermoelements and the W-25 percent Re thermoelements are "undoped."

As part of the characterization of the "as received" thermoelements, the thermal emfs of representative thermocouples from all matched lots of thermocouple wire were measured at 200 K increments from 673 to 2073 K. The thermocouples were tested by intercomparison with W-3 percent Re vs. W-25 percent Re thermocouples that were taken from a matched lot of previously calibrated wire.<sup>11</sup> The measurements showed that the emf-temperature relationship of the "as received" thermocouples from each matched lot (as determined with increasing temperature) complied with the suppliers corresponding standard calibration table<sup>12,13</sup> to within the equivalent of  $\pm 1$  percent of the temperature. Mass spectrographic analyses of representative samples were reported previously.<sup>1,3</sup> The W-3 percent Re wires typically had impurities of K, Al, Mo and Fe present in the range 300 to 50 ppmw, with other impurities totaling less than 50 ppmw. The W-25 percent Re wires typically had impurities of Mo, Si, Al, P, K, Cr, Ni, and Fe present in the range 200 to 20 ppmw, with other impurities totaling less than 100 ppmw.

In addition to the matched lots of wire obtained from the thermocouple wire suppliers, a lot of doped W-3 percent Re wire and a lot of W-25 percent Re wire were obtained directly from major wire manufacturers for special use in aging studies. Both lots were 0.25 mm diameter wire. The W-3 percent Re wire was cleaned and straightened by the manufacturer after being drawn, but was not given a stress-relief anneal. The manufacturer of the W-25 percent Re wire reported that, after drawing, the wire was subjected to a temperature of about 1200 K for a short period ( $< 1$  minute) during a cleaning and straightening process. In contrast, the matched lots of wire obtained from the thermocouple wire suppliers were heat treated to reduce the effects of the mechanical working (received during the wire drawing proc-

ess) upon the thermoelectric properties of the wire.

### BeO Insulators

For tests with BeO-insulated thermoelements and thermocouples, high purity, sintered, double-bore BeO tubing with 0.3 mm diameter bores, 1.1 mm outer diameter, and 0.125 mm  $\pm$  0.025 mm web size (space between bores) was used. All tubing was from the same batch which was supplied by the manufacturer in random lengths between 10 and 25 cm long. Quantitative spectrochemical analyses of representative "as received" samples from the batch of tubing indicated purities to be in excess of 99.8 percent. The major impurities detected were C (230 ppmw), Al (200 ppmw), Si (120 ppmw), and Mg (90 ppmw). The total detectable impurities were less than 800 ppmw (see the results section for a more detailed analysis).

### Tantalum

Seamless tantalum tubing was used in the construction of the blackbody enclosure for the ultra-high vacuum furnace. Before being used, the blackbody enclosure was given a vacuum degas, during which it was heated to 2370 K and the pressure was maintained at less than  $1 \times 10^{-6}$  Torr. A mass spectrographic analysis of the tantalum components after degassing was reported previously.<sup>3</sup>

### Gases

Each of the argon, hydrogen, helium and nitrogen gases used in the experiments were an ultra-high purity grade of commercially available compressed gas. The helium, argon, and hydrogen gases were certified by the supplier to contain less than 10 ppmv total impurities,<sup>14</sup> and within detectable limits, this was supported by analyses at NBS. The nitrogen gas was certified by the supplier to contain less than 30 ppmv total impurities, and an analysis at NBS indicated that it contained less than 0.1 ppmv hydrocarbons, less than 5 ppmv H<sub>2</sub>O, and less than 1 ppmv O<sub>2</sub>. Hydrogen and nitrogen were employed in some experiments since these gases are commonly used in annealing of the thermoelements.

## RESULTS OF TESTS WITH BARE THERMOELEMENTS

### Changes in Thermoelectric Properties

It is convenient to describe the initial changes that occur during a short-term, high temperature exposure of the "as received" thermoelements as a *shift* in the emf-temperature relationship. It is apparent from the tests to be described that the thermoelectric properties of the thermoelements are essentially stabilized in a very short period of time if the exposure temperature is sufficiently high. After the thermoelements have been stabilized, it is convenient to characterize any additional long-term changes that occur as a *drift* in the emf-temperature relationship.

### Short-term behavior

Bare-wire samples from the matched lots of thermocouple wire that were obtained from the commercial suppliers were uniformly exposed to high temperatures in the stainless steel test chambers. After the exposure, the thermoelements exhibited a change in their emf-temperature relationship. Typical results are given in Table I, where the data are for seven different matched lots of W-3 percent Re and W-25 percent Re thermoelements that had been exposed in argon at 2400 K for 1 and 50 hours. The change in the emf-temperature relationship of the thermoelements was essentially complete after an exposure for 1 hour at 2400 K. The initial change, or shift, varied with the lot of wire, as shown in Table I. Thermocouples from the seven different lots exhibited changes in indicated temperature ranging from about 0.1 percent to 1 percent at 2073 K. The measured shifts at temperatures below 2073 K were reduced by an amount roughly in proportion to the temperature.

For the doped W and W-5 percent Re thermoelements, the undoped W-5 percent Re thermoelement, and for the W-25 percent Re thermoelements that were matched with these positive thermoelements, a similar initial shift in the thermal emf occurred within the first 50 hours of exposure at 2400 K in argon. For the positive thermoelements, the equivalent  $\Delta T$  at 2073 K after exposure for 1 hour at 2400 K was typically +20 to +30 K. For the negative thermoelement (W-25 percent Re thermo-

TABLE I. AVERAGE CHANGE IN THE EMF-TEMPERATURE RELATIONSHIP AT 2073 K FOR THERMOELEMENTS AND THERMOCOUPLES FROM DIFFERENT MATCHED LOTS AFTER EXPOSURE AT 2400 K IN ARGON (1 atm).

Exposure Time →	Equivalent $\Delta T$ at 2073 K in Kelvins					
	1 Hour			50 Hours		
	Lot	W-3% Re Element	W-25% Re Element	Thermocouple	W-3% Re Element	W-25% Re Element
A	+ 6	- 4	+ 2	+ 7	- 4	+ 3
B	+23	- 5	+18	+24	- 7	+17
C	+ 9	- 3	+ 6	+ 8	- 2	+ 6
D	+ 9	+ 1	+10	+ 9	+ 1	+10
E	+20	- 2	+18	+20	- 2	+18
F	+18	- 3	+15	+20	- 8	+12
G	+15	- 3	+12	+16	0	+16

element), the change was small, averaging about  $-3$  K at 2073 K. The positive thermoelements all exhibited a small additional change (ranging from the equivalent of  $+5$  to  $+10$  K) in thermal emf between 1 and 50 hours of exposure at 2400 K. A second lot of matched thermoelements was also tested, and also exhibited shifts of the same magnitude.

The shifts for thermoelements taken from the same lot of wire were also determined after the thermoelements had been exposed in environments of hydrogen, helium and nitrogen. For the W-3 percent Re thermoelement the shift depended slightly on the environmental gas that was used. For the W-25 percent Re thermoelement, no variation of the shift with the different environmental gases was found. Table II summarizes the shifts (expressed in equivalent  $\Delta T$  at 2073 K) for the W-3 percent Re thermoelements after exposures at 2400 K

TABLE II. AVERAGE SHIFT IN THE THERMAL EMF-TEMPERATURE RELATIONSHIP AT 2073 K FOR W-3% Re THERMOELEMENTS FROM THE SAME LOT AFTER EXPOSURE AT 2400 K IN VARIOUS GASEOUS ENVIRONMENTS (1 atm).

Exposure Time h	Equivalent $\Delta T$ at 2073 K in Kelvins			
	Hydrogen	Helium	Nitrogen	Argon
1	+ 3	+ 5	+ 4	+ 9
50	+ 4	+ 6	+ 6	+ 9

for 1 and 50 hours. The differences between the shifts in hydrogen and argon are considered measureably significant. Three different lots of W-3 percent Re wire have been tested in both environments. Whereas each lot exhibited a different initial shift, the difference between the shift in argon and the shift in hydrogen was about the same for all three lots and was equal to  $100 \pm 30$   $\mu V$  at 2073 K (equivalent to an indicated difference in temperature of about 6 K).

### Long-term behavior

Exposure of bare-wire thermoelements for extended periods (greater than 50 hours) in the different gaseous environments at 2400 K resulted in no significant changes (drift) in the emf-temperature relationship. For the W-3 percent Re and W-25 percent Re thermoelements that were exposed for periods of 1, 50, 100, 250, 500, 750 and 1000 hours in argon, no significant trend with increasing exposure time was apparent.<sup>1,2</sup> Similar results were obtained with these thermoelements when they were exposed for periods up to 1000 hours in nitrogen and when they were exposed for periods up to 500 hours in helium and hydrogen. Thermoelements of doped W, and both doped and undoped W-5 percent Re, also gave no evidence of any drift during exposures at 2400 K in argon for periods up to 500 hours.<sup>3</sup>

W-3 percent Re and W-25 Re thermoelements, when exposed in high vacuum ( $< 1 \times$

10<sup>-8</sup> Torr) at temperatures above 2200 K, did exhibit a drift in their emf-temperature relationship.<sup>1,2</sup> Exposure of the thermoelements at 2400 K for 500 hours resulted in a change for the composite thermocouple (constructed from the exposed thermoelements) of about -180 K at 2073 K. A similar change was experienced after only 50 hours of exposure at 2600 K. At 2200 K, the change after 500 hours of exposure was negligible (< 5 K). The change in the composite thermocouple is largely the result of the change that occurs in the W-25 percent Re thermoelement. Examinations of the thermoelements by electron probe microanalysis showed that the drift was caused by the preferential loss of Re from the thermoelements. After 500 hours of exposure at 2400 K, the fractional loss of Re from both alloys was about 20 percent.

### Aging Studies

Because of the short-term behavior exhibited in the earlier experiments, it became desirable to develop time-temperature parameters that could be applied to stabilize the thermoelectric properties of the thermoelements prior to their usage. Studies were performed with the W-3 percent Re wire and the W-25 percent Re wire that had been obtained directly from wire manufacturers and that had not received the usual heat treatment that is normally performed by the thermocouple wire suppliers.

The aging studies were performed in argon and in hydrogen gases, and the thermoelements were exposed to temperatures that ranged from 1200 to 3000 K and for time periods between 2 minutes and 50 hours. In Fig. 1, the changes in the emf at 2073 K of the W-3 percent Re thermoelements (relative to an as received wire from the same lot) after aging in argon and hydrogen for 1 hour are plotted as a function of the aging temperature. Above about 2200 K the change in the thermal emf is essentially independent of the aging temperature for a 1 hour exposure period. Further, the change in thermal emf of the thermoelements aged in hydrogen is somewhat less than that of the thermoelements aged in argon (about 100  $\mu\text{V}$  or 10 percent of the overall change in argon). The time dependency of the change in thermal emf of the W-3 percent Re thermoelements is shown in Fig. 2 for aging in argon at temperatures of 1400, 2000, 2200 and 2400 K. About

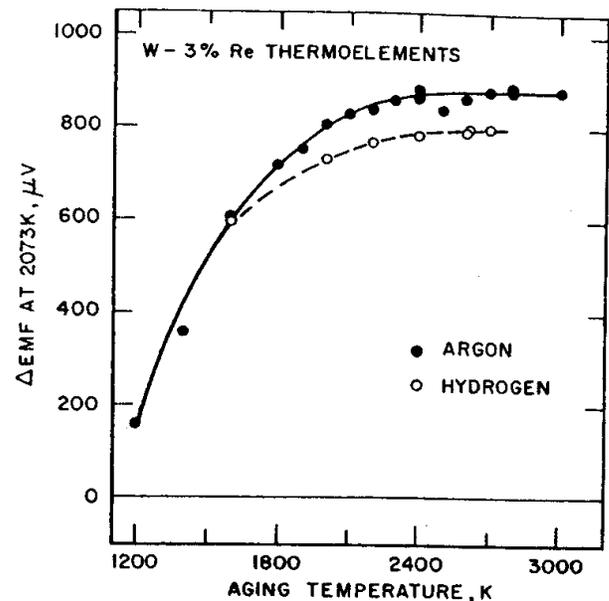


Fig. 1. Change in the thermal emf at 2073 K of W-3% Re thermoelements from one lot as a function of aging temperature in argon or hydrogen. The aging time was 1 hour.

90 percent of the change in emf occurs after exposure for 2 minutes at 2400 K, or for 1 hour at 2000 K. At 1400 K, a gradual and continual change in thermal emf occurs, and extrapolation of the curve indicates that aging for about 1000 hours at this temperature would be required to complete 90 percent of the change (shift) in thermal emf.

The changes in emf at 2073 K of the W-25 percent Re thermoelements after aging in argon and in hydrogen for 1 hour are plotted as a function of aging temperature in Fig. 3. In contrast to the W-3 percent Re thermoelement, a relatively small shift (about -150  $\mu\text{V}$  at 2073 K) occurs with aging for 1 hour at temperatures above 1900 K. No significant difference in the thermoelectric properties of the W-25 percent Re thermoelements with aging in the two environments was found. The time dependency of the change in thermal emf of the W-25 percent Re thermoelements for aging temperatures of 2000 and 2400 K is shown in Fig. 4. One hour at 2000 K or a few minutes at 2400 K in either argon or hydrogen is sufficient to virtually eliminate the initial shift in thermal emf.

### Changes in the Microstructure and in the Ductility

Chemically doped W, W-3 percent Re and W-5 percent Re wires in the "as drawn" con-

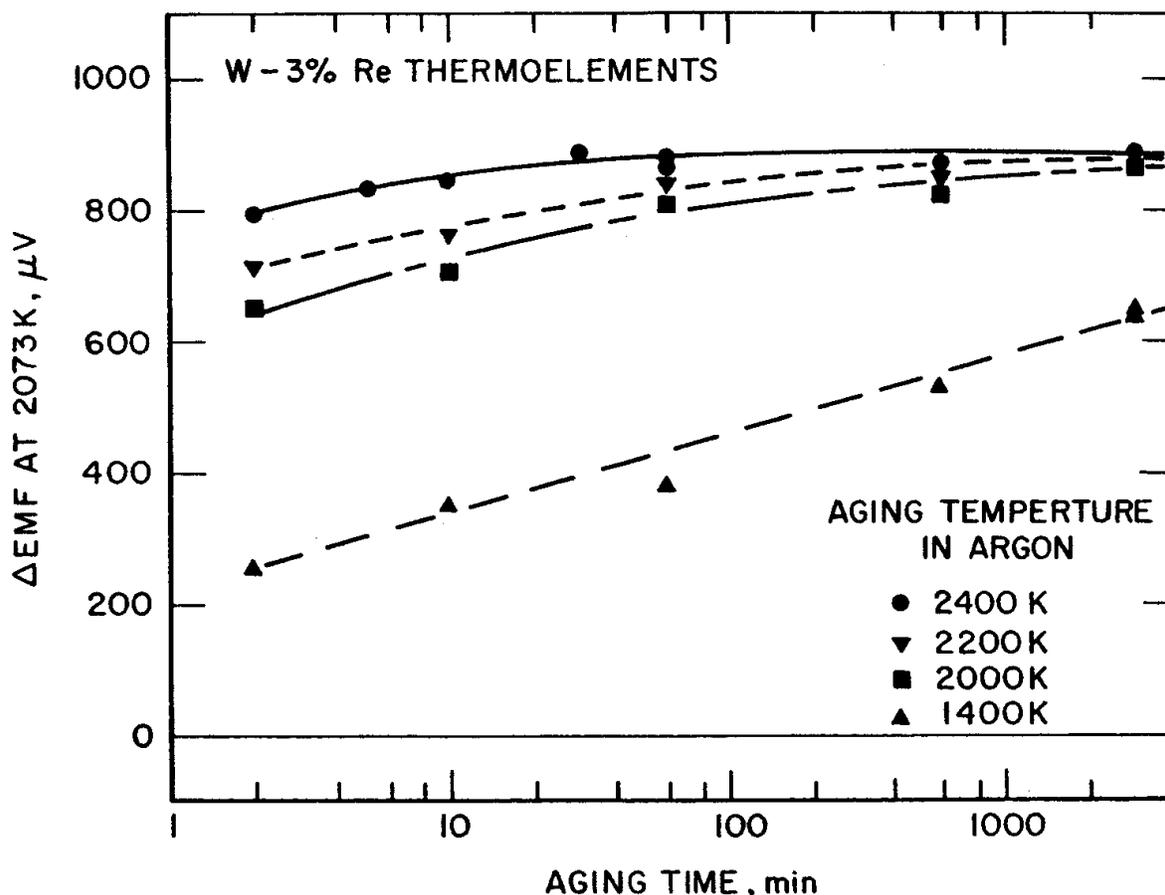


Fig. 2. Change in the thermal emf at 2073K of W-3% Re thermoelements from one lot as a function of the aging time in argon at the indicated temperature.

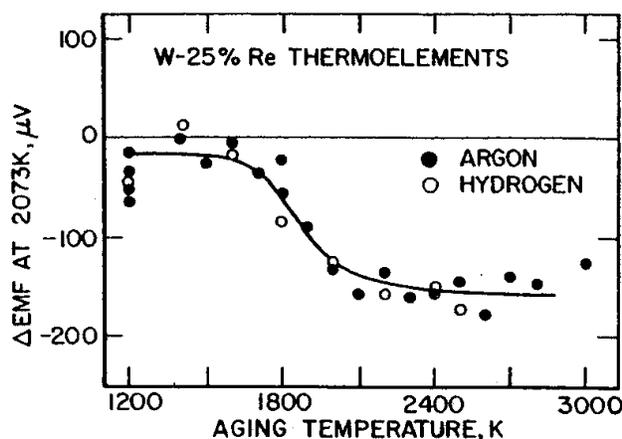


Fig. 3. Change in the thermal emf at 2073K of W-25% Re thermoelements from one lot as a function of the aging temperature in argon or hydrogen. The aging time was 1 hour.

dition (obtained from wire manufacturers) have a fine, fibrous structure, with very long fibers running parallel to the axis of the wire. Typically, the chemically doped thermoelements that were "as received" from the commercial thermocouple wire suppliers exhibited microstructures that were slightly advanced from the

"as drawn" structure, in that some broadening in the fibrous structure was usually apparent. For the W-3 percent Re thermoelements that were exposed for 1 hour at 2400 K in the argon, helium, or nitrogen environments, some further broadening in grain structure occurred, and small elongated grains developed. The microstructures of the W-3 percent Re thermoelements that were exposed at 2400 K for long periods (up to 1000 hours) in these environments were virtually the same as those exhibited by the thermoelements exposed for 1 hour. That is, the microstructure was stabilized within the first hour of exposure at 2400 K and essentially no grain growth occurred during subsequent exposures. An example of the stabilized microstructure exhibited by the W-3 percent Re thermoelements is shown in Fig. 5(a).

In the aging studies where W-3 percent Re thermoelements were exposed in argon for 1 hour at temperatures ranging from 1200 to 3000 K, those thermoelements exposed at 2700 K or above exhibited a structure of very large interlocking elongated grains (secondary

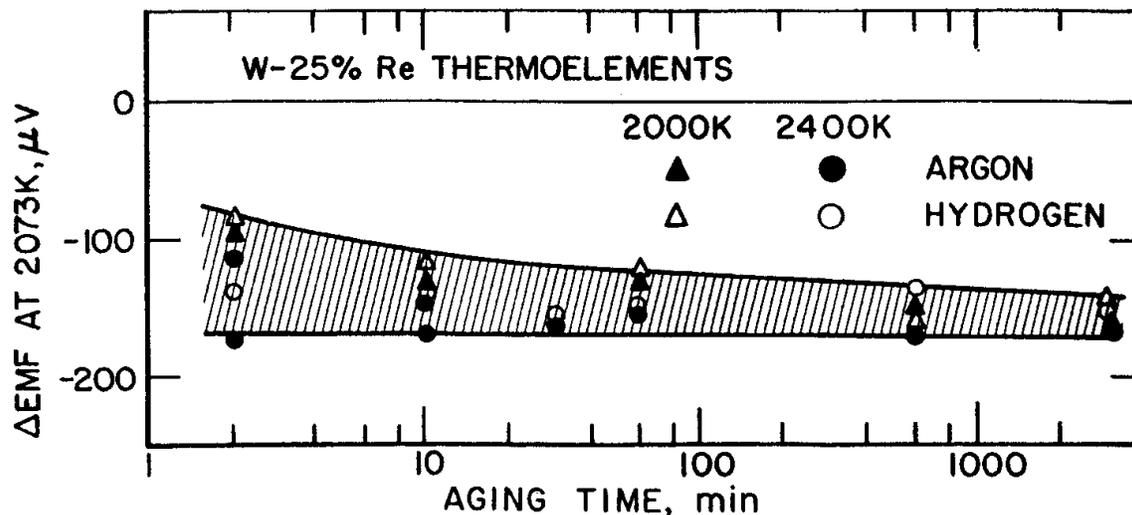


Fig. 4. Change in the thermal emf at 2073 K of W-25% Re thermoelements from one lot as a function of the aging time in argon or hydrogen at the indicated temperature.

recrystallization). A typical example of the resulting microstructure is shown in Fig. 5(b).

The microstructures of W-3 percent Re thermoelements after exposure at 2400 K in vacuum or hydrogen for 50 hours or longer were characterized by a central core of large, interlocking elongated grains surrounded by the small-grained structure.<sup>1</sup> There was no appreciable change in the structure after the first 50 hours of exposure, since the size of the core was not noticeably enlarged in the thermoelements that were exposed for times up to 500 hours. Similar structures were observed for W-3 percent Re thermoelements after exposure in vacuum at 2200 K for times of 250 hours or longer, or at 2600 K for times between 5 and 50 hours.

Only one lot of the chemically doped W and W-5 percent Re thermoelements was examined metallographically. For these lots, exposure in argon at 2400 K for 1 hour resulted in the formation of a grain structure very similar to that shown in Fig. 5(a) for the W-3 percent Re thermoelement. Thermoelements exposed for periods in excess of 50 hours at 2400 K exhibited secondary recrystallization, and a large interlocking elongated grain structure was produced similar to that shown in Fig. 5(b).

The W-25 percent Re thermoelements, in the as received condition from the thermocouple wire supplier, in most cases exhibited a very fine-grained, partially recrystallized structure. Exposure to high temperatures for a very short

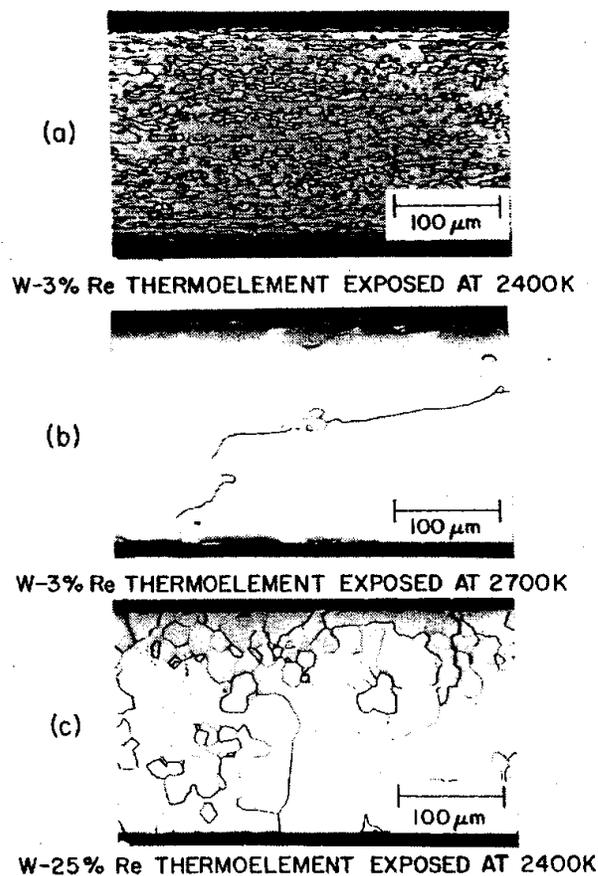


Fig. 5. Typical microstructure of the thermoelements after exposure for 1 hour in argon at the indicated temperature, as exhibited in a longitudinal cross section.

period of time resulted in full recrystallization and some grain growth. Large, equiaxed grains were formed with 1 hour of exposure at

2400 K, as illustrated in Fig. 5(c). Grain growth was continuous with exposure at high temperatures, with the wires exhibiting grains roughly 100  $\mu\text{m}$  to one wire diameter in size after exposure for 1000 hours at 2400 K in argon. No difference in the recrystallization behavior was observed between W-25 percent Re thermoelements that were exposed in the different environments.

A number of the "as received" lots of wire exhibited radial cracks, with some cracks as deep as one wire radius. These cracks were not localized, but ran for long lengths along the wire. While they were more predominate in the W-25 percent Re thermoelement, where about one-half of the as received wire lots exhibited cracks, similar radial cracks were observed in a few lots of W-3 percent Re and W-5 percent Re thermoelements as well. The cracks probably have no significant effect on the thermoelectric properties. However, they can hinder the formation of reliable hermetic seals. In addition, they increase the surface to volume ratio of the thermoelements, thereby making the thermoelements more susceptible to possible chemical contamination.

For typical applications, the thermoelements must be sufficiently ductile at room temperature subsequent to the aging process to permit reliable thermocouple fabrication and installation. A simple test, consisting of attempting to coil the exposed thermoelements around a mandrel of known diameter, was performed to give a semi-quantitative measure of their bend ductility at room temperature.

The doped W-3 percent Re thermoelements exposed to high temperatures in such a manner that either only primary recrystallization resulted (such as occurred in the thermoelements exposed in argon below 2600 K), or secondary recrystallization was only partially complete (such as occurred in thermoelements exposed in vacuum or hydrogen), were quite ductile in that coiling of the thermoelements for many turns around a 1 mm diameter mandrel was usually possible. Thermoelements that exhibited these microstructures after exposure for long periods of time were essentially as ductile as those exposed for 1 hour or less. The doped thermoelements that were exposed in such a manner that secondary recrystallization was completed, such as occurred for W-3 percent Re thermo-

elements exposed at 2700 K or above, gave variable results in ductility and in most cases the thermoelements broke when attempting to coil them one full turn around the 1 mm mandrel. For aging of the W-3 percent Re thermoelement, it would therefore be desirable to retain the fine-grained structure. Aging of the thermoelement for 1 hour in argon at 2400 K ensures this and is sufficient to stabilize the thermoelectric properties (essentially complete the initial emf shift).

For the W-25 percent Re thermoelement, full recrystallization occurs during a short exposure at temperatures above about 1800 K, and equiaxed grains are formed. As the high temperature exposure is continued, the equiaxed grains grow rather rapidly and, as the grain size increases, the thermoelement becomes less pliable at room temperature. At grain sizes larger than about 25  $\mu\text{m}$  the thermoelement becomes rather brittle and it is not well suited for thermocouple assembly. Aging of the W-25 percent Re thermoelement for 1 hour at 2000 K or a few minutes at 2400 K which is sufficient to essentially eliminate the initial emf shift, leaves it fully recrystallized but with only a moderate amount of grain growth (average grain size typically 10 to 20  $\mu\text{m}$ ). Aged in this manner, the thermoelement is pliable enough at room temperature to be repeatedly coiled about a 20 mm diameter mandrel. When extreme pliability is required, the average grain size should be kept to less than 5  $\mu\text{m}$ .

#### Some General Remarks on Bare-Wire Behavior

It is well known that commercial W-Re thermocouple materials will experience some shift in their emf-temperature relationship on initial heating to elevated temperatures.<sup>15,16</sup> However, these results demonstrate that thermocouple wire, which will exhibit only a very small initial shift (0.1 percent to 0.2 percent), can be supplied commercially. It is clear that, with further careful aging of the wires by the user or the sensor fabricator, both the W-3 percent Re and the W-25 percent Re thermoelements can be essentially stabilized while retaining reasonably good room temperature ductility for fabrication purposes. However, the time-temperature parameters required to essentially completely age the wires may be difficult

to achieve in commercial production. For applications where highly ductile properties may be required, such as in the construction of metal-sheathed, compacted-insulated thermocouple sensors, complete stabilization of the wire prior to its assembly into sensor units may not be possible. Nevertheless, with improved controls in the processing of the wires, the authors feel that positive thermoelements could be dependably supplied that will have desirable mechanical properties and yet exhibit only relatively small initial shifts. Efforts along this line have been recently reported by one supplier.<sup>12</sup>

The shifts presented here for the various positive thermoelements are probably largely the result of further relieving of the residual amounts of cold work left in the thermoelements. For the doped W-3 percent Re thermoelement, the small difference in shifts with exposure in the different environments suggests that various small chemical changes in the thermoelements might be occurring as well. In the W-25 percent Re thermoelement, the shift has been relatively small in all lots. The nature of the shifts in the thermoelement (both negative and positive) indicate that chemical or other physical changes in the material may predominate. However, attempts to support this with conventional spectrographic techniques for analysis of residual impurities have not been successful.

The recrystallization behavior that was observed in the W-3 percent Re thermoelement appears to be similar to the two-stage recrystallization process described by Davis<sup>17</sup> for doped tungsten wire, and for this reason we have applied the same terminology to the W-3 percent Re thermoelement. Davis gives a discussion of a number of variables that influence the recrystallization behavior of the doped W wire, and these are probably applicable to the doped W-3 percent Re wires as well. For the particular lots of 0.25 mm diameter doped W-3 percent Re thermoelements that were examined in the current studies, the transition temperature for the onset of secondary recrystallization was found to be above 2400 K in the argon, helium, or nitrogen environments.

For those applications where an accuracy of only a few percent is required, the shift in the

“as supplied” wire is sufficiently small in comparison to the desired measurement accuracy so that its effect may be neglected, and no special aging of the wire by the user is necessary. Furthermore, in typical thermocouple installations and applications, high temperature exposure of the thermocouple is such that the thermocouple wire is not fully aged along its entire length. For a given lot of wire, the shift then, in general, would be less than the shift reported here. Nevertheless, the occurrence of such shifts tends to restrict the accuracy obtainable. For those applications where the ultimate in performance and accuracy is sought, additional thermal aging to eliminate the shift will probably prove desirable.

For a particular lot of wire, the time-temperature parameters for thermal aging will undoubtedly depend upon its previous thermal and metallurgical history as well as the amounts and nature of the chemical impurities present. For this reason, the time-temperature parameters presented here provide only a guide that can be applied for stabilizing other lots of 0.25 mm diameter thermocouple wire.

## RESULTS OF TESTS WITH BeO-INSULATED THERMOELEMENTS AND THERMOCOUPLES

### Thermoelectric Behavior of Insulated Thermocouples

The drift in the thermal emf of three BeO-insulated W-3 percent Re versus W-25 Re thermocouples was determined during exposure at 2073 K in an environment of argon (1 atm) over a period of 1029 hours. The test was performed in the UHV furnace with the thermocouples inserted into the tantalum blackbody enclosure. Preliminary to this, a similar test was performed at 2000 K for 214 hours with four thermocouples, but it will not be discussed in detail since comparable results were obtained.

Prior to these tests, both the thermoelements<sup>18</sup> and the BeO insulating tubing were given preparatory heat treatments. The thermoelement preparation consisted of heating the thermoelement at about 1570 K in vacuum ( $<5 \times 10^{-8}$  Torr) for 1 hour (primarily a surface degas), and then aging the thermoelement in argon at 2400 K for a time period sufficient to eliminate the initial shift in the thermal emf.

The BeO tubing was vacuum degassed in the UHV furnace, during which it was supported in the hot-zone with a basket formed from W-3 percent Re wire. For the degas of the BeO the furnace temperature was increased over a 5-hour period to about 1100 K, held at this temperature for 20 hours, and then increased during a 5-hour interval to about 1800 K where it was maintained for 4 hours. During most of the degas, the pressure in the furnace chamber was less than  $5 \times 10^{-8}$  Torr, but occasionally it briefly increased to about  $5 \times 10^{-7}$  Torr following an increase in the furnace temperature.

After these preparatory treatments, the measuring junctions of the thermocouples were formed by welding with a dc arc in a helium atmosphere, the double-bore insulating tubes were gently slipped onto the thermoelements, and the thermocouples were installed in the furnace. The insulated thermocouples were then vacuum degassed in situ for 2-hour periods at 1000, 1100 and 1300 K. The furnace chamber was cooled to room temperature, backfilled with argon, and finally over a 5-hour period the temperature of the furnace was slowly increased and stabilized at about 2073 K to initiate the test.

At 20- to 30-hour intervals during the course of the test, the temperature of the blackbody enclosure was determined with the visual optical pyrometer (two different observers made readings) and with the automatic photoelectric optical pyrometer; the corresponding values of thermal emf of each thermocouple were also measured. For determining the drift of the thermocouples, the measured values of emf were adjusted to correspond to 2073 K by making a small correction that was equivalent to the difference between the temperature determined with the optical pyrometer and 2073 K.

The thermal emf of one thermocouple was continuously monitored on a recorder throughout the test as a check on the temperature stability of the blackbody enclosure. This, together with the periodic measurements made with the optical pyrometers, indicated that the temperature of the blackbody enclosure was stable within  $\pm 4$  K for the duration of the test. Over a 24-hour period, the temperature stability was typically  $\pm 2$  K and for shorter periods (20 to 30 minutes),  $\pm 0.5$  K. The determina-

tions made with the optical pyrometer indicated that the average temperature during the test was about 2070 K. Since the temperature was closely controlled near 2073 K, the adjustment of the measured emfs to the 2073 K equivalency could be made without introducing any significant uncertainty in the drift results by using an approximate value for the thermoelectric power of the thermocouples.

The values of thermal emf determined at 2073 K for each thermocouple are plotted against the time of exposure at 2073 K in Fig. 6. The data presented are based upon the measurements made with the automatic photoelectric pyrometer. The thermocouples exhibit an apparent small positive linear drift at 2073 K equivalent to 2.3, 2.5 and 2.9 mK/h (or a total change equivalent to about 2.4, 2.6 and 3.0 K after 1029 hours). In each case, the standard deviation of the residuals was equivalent to about 0.4 K and the standard deviation of the slope of the line was equivalent to about 0.2 mK/h. The slopes, while small, are considered statistically significant since they are more than three times the standard deviation of the slope. The measurements made with the visual optical pyrometer gave almost identical values for the drift, although the scatter in the measurements was somewhat larger (i.e., the standard deviation of the residuals was equivalent to about 0.6 K for one observer and about 1.2 K for the other).<sup>3</sup>

For the measurements made with the automatic photoelectric pyrometer, the sum of the absolute values of the estimated measurement errors was about 2 K.<sup>3</sup> Since the observed changes in the thermal emf of the thermocouples are equivalent to slightly more than this, we conclude that at least part of the observed changes results from an actual drift in the thermocouples.

### Metallurgical and Chemical Behavior of Materials

#### Preliminary short-term tests with BeO-insulated thermoelements

Prior to the studies of long-term performance, a series of short-term tests<sup>3</sup> were performed in argon with BeO-insulated thermoelements to gain a working knowledge of the possible effects of materials preparation upon

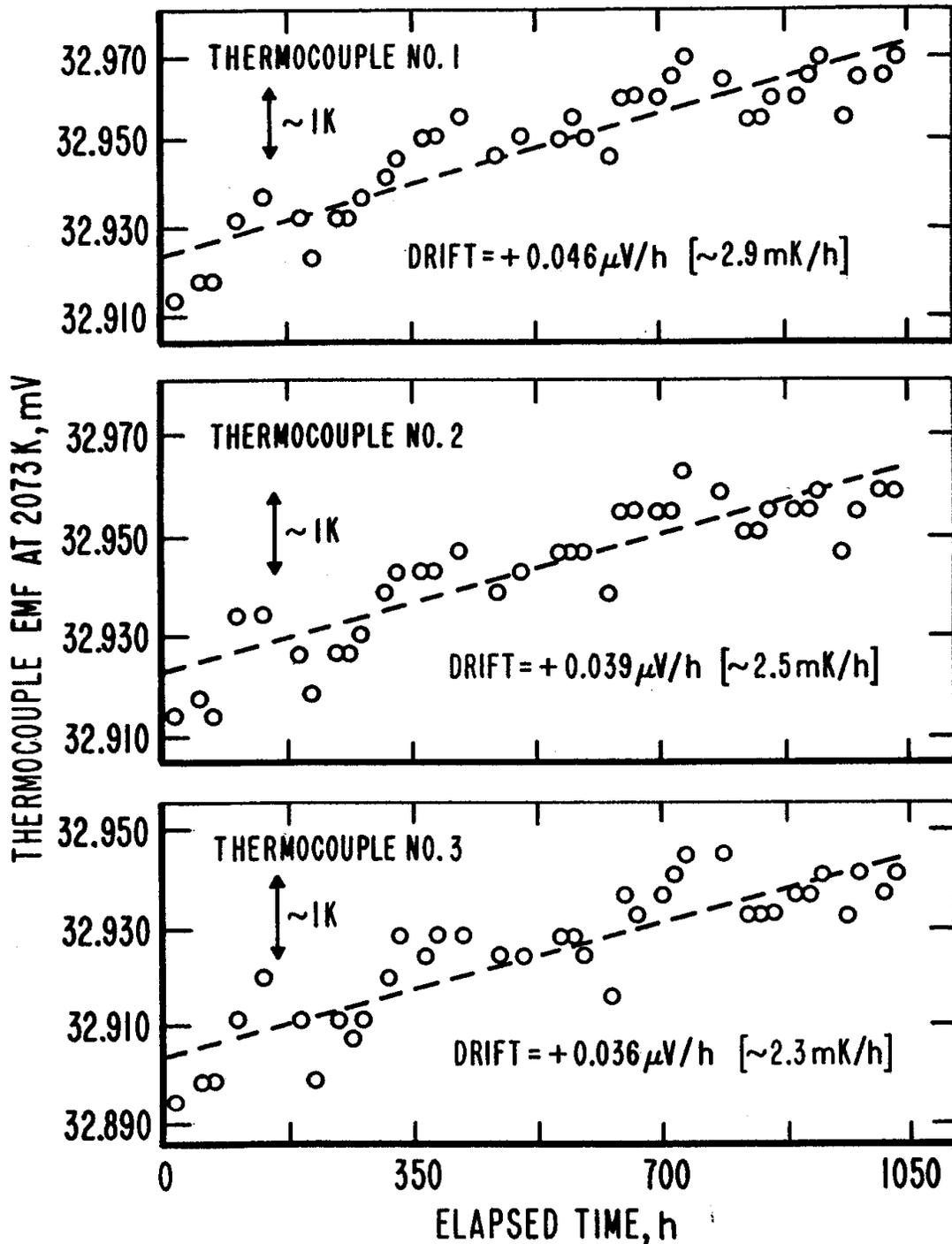


Fig. 6. Drift in the thermal emf of BeO-insulated W-3% Re versus W-25% Re thermocouples exposed at 2073 K in argon for 1029 hours while in the presence of tantalum. The curve through the data points is a straight line fit to the data by the method of least squares. The temperature was measured with an automatic photoelectric optical pyrometer.

the subsequent thermocouple performance at high temperatures. Some of these preliminary findings are summarized here because of their unusual nature.

The preliminary tests were performed by exposing BeO-insulated W-3 percent Re and W-25 percent Re thermoelements<sup>18</sup> in argon at

about 2000 K for periods up to 50 hours. Two methods for exposing the insulated thermoelement were employed. In one method, lengths of the BeO insulating tubing were strung onto the thermoelement and the assembly was hung from two electrodes in the test chamber. The thermoelement was heated electrically, and its temperature was ascertained

from measurements of its electrical resistance. In the second method, the insulated thermoelement was suspended directly in the hot-zone of the furnace for exposure (the blackbody enclosure was removed).

The behavior exhibited by the BeO-insulated thermoelements varied with the method of exposure. For the BeO-insulated thermoelements that were tested by electrical heating, gross erosion of the thermoelements occurred if little or no high-temperature degassing of the BeO tubing was performed prior to the test. Transport of predominantly W from the thermoelements occurred. Much if not all of the W was deposited as a coating upon the bore of the BeO tubing. A small amount of Re, a few tenths of 1 percent was sometimes found in the coating as well. The transport of W was most severe in regions where adjacent lengths of BeO tubing joined. This resulted in a localized reduction in the wire cross-sectional area, which produced hot spots in the thermoelement and often led to its premature failure during test. Because of such effects, the average temperature of the thermoelement could be determined to no better than  $\pm 150$  K during most of these tests. The W-3 percent Re thermoelements tested in this manner experienced as much as a 10 percent reduction in diameter after a 50 hour exposure. While no increase in Re concentration of the W-3 percent Re thermoelements was detected with electron probe microanalysis, changes in the emf-temperature relationship of the thermoelements after exposure were found to be in a direction expected for a small increase in Re concentration.<sup>3</sup> The W-25 percent Re thermoelements experienced no significant changes in diameter but metallographic examination revealed a porous surface layer which for some samples ranged up to 35  $\mu\text{m}$  deep. The central portion of the thermoelements had large, equiaxed grains with no apparent structural anomalies. Electron probe microanalysis revealed no detectable changes in Re concentration in the central portion of the W-25 percent Re thermoelements. In the porous surface layer, grains were Re enriched to as much as W-45 percent Re, and in some samples a second phase was observed, most probably the W-Re sigma phase. Mass spectrographic analyses of samples taken from the exposed thermoelements revealed no significant

changes in the concentration of the metallic impurities. The transport of W from the thermoelements could be reduced, but not eliminated, if high temperature vacuum degassing of the BeO tubing prior to assembly was performed. For example, when degassing procedures similar to one described in the previous section were followed, the porous surface layers exhibited by the W-25 percent Re thermoelement were about 5  $\mu\text{m}$  deep or less.

In tests where the insulated thermoelements were exposed in the furnace, the erosion of the thermoelements after 50 hours at 2000 K was negligibly small. For most of the tests in the furnace, the BeO tubing was degassed for extended periods at temperatures up to 1850 K in the furnace before being assembled onto the thermoelement. In the case of W-25 percent Re thermoelements, no porous layer occurred at the surface on the thermoelements after exposure, and for the most part the surface had essentially the same appearance as for a non-insulated thermoelement exposed in argon. However, a very slight amount of attack was noted at the surface of the W-25 percent Re thermoelement at regions near the ends of BeO tubing segments. For W-3 percent Re thermoelements, there was no visual evidence of any degradation. In addition, in all of these tests the bore of the BeO tubing remained free of any visible coating.

A special test was performed in the furnace with a BeO-insulated W-25 percent Re thermoelement, in which no prior high temperature vacuum degassing of the BeO tubing was performed. After this test, the bore of the BeO tubing was again free of any visible coating, and most of the surface of the thermoelement was again similar in appearance to bare (non-insulated) thermoelements exposed in argon. However, at approximately 5 mm intervals, the thermoelement was found to be fused to the inner bore of the BeO tubing. The fusion regions occurred alternately on opposite sides of the BeO tubing. While the thermoelement normally remains straight after a test, in this case its shape was distorted by the adhesion to the BeO.

In the tests where the thermoelements were electrically heated, the tungsten (and some rhenium) that is removed is probably in the

form of a volatile oxide. The microstructure of the W-25 percent Re thermoelements is very similar to that observed by Wagner<sup>19</sup> in experiments in which W-25 percent Re wires were exposed to high temperatures in oxygen at pressures of  $10^{-4}$  to  $10^{-5}$  Torr. While no clear explanation can be given for the difference in the material behavior between the two methods of exposure, it may be that the tungsten transport that occurs in the electrically heated assemblies is hastened by the radial temperature gradient that exists at the BeO-thermoelement interface.

#### Long-term drift tests with BeO-insulated thermocouples

The thermocouple drift test which exposed BeO-insulated thermocouples for 1029 hours at 2073 K in argon and in the presence of tantalum (Fig. 6) resulted in no observable gross degradation of the thermoelements, BeO tubing or tantalum. During the test, the BeO insulator did adhere to the tantalum in the region near the entrance to the blackbody enclosure. Most likely this was one of the few areas of intimate contact between the tantalum and the BeO insulators. As in the previous short-term tests in the furnace, there was no evidence of any serious chemical incompatibility between the thermoelements and the BeO tubing. Effects such as changes in wire diameter, porous surface layers in the W-25 percent Re alloy, and W coating in the bore of the BeO tubing were not observed. In the W-25 percent thermoelements, a small amount of erosion on the wire surfaces was apparent at regions where small gaps ( $< 1$  mm) occurred between adjacent BeO insulating sections within the furnace hot-zone region; the erosion was confined to the uncovered portions of the thermoelements. No evidence for similar behavior in the W-3 percent Re thermoelements could be found.

The portions of the BeO insulators that were in the hot-zone region of the furnace during the test attained a translucent appearance. Photomicrographs of BeO cross sections revealed that the grain size of the translucent BeO was between 30 and 60  $\mu\text{m}$ . "As received" BeO tubing exhibited grain sizes of the order of 1 to 5  $\mu\text{m}$ , and the preparatory degassing procedure resulted in no appreciable change in grain size. Grain growth in the BeO was also observed

after the preliminary drift test. This test exposed thermocouples to 2000 K for 214 hours in argon while the thermocouples were in the presence of tantalum. The result contrasts with that obtained in experiments which exposed BeO-insulated thermoelements in argon for somewhat shorter times (50 hours) with no tantalum present; under these conditions no appreciable change from the original grain size occurred.

A spectrochemical analysis<sup>20</sup> of the BeO tubing was performed on the "as received" material, on degassed material, on material after exposure in argon at 2000 K for 214 hours in the presence of tantalum, and on material after exposure in argon at 2073 K for 1029 hours in the presence of tantalum. Table III gives the principal impurities detected in these materials. In most cases there was a reduction in the impurity level as the material was first degassed and then thermally exposed in argon in the presence of tantalum for extended time periods. The largest change that occurred with degassing was the removal of Si from 120 ppmw to below detection limits (about 2 ppmw). Ta and W were not detected in any of the samples but are listed to emphasize the relatively high detection levels for these elements. Exposure of the BeO tubing in argon while in the presence of Ta resulted in a reduction of the total detectable impurities by almost an order of magnitude, to a total of 69 ppmw. Large changes in the impurity levels occurred for Al, Ca, and Mg; these elements had experienced little or no reduction in impurity levels after degassing.

Since the BeO tubing was of high purity, the degassing procedure was designed primarily to remove sorbed gases, and the procedure was limited to relatively moderate temperatures ( $< 1850$  K) to prevent gross physical changes in the tubing (such as warpage, grain growth and dimensional changes due to evaporation). Nevertheless, the preceding results demonstrate that the degassing was also effective in reducing some of the metallic impurity levels, and it might be possible to derive a procedure which will further purify the BeO tubing as well. Droege et al.<sup>21</sup> have reported a decrease in the impurity level of sintered BeO insulating tubing that contained starting impurity levels of

TABLE III. CHEMICAL ANALYSIS OF SINTERED, DOUBLE-BORE BeO INSULATING TUBING.

Principal Impurities <sup>a</sup>	ppmw			
	"As received" material	Degassed material	Material exposed for 214 hours at 2000 K in argon in the presence of tantalum	Material exposed for 1029 hours at 2073 K in argon in the presence of tantalum
Aluminum	200	300	90	15
Calcium	30	30	10	6
Carbon	230	115	42	42
Copper	ND (< 1) <sup>b</sup>	ND (< 1)	1	1
Iron	20	7	2	2
Magnesium	90	80	ND (< 1)	1
Nickel	2	ND (< 2)	ND (< 2)	ND (< 2)
Potassium	30	15	15	ND (< 2)
Silicon	120	ND (< 2)	ND (< 2)	2
Sodium	40	20	20	ND (< 2)
Strontium	ND (< 5)	10	ND (< 2)	ND (< 2)
Tantalum	ND (< 500)	ND (< 500)	ND (< 500)	ND (< 500)
Titanium	7	ND (< 5)	ND (< 5)	ND (< 5)
Tungsten	ND (< 500)	ND (< 500)	ND (< 500)	ND (< 500)
Total Detected Impurities	769	577	180	69

<sup>a</sup>Samples were analyzed for 42 metallic elements.

<sup>b</sup>ND, not detected. The values in brackets are estimated detection limits.

several tenths of a percent, after high temperature exposure in vacuum.

Representative samples taken from the thermoelements that were exposed within the BeO tubing for 1029 hours at 2073 K were chemically analyzed by general mass spectrographic methods. Metallic impurities were detected in the samples at the same levels, within a factor of ten, as in unexposed thermoelements from the same lots. Consequently, chemical contamination of the thermoelements by metallic impurities transferred from the BeO tubing or surroundings was not a serious problem.

### SUMMARY

Some studies of the effects of high temperature exposure of bare-wire W-Re alloy thermoelements and BeO-insulated W-3 percent Re and W-25 percent Re thermoelements have been presented. Bare-wire W-Re alloy thermo-

elements of W, W-3 percent Re, W-5 percent Re and W-25 percent Re exposed in the gaseous environments (Ar, He, H<sub>2</sub> and N<sub>2</sub>) exhibited no significant change (drift) in the emf-temperature relationship for time periods up to 1000 hours, after an initial shift was completed. Aging studies of the bare-wire thermoelements indicated that exposure of the unaged W-3 percent Re thermoelement for 1 hour at 2400 K and exposure of the unaged W-25 percent Re alloy for a few minutes at 2400 K was sufficient to essentially remove the shift in the emf-temperature relationship and yet leave the thermoelements sufficiently ductile at room temperature for sensor fabrication purposes.

Exposure in argon of BeO-insulated W-Re thermocouples to high temperatures (2073 K) while in the presence of tantalum can result in highly reliable thermocouple performance for extended periods. Drifts in the W-3 percent Re versus W-25 percent Re thermocouples of only

a few millikelvins per hour were exhibited during an exposure period of 1000 hours. The result is possible if high purity BeO is used, if the BeO is carefully degassed prior to use, if the thermoelements are properly aged, and if a high purity argon environment is maintained.

### References

- <sup>1</sup>G. W. Burns and W. S. Hurst, Natl. Bur. Standards Final Report (NASA CR-72639), March 10, 1970.
- <sup>2</sup>G. W. Burns and W. S. Hurst, J. Research Natl. Bur. Standards 75C, No. 2, 99-106 (April-June 1971).
- <sup>3</sup>G. W. Burns and W. S. Hurst, Natl. Bur. Standards Summary Report (NASA CR-72884), Feb. 1972.
- <sup>4</sup>1 atmosphere =  $1.01325 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ .
- <sup>5</sup>1 Torr =  $(1.01325 \times 10^5 / 760) \text{ N}\cdot\text{m}^{-2}$ . The pressure is equivalent indicated nitrogen pressure.
- <sup>6</sup>The change in the emf-temperature relationship of a thermoelement is defined as the emf-temperature relationship of a thermocouple that is comprised of that thermoelement versus an unheated "as received" thermoelement from the same spool (lot) of wire, when the reference junctions are maintained at 273.15 K and the unheated "as received" thermoelement is designated as the negative leg of the thermocouple.
- <sup>7</sup>The equivalent  $\Delta T$ 's given here were obtained by dividing the values of emf by the thermoelectric power of the W-3 percent Re versus W-25 percent Re thermocouple. The thermoelectric uniformity of some spools (lots) of wire was better than for others, and for these lots the uncertainties in the measurements are estimated to be somewhat less than that given here (see reference 2 for a discussion of measurement uncertainties).
- <sup>8</sup>The calibration of the pyrometers was performed by the Radiation Thermometry Section at NBS. See NBS Monograph 41 for the calibration procedure.
- <sup>9</sup>A "matched lot" of thermoelements is one in which the positive and negative thermoelements have been selected by the supplier so that the emf-temperature relationship of the thermocouple complies to a table within specified limits. One supplier designates the negative thermoelement as W-26 percent Re when matched with the unalloyed W or the W-5 percent Re thermoelement, and designates the negative thermoelement as W-25 percent Re when matched with the W-3 percent Re thermoelement. All Re concentrations are nominal values only. We have chosen to designate the negative thermoelement of the three types of thermocouples as W-25 percent Re in this paper as a matter of convenience.
- <sup>10</sup>J. W. Pugh, L. H. Amra, and D. T. Hurd, Trans. Am. Soc. Metals 55, 451-461 (1962).
- <sup>11</sup>Representative thermocouples from this lot were calibrated by intercomparison with Pt-Rh type thermocouples in the 673 to 1473 K range, and by intercomparison with the visual optical pyrometer in the 1273 to 2073 K range.
- <sup>12</sup>Y. Tseng, S. Schnatz, and E. D. Zysk, Engelhard Ind. Tech. Bull. XI, 12-18 (1970).
- <sup>13</sup>Anon., Product Literature on Tungsten-Rhenium Thermocouple Materials, Hoskins Manufacturing Company, Detroit, Michigan.
- <sup>14</sup>The helium gases are assumed to be free of neon, and the hydrogen gases are assumed to be free of helium.
- <sup>15</sup>B. E. Walker, C. T. Ewing, and R. R. Miller, Rev. Sci. Instr. 36, 816-825 (1965).
- <sup>16</sup>B. F. Hall, Jr., and N. F. Spooner, Los Angeles, California, Sept. 23-27, 1963, Paper 750C (Society of Automotive Engineers, Inc., New York, N.Y.).
- <sup>17</sup>G. L. Davis, Metallurgia 58, 177-184 (1958); 228-232 (1958).
- <sup>18</sup>The thermoelements for these tests were selected from matched lots of wire that had been given a special surface cleaning treatment by the thermocouple wire supplier. The surface cleaning process, which includes ultrasonic degreasing, abrading and electro-etching, was performed to more thoroughly remove surface contaminants introduced during the wire manufacturing processes.
- <sup>19</sup>R. L. Wagner, IEEE 1969 Thermionic Conversion Specialist Conference, Carmel, California, Oct. 21-23, 1969.
- <sup>20</sup>Carbon was determined by combustion-gas chromatography.
- <sup>21</sup>J. W. Droege, N. E. Miller, M. E. Schimek, V. E. Wood, and J. J. Ward, Report No. BMI-X-10246, Battelle Memorial Institute, Columbus, Ohio (November, 1968).