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HIGH RELIABILITY SHEATHED, BERYLLIA INSULATED, TUNGSTEN-RHENIUM ALLOY THERMOCOUPLE ASSEMBLIES – THEIR FABRICATION AND EMF STABILITY

by

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16. Abstract

   1.6 mm diameter tantalum sheathed, BeO insulated, W-3% Re/W-25% Re thermocouple assemblies have been fabricated and their emf drift determined during 2059 hours of exposure at 2073 K in a gaseous helium environment. The sheathed thermocouple assemblies were constructed from aged thermoelements, specially heat-treated BeO insulators, and specially cleaned and etched tantalum sheaths. Their thermal emf drifts ranged from the equivalent of only -0.3 to -0.8 K drift per 1000 hours of exposure at 2073 K. No evidence of any gross chemical attack or degradation of the component materials was found. The emf drift and material behavior of some unsheathed, BeO insulated, W-3% Re/W-25% Re thermocouples at 2250 and 2400 K were also determined. Unsheathed thermocouples tested in an argon environment at 2250 K for 1100 hours and at 2400 K for 307 hours exhibited changes in thermal emf that typically ranged from the equivalent of a few degrees K to as much as +11 K. Post-test examinations of these thermocouples revealed some undesirable material degradation and interaction which included erosion of the BeO insulators and contamination of the thermoelements by tantalum from the tantalum blackbody enclosure in which the thermocouples were contained. Preliminary tests to examine the chemical compatibility of sintered BeO insulators with Ta sheaths in an argon environment at 2073, 2250, and 2400 K were also conducted. They revealed gross erosion of the insulator after only 50 hours exposure at 2400 K. A 50% reduction in the insulator diameter at the open end of the sheath was typical. Well inside the sheath, where gaseous reaction products were confined, the erosion was considerably less. Similar behavior occurred with long exposure (1100 hours) at 2250 K. Serious problems with the BeO insulators were not apparent in tests at 2073 K.

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THEIR FABRICATION AND EMF STABILITY

by

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SUMMARY

This report presents information on the fabrication and the performance of 1.6 mm diameter tantalum sheathed, beryllium oxide (BeO) insulated, W-3% Re vs W-25% Re thermocouple assemblies. The thermocouple assemblies were tested at 2073 K for 2059 hours. Tests were also performed with unsheathed, BeO insulated W-3% Re vs W-25% Re thermocouples. These thermocouples were exposed at 2250 and 2400 K for periods up to 1100 hours. In addition, studies of the chemical compatibility of sintered BeO insulators with tantalum sheaths at 2073, 2250, and 2400 K are also presented. All of the investigations were conducted in gaseous environments of high purity argon or helium at a pressure of nominally 1 atm. Material characterization included metallographic examination and chemical analyses both before and after the high temperature exposures.

The sheathed thermocouple assemblies were constructed from aged W-3% Re and W-25% Re thermoelements, specially heat treated sintered BeO insulators, and specially cleaned and etched tantalum sheaths. Four such assemblies were constructed. After evacuating, baking, and helium leak testing the assemblies, they were filled with high purity argon gas and hermetically sealed. The thermal emf drift of the assemblies was then determined during an exposure in a gaseous helium environment at 2073 K for 2059 hours. The measured thermal emf drifts were smaller than the estimated measurement uncertainties and ranged from the equivalent of only 0.3 to 0.8 K downward drift per 1000 hours of exposure at 2073 K. Rapid cooling (at a rate of about 400 K/min during the first 2 minutes) of the thermocouple assemblies to room temperature after exposure for 88, 252, 553, and 1680 hours did not appreciably alter their values of thermal emf at 2073 K. Post test examinations of the component materials revealed no evidence of any gross chemical attack. However, some minor contamination at the surface of the thermoelements was observed along those portions that were in a steep temperature gradient during the test.

The unsheathed, BeO insulated W-3% Re vs W-25% Re thermocouples were tested in argon at 2250 K for 1100 hours and at 2400 K for 307 hours. Their values of thermal emf at the test temperature typically increased by the equivalent of a few degrees K to as much as 11 K. While these changes are small, they nevertheless are substantially larger than the changes observed in the test of the sheathed thermocouple assemblies. The unsheathed thermocouples exhibited undesirable material degradation and interaction effects in both tests. These effects included erosion and a reduction in the diameter of BeO insulators in the hot-zone of the furnace, coatings of tantalum on bared portions of the thermoelements, coatings of beryllium on the BeO insulators in the temperature-gradient zone of the furnace and microcracking of the BeO insulators in cases where the exposure temperature exceeded the phase transformation temperature of the BeO.

Studies of the chemical compatibility of the BeO insulators with the tantalum sheaths were performed by exposing open-ended tantalum sheaths that contained a specimen of BeO tubing. Tests were run at 2073, 2250, and 2400 K in an argon environment. Gross erosion of the BeO insulator occurred with only 50 hours exposure at 2400 K, particularly at the open end of the sheath (greater than 50% erosion was typical). Erosion was markedly less inside the sheath, where the gaseous reaction products were confined. Microcracking of

the BeO also occurred. With 1100 hours of exposure at 2250 K similar erosion of the BeO
was observed but no microcracking was evident. Serious problems with the BeO were not
apparent in tests at 2073 K. At this temperature the BeO insulators exhibited shrink-
age of about 10 percent in diameter. This was also observed in earlier tests (ref. 1) in
which BeO insulators were exposed to high temperatures in the presence of tantalum. The
shrinkage results from further densification of the sintered insulator and is accompanied
by a reduction in the impurity level.

INTRODUCTION

This report presents results of a continuing study (refs. 2 and 3), which has been
directed towards improving the general reliability of metal-sheathed, ceramic-insulated,
W-Re type thermocouple sensors. Reliable sensor operation for prolonged periods of time
(for many thousands of hours) at temperatures above 1800 K has been of primary concern.
Useful criteria have been sought regarding the selection, preparation, and performance of
materials that might be applied in the design and construction of suitable sensors.

Previous studies were concerned with the behavior of bare (non-insulated) commercially
available W-Re alloy thermoelements and with the behavior of these thermoelements when
fabricated as a thermocouple and insulated with high purity BeO. In the initial studies
(ref. 4) 0.25 mm diameter W-3% Re and W-25% Re thermoelements were exposed at temperatures
of 2200 to 2600 K in environments of high purity argon or hydrogen (nominally 1 atm
pressure) or in high vacuum of less than 1.3 x 10^{-6} Pa (1 x 10^{-8} torr)[1] for periods up to
1000 hours. With exposure in the gaseous environments, initial changes[2] (shifts) in the
emf-temperature relationship of the thermoelements were found to occur usually within 50
hours or less of exposure[3]. With continued high temperature exposure of the thermoelements
in the gaseous environments, the subsequent long term changes (drift) in the emf-temper-
ature relationship were negligible. Conventional metallographic and chemical analyses
were performed to more fully characterize the thermoelements. The thermoelements exposed
in vacuum at temperatures above 2200 K exhibited a continual drift in their emf-temperature
relationship as a result of the preferential evaporation of Re.

Subsequent work (ref. 1) extended the bare-wire studies to include other commercially
available W-Re alloy thermoelements. Parameters for aging were developed that would
minimize the initial shift in the thermal emf and yet leave the thermoelements with
sufficient room temperature ductility to permit subsequent fabrication of thermocouple
sensors. In addition, studies were initiated to examine the behavior of thermoelements and
thermocouples when insulated with high purity sintered BeO tubing. W-3% Re vs W-25% Re
thermocouples, fabricated from thermally aged thermoelements and insulated with well de-
gassed sintered BeO tubing, exhibited drifts of only 2 to 3 K during exposure in argon at
20 5 K for 1029 hours.

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[1] 1 torr = (1.01325 x 10^5/760) Pa. All values of pressure are indicated equivalent
nitrogen pressures.

[2] 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.

[3] Efforts to minimize the shift have been reported. See for example, Tseng et al.,
ref. 8.

This work presents further studies of the thermoelectric stability of BeO-insulated W-3% Re versus W-25% Re thermocouples during exposure in argon at 2250 K for 1100 hours and at 2400 K for 307 hours. Studies of the compatibility of BeO with Ta sheaths at 2073, 2250 and 2400 K are presented. Finally, using carefully prepared and cleaned materials, Ta sheathed, BeO insulated W-3% Re vs W-25% Re thermocouples were fabricated and tested in helium at 2073 K for 2059 hours. The thermal emf test results and the post-test analyses of the component materials are presented.

EXPERIMENTAL PROCEDURES AND APPARATUS

DRIFT TEST WITH SHEATHED THERMOCOUPLE ASSEMBLIES

Preparatory heat treatments and chemical cleaning of materials. Four 1.6 mm diameter tantalum sheathed, BeO-insulated, W-3% Re versus W-25% Re thermocouple assemblies were fabricated for testing at 2073 K. Prior to the fabrication, the component materials were subjected to preparatory heat treatments and cleaning procedures.

The thermoelements were cleaned with ether and then heated for about 1 hour at 1570 K in vacuum (<5 x 10^-8 torr), using test chambers described previously (refs. 2 and 4). This was followed by aging at 2400 K in high purity argon (<10 ppm total impurities) in order to essentially remove the initial emf shift (refs. 1 and 3). The W-3% Re thermoelements were aged for 1 hour and the W-25% Re thermoelements were aged for 10 minutes.

The BeO insulators were vacuum degassed in an ultra-high-vacuum (UHV), high temperature furnace. The furnace, described previously, employs a tungsten wire mesh heating element, tungsten radiation shields and a copper cold wall, and is pumped with an ion pump and an optional titanium sublimation pump (refs. 1 and 2). For the degas, the BeO insulators were suspended in the 30 cm long hot-zone of the furnace in a W-Re basket. The furnace temperature was increased to about 1525 K and held for about 12 hours, and then increased to about 1700 K where it was held for 9 hours. The pressure in the furnace was maintained at less than 5 x 10^-7 torr by continuous pumping during the degas.

The tantalum sheaths were cut to approximately the desired length with a 0.15 mm thick Al₂O₃ cut-off wheel. The sheaths were rinsed in methanol and trichloroethylene, and then etched for about 2.5 minutes in a solution of 33% HNO₃, 33% HF and 33% lactic acid. Following the acid etch, the sheaths were rinsed for 5 minutes in tap water and then rinsed again in the above solvents. The sheaths were cut to final size (about 29 cm long) by cutting off one end with a tube cutter that had a hardened steel cutting wheel and was modified so that its steel rolling surfaces were replaced with a strip of Ta. The cut end of the sheath that was partially closed by the tube cutter was then welded closed with a tungsten inert gas welder under cover of argon gas. The sheaths were then put in a Ta holder and placed in the UHV furnace for vacuum degassing. For degassing, the furnace temperature was increased slowly over a period of 10 hours to about 1875 K, held at this temperature for about 16 hours and then increased to about 2175 K where it was maintained for about 1 hour. The furnace was then cooled in steps to room temperature in about 2 hours. During the degas, the pressure was maintained at less than 5 x 10^-7 torr.

Fabrication and installation of the thermocouple assemblies. Following the heat treatments of the component materials, the components were stored in a vacuum until the construction of the thermocouple assemblies was undertaken. For assembly, the measuring junctions of the four thermocouples were formed by welding with a dc arc in a helium atmosphere. The double-bore BeO insulators were then gently slid onto the thermoelements and the thermocouples were slipped into the tantalum sheaths until the measuring junctions were approximately 5 mm from the closed-end of the sheath. All material handling was done with polyethylene gloves and chemically-cleaned tools.

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[4] 1 torr = (1.01325 x 10⁵/760)Pa. All values of pressure are indicated equivalent nitrogen pressures.

The four tantalum sheathed thermocouple assemblies were installed in a tantalum blackbody enclosure that was suspended in the hot-zone of the UHV high-temperature furnace as shown in Fig. 1. The apparatus is designed so that, after testing, the blackbody and top radiation shield pack can be removed along with the 15 cm diameter top access flange in such a manner as to not load any of the sheaths. Dismantling of the sheaths after testing can then be done outside of the furnace in as non-destructive a manner as possible. The blackbody enclosure closely approximates an ideal blackbody if the walls of the enclosure are at a uniform temperature. Using calculations derived by DeVos (ref. 5), it is estimated that the effective emittance of the enclosure is greater than 0.995.

The mounting of the sheath into the stainless steel access flange is shown in Fig. 1. Underneath the flange, the Ta sheath is held in a stainless steel three-piece compression type fitting. A 0.15 mm thick gold O-ring is inserted into the fitting and provides the primary vacuum seal at the end of the Ta sheath. The stainless steel tee mounted on the top of the flange is an UHV coupling that employs copper gaskets. The thermoelements are brought out through a Kovar-seal header, and the thermoelements are sealed with a solvent-free epoxy resin to the Kovar feedthrough tubes in the header. A connection from each tee is made a manifold through a 6.3 mm diameter stainless steel bellows and a stainless steel UHV valve. The manifold is also of stainless steel, of UHV construction, and is equipped with a 200 liter/s ion pump, an ultra-high purity argon gas supply, and a partial-pressure analyzer.

Initiation of the drift test and test procedures. After installing the blackbody enclosure with the thermocouple assemblies in the UHV furnace, the furnace and manifold were evacuated and baked for about 10 hours at about 525 K. The thermocouple assemblies were then vacuum degassed in situ: The furnace temperature was increased to about 975 K over a 3-hour period, held at this temperature for about 22 hours, and then increased to about 1325 K and held for 2 hours. The pressure in the thermocouple manifold was maintained at less than 2 x 10^{-7} torr during these processes. Following the in situ degas, the thermocouple assemblies were cooled to room temperature and the furnace chamber was backfilled with helium gas. The thermocouple manifold was backfilled with argon gas. The temperature of the furnace was then slowly increased (over a 4-hour period) to about 2073 K and stabilized to initiate the drift test. The thermocouples were calibrated against a visual optical pyrometer at about 1195, 1395, 1590 and 1795 K on bringing them to test temperature. (With the furnace at 2073 K, the pressure in the furnace chamber was about 840 torr and the pressure in the thermocouple manifold was about 780 torr.) The isolation valves to each thermocouple assembly were closed after reaching the test temperature.

During the 2059 hours of test, temperature measurements were made about every 24 hours with an automatic photoelectric optical pyrometer and about every 70 to 100 hours with a visual optical pyrometer (using two observers). Corrections were applied to account for the transmittance of the view port of the furnace. A mechanical shutter was used to shield this view port from the blackbody whenever temperature measurements were not being made. The pyrometers used were of commercial design and were calibrated[5] by relating the pyrometer lamp current to the brightness or blackbody temperature. In use, the pyrometer lamp current was determined by measuring the voltage drop across a 1 ohm standard resistor in series with the lamp. The reference junctions of the thermocouples were maintained at 273.15 K in an ice bath during the test. The values of thermal emf were measured with a digital voltmeter (DVM) having an absolute voltage accuracy of ±(0.004% of voltage measured +2 µV). The DVM was intercompared with a standard cell and also with a precision potentiometer after every several hundred hours of test. Following procedures similar to those used in previous tests (ref.1), the measured values of emf were adjusted to correspond to a temperature of 2073 K by making a small correction equivalent to the difference between the temperature determined with the optical pyrometer and 2073 K.

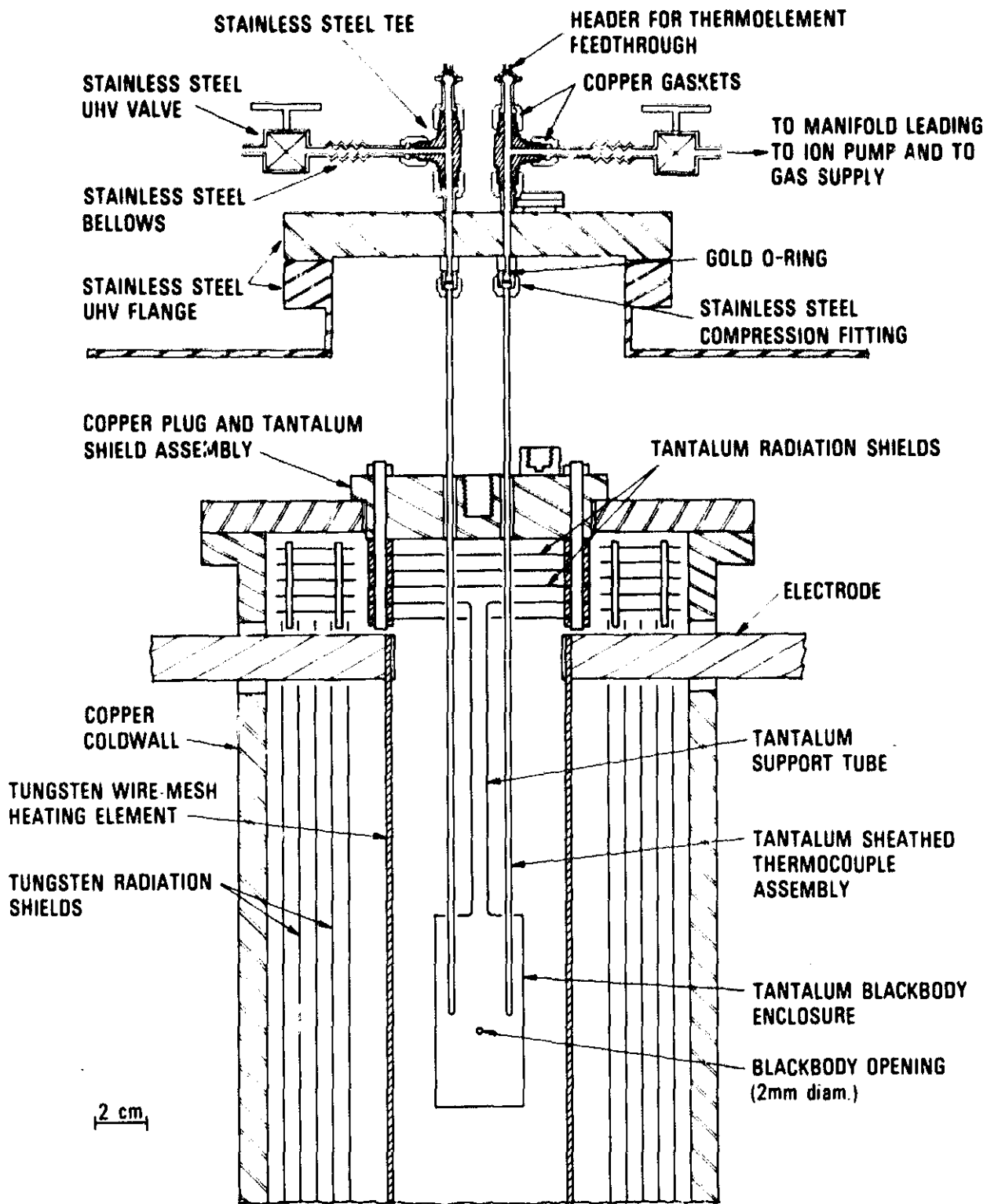[5] Calibration was performed by the Optical Radiation Section of the NBS.

Figure 1. Features of experimental apparatus illustrating the installation of the sheathed thermocouple assemblies for drift testing. Four assemblies were installed.

DRIFT TESTS WITH UNSHEATHED THERMOCOUPLE ASSEMBLIES

Tests were conducted to evaluate the performance of unsheathed BeO-insulated W-3% Re versus W-25% Re thermocouples in argon at temperatures above 2073 K. Test temperatures of 2250 and 2400 K were employed. The preparation of the W-Re thermoelements and the BeO insulators was the same as that described for the sheathed thermocouple drift test. For the tests, the thermoelements were inserted into the BeO, and the assembly was placed into a tantalum blackbody (similar to that in Fig. 1) so that the measuring junction was within the blackbody enclosure. The insulated thermocouples were inserted into the blackbody enclosure through the 6.35 mm diameter tantalum supporting tube (as described in more detail in ref. 1). Usually, four thermocouples were inserted into the blackbody. Prior to testing, the thermocouples were vacuum degassed in situ with 2 hour exposures at temperatures of 1000, 1100 and 1300 K. The procedure for testing of the thermocouples was very similar to that described for the sheathed thermocouple assemblies in the previous section.

COMPATIBILITY STUDIES OF BeO INSULATORS WITH TANTALUM SHEATHS

A series of tests were run exposing the BeO insulators contained in the tantalum sheaths to high temperatures. In preparation for these tests, the BeO insulators were degassed in the same manner as that described for the drift tests. The procedures for cleaning and vacuum-degassing of the tantalum sheaths were also similar to that previously described, except that the sheaths were not etched. (Later, similar tests were performed in which etched sheaths were used and virtually identical results were obtained.) Short lengths (typically 5 to 6 cm) of the Ta sheathing were cut with the Al_2O_3 cut-off wheel, cleaned, vacuum degassed, and then pinched closed at one end. The degassed BeO insulators were broken into lengths about 1 cm longer than the Ta sheaths, and placed in the sheaths. Hence, about 1 cm of the insulator extended beyond the open end of the sheath. The BeO-Ta sheath assemblies were then strapped with Ta wire on the outside of a Ta blackbody. The blackbody, which was similar to the one shown in Fig. 1, was then placed in the UHV furnace, and the usual bake-out of the furnace and a low temperature degas of the assemblies (at about 1000 to 1300 K for 3 to 6 hours at pressures of less than 5×10^{-7} torr) were performed. After cooling the furnace to ambient temperature, it was back-filled with ultra-high-purity argon gas in preparation for the high temperature exposure.

<div align="center">

MATERIALS TESTED

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The W-3% Re and W-25% Re thermoelements for the tests were taken from a matched lot of thermocouple wire that was obtained from a leading commercial supplier. The thermoelements were nominally 0.25 mm in diameter. They were given a special surface cleaning treatment by the supplier in order to more thoroughly remove surface contaminants introduced during the manufacturing processes. The cleaning treatment included ultrasonic degreasing, abrading, and electro-etching, and is described in detail by Toenshoff, et al. (ref. 6). The W-3% 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, act to produce metallurgical structural changes in the wire when it is exposed to high temperatures that result in improvements in the mechanical properties (ref. 7). The W-25% Re thermoelement is not "doped".

Typical mass spectrographic analyses for specimens from these lots of thermoelements were reported previously (ref. 1). For the W-3% Re thermoelement the major impurities detected were K (100 ppm), Mo (100 ppm), and Fe (50 ppm), while impurities of Na, Mg, Al, Si, Cl, Ca, V, Cr, Ni, Cu, Ge, and Ta were detected at the 1 to 20 ppm level. For the W-25% Re thermoelement, Mo (100 ppm) and Fe (50 ppm) were the major impurities detected, with Na, P, K, Cr, Ni, Ge, and Ta detectable at the 10 to 20 ppm level.

Representative thermocouples from the matched lot of thermocouple wire were calibrated in an argon atmosphere by intercomparison with Pt-Rh type thermocouples in the 673 to 1473 K range and by intercomparison with an automatic photoelectric optical pyrometer at temperatures to 2400 K. The emf-temperature relationship of the thermocouples, as derived

from these calibrations, deviated by less than ±1% from the tabular values of emf and temperature that were reported for the W-3% Re vs W-25% Re thermocouple by Tseng et al. (ref. 8).

High purity sintered beryllium oxide (BeO) double-bore insulating tubing with 0.3 mm diam. bores, 1.1 mm outer diameter and 0.13 ±0.03 mm web size (space between bores) was used in the experiments. All the tubing was from the same production batch and was supplied by the manufacturer in random lengths between 10 and 25 cm long. Quantitative spectrochemical analyses of representative "as received" samples from this batch of tubing were reported previously (refs. 1 and 3). The major impurities detected were Al (200 to 300 ppm)[6], C (120 to 230 ppm), Si (120 to 150 ppm), Mg (90 ppm), and Ca (30 to 50 ppm), while the total detectable impurities (metallic and carbon) were less than 1000 ppm. The grain size of the "as received" tubing, as determined from examinations of polished and etched specimens, ranged from about 1 to 5 μm.

Tantalum tubing with a nominal 1.6 mm o.d. and 1.3 mm i.d. was used in the experiments. The tubing was all taken from the same production lot, which was made by a seamless method from electron-beam melted raw material. A variation of about 10 percent was observed in the inner diameter of tubing from this lot. The tubing was supplied by the manufacturer in an as-drawn, straightened, and cleaned condition. The manufacturer reported that the cleaning process consisted of vapor degreasing in hot trichloroethylene after drawing to final size. A typical mass spectrographic analysis of the tantalum tubing is given in the Experimental Results and Discussion section. Niobium (50 ppm) was the principal metallic impurity detected, while other impurities such as F, K, Cu, Zn, and W were detected at the 1 to 10 ppm level. A report of chemical analysis furnished by the manufacturer of the tantalum tubing indicated carbon at 25 ppm, O_2 at < 50 ppm, H_2 at < 5 ppm and N_2 at < 10 ppm.

The argon and helium gases used in the various tests were taken from cylinders of ultra-high purity compressed gas. The gases were certified by the commercial supplier to contain less than 10 ppm by volume total impurities[7] and within detectable limits this was supported by chemical analyses performed by the Analytical Chemistry Division of the NBS.

Concurrent with these studies, a program was sponsored by NASA for development of commercial thermocouple assemblies. This has been reported by Toenshoff, Zysk and Fleischner (ref. 6). The thermocouples they produced had the same general design as those described in this report. The materials used in both programs were of similar quality.

EXPERIMENTAL RESULTS AND DISCUSSION

TESTS WITH SHEATHED THERMOCOUPLE ASSEMBLIES

Thermal emf drift. The thermal emf drift of four 1.6 mm o.d. tantalum sheathed, BeO insulated, W-3% Re versus W-25% Re thermocouple assemblies was determined during exposure at 2073 K for 2059 hours in helium (1 atm). The methods used during the test to obtain the experimental data are discussed in the section on experimental procedures and apparatus.

The four thermocouple assemblies exhibited virtually identical behavior during the test. The values of thermal emf determined for one of the thermocouple assemblies are plotted against time of exposure at 2073 K in Fig. 2. The data presented are based upon measurements made with the automatic photoelectric optical pyrometer. A straight line is fitted to the data by the method of least squares to show the general trend of the data (the drift). The slope of the line is -0.013 μV/h, which is equivalent to about -0.8 K per 1000 hours. While some systematic variation of the data points about the straight line is

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[6] The values in parentheses give the range in the composition of the element in parts per million by weight as determined from analyses of several specimens.

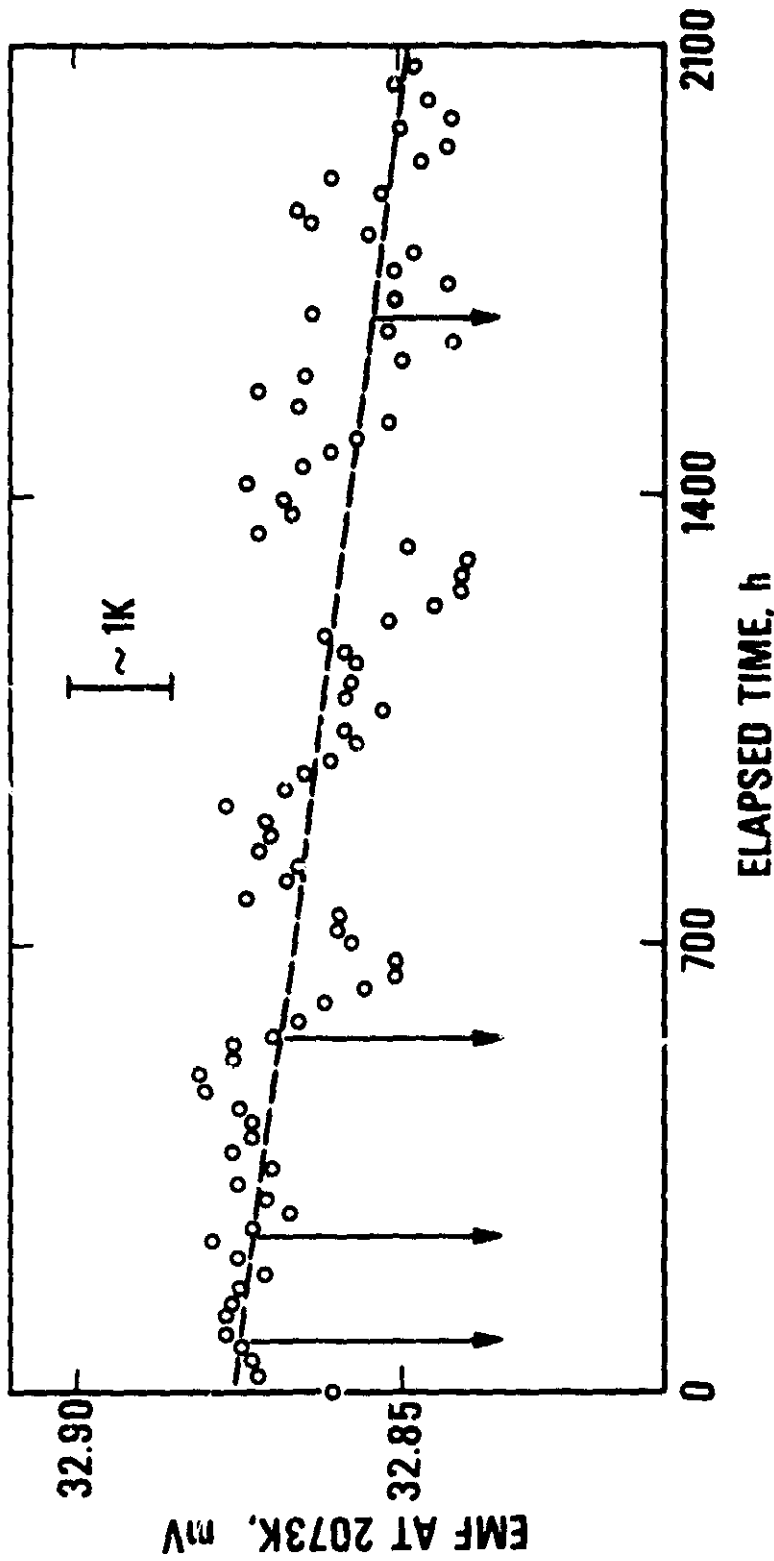[7] This assumes the helium gas to be free of neon.

Figure 2. Drift in the thermal emf of a tantalum sheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple assembly during exposure in helium for 2059 hours at 2073 K. The thermocouple assembly was installed in a tantalum blackbody enclosure that was heated in a high temperature furnace and the temperature was measured with an automatic photoelectric optical pyrometer. The reference junctions of the thermocouple were maintained at 273.15 K. The curve through the data points is a straight line fit to the data by the method of least squares. The thermocouple assembly was rapidly cooled to room temperature at the times indicated by the arrows (see Fig. 4 for rate of cooling).

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evident, the maximum deviation of any data point from the line is equivalent to only 1.2 K. The standard deviation of residuals is equivalent to 0.5 K and the standard deviation of the slope is equivalent to 0.09 K per 1000 hours. The use of higher order terms to achieve a more precise fit of the experimental data seemed unwarranted. The oscillatory nature of the experimental data is thought to have resulted principally from some instability in the automatic photoelectric optical pyrometer.

Such oscillations were also apparent in the data obtained for the other three thermocouple assemblies. Similar treatment of the experimental data for the other thermocouple assemblies gave values for the drift at 2073 K of -0.5, -0.7, and -0.8 K per 1000 hours. Measurements with the visual optical pyrometer yielded values for the drift that agreed within 0.2 K per 1000 hours with those derived from the automatic photoelectric pyrometer measurements. Typical results, based upon measurements with the visual optical pyrometer, are shown in Fig. 3. The data of both observers are plotted against exposure time at 2073 K for the same thermocouple assembly as the one used in Fig. 2. The straight line fitted to the data has a slope of -0.010 μV/h, which is equivalent to -0.6 K per 1000 hours. The standard deviation of residuals is equivalent to 0.7 K and the standard deviation of the slope is equivalent to 0.15 K per 1000 hours. The test results for all four thermocouple assemblies are summarized in Table 1.

As indicated in Figs. 2 and 3 the thermocouple assemblies were cooled to room temperature (~ 295 K) on four occasions during the test; after about 88, 252, 553, and 1680 h of exposure. The rate of cooling on all four occasions was approximately the same and is shown in Fig. 4. The average rate of cooling during the first 2 minutes was about 400 K/min. After cooling, the thermocouple assemblies were heated to 2073 K over a period 1 to 4 hours in order to resume the test. It is evident from the results presented in Figs. 2 and 3 that the thermal cycling had no appreciable effect upon the thermal emf of the thermocouple at 2073 K. During the thermal cycles which occurred after 252 and 553 h of exposure, the thermocouple assemblies were calibrated by intercomparison with the visual optical pyrometer at about 1195, 1395, 1590, 1795, and 2073 K. The calibrations were performed during the heating portion of the cycle and two observers made readings with the pyrometer. A similar calibration was also performed both before and after the test. The differences between the calibrations that were performed after 252, 553 and 2059 hours of exposure and the calibration performed before the test are shown in Fig. 5 for two of the thermocouple assemblies. They are the assemblies which had the largest and the smallest measured drifts at 2073 K (see Table 1, thermocouple Nos. 2 and 3, respectively). These data indicate the drift was also less than the equivalent of 1 K per 1000 hours for calibration temperatures below 2073 K. While a small deviation between the initial calibration and the subsequent calibrations is apparent at the lower temperatures, the calibrations after 252, 553 and 2059 hours of exposure agree within estimated observer precision.

Before any significance can be attached to the small drifts that were derived from the experimental data, the measurement uncertainties must be considered. Drift in the calibrations of the optical pyrometers and changes in the spectral transmittance of the furnace window during the test are the principal factors contributing to the measurement uncertainties. The calibrations of both pyrometers were checked at about 2060 K before, near the middle, and after the 2059 hour drift test by the Optical Radiation Section at the NBS. The pyrometers were intercompared with the NBS standard photoelectric pyrometer (ref. 9) using a vertical resistive-heated graphite blackbody as a transfer source. A small change, equivalent to about 1.8 K, was detected in the calibration of the automatic photoelectric pyrometer and a small correction was applied to the experimental data to account for it. It is estimated that this reduced the uncertainty in the measurements, due to any drift in the calibration of the automatic photoelectric pyrometer, to less than the equivalent of 1 K. There was no significant change ($\leq$ equivalent of 1.5 K) detected in calibration of the visual optical pyrometer. The spectral transmittance of the furnace window was also checked before and after the test and no significant change was apparent in it ($\leq$ equivalent of 0.5 K). The calibration of the DVM was checked periodically during the test by the method described in the section on experimental procedures and apparatus. These checks indicated that uncertainties in the measurements arising from any drift in its calibration were less than the equivalent of 0.2 K. Systematic errors introduced by other means, such as a gradual change in blackbody conditions, are thought to be small ($\leq$ equivalent of 0.2 K).
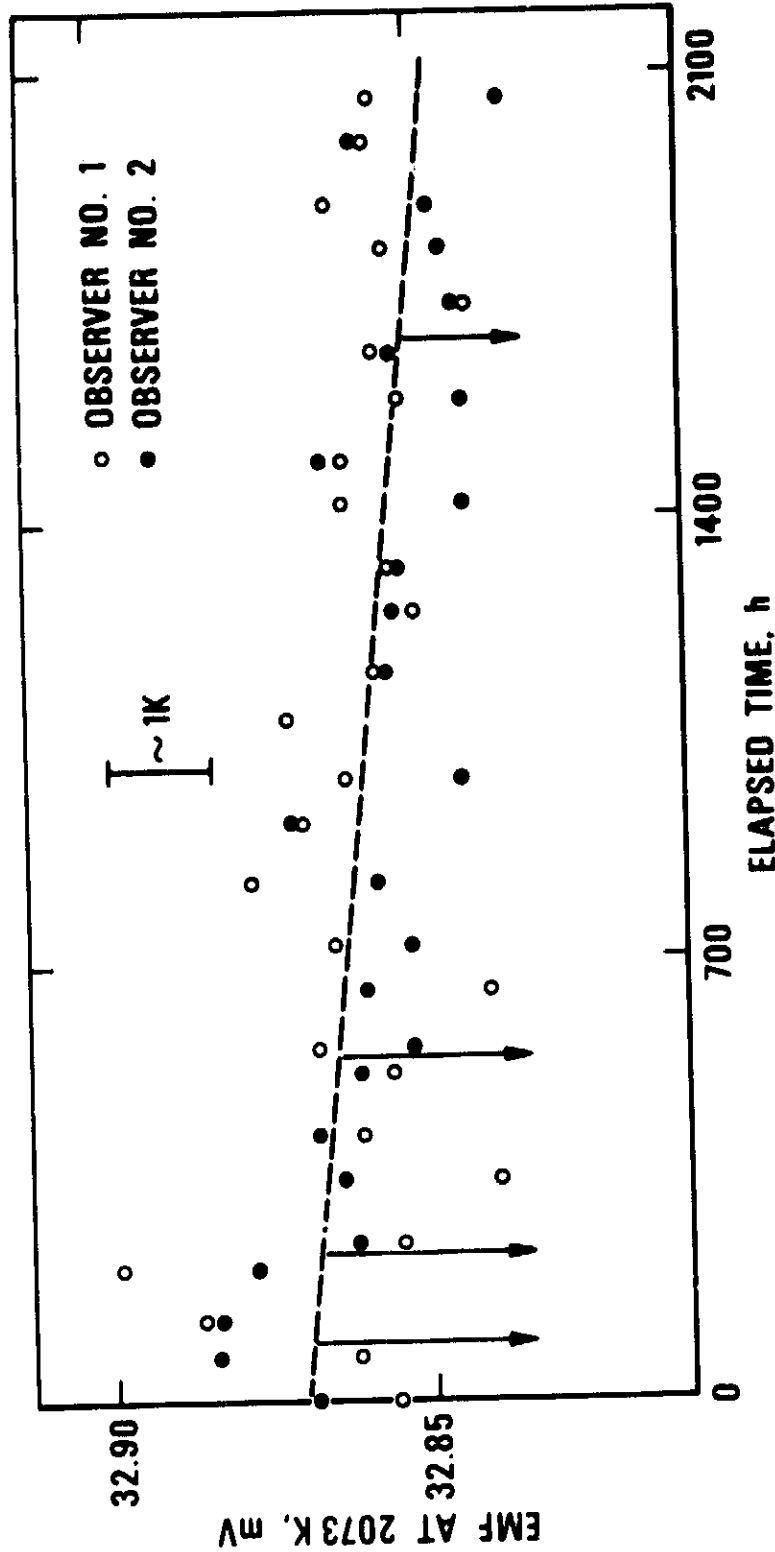
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Figure 3. Drift in the thermal emf of a tantalum sheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple assembly during exposure in helium for 2059 hours at 2073 K. The thermocouple assembly was installed in a tantalum blackbody enclosure that was heated in a high temperature furnace and the temperature was measured with a visual optical pyrometer (two observers made readings). The reference junctions of the thermocouple were maintained at 273.15 K. The curve through the data points is a straight line fit to the data by the method of least squares. The thermocouple assembly was rapidly cooled to room temperature at the times indicated by the arrows (see Fig. 4 for rate of cooling).

TABLE 1. SUMMARY OF THE RESULTS OF THE 2059 HOUR DRIFT TEST AT 2073 K WITH TANTALUM SHEATHED, BeO INSULATED, W-3% Re VERSUS W-25% Re THERMOCOUPLE ASSEMBLIES.

RESULTS EXPRESSED IN TEMPERATURE EQUIVALENTS

THERMOCOUPLE NO.	AUTOMATIC PHOTOELECTRIC OPTICAL PYROMETER AS TEMPERATURE REFERENCE[a]			VISUAL OPTICAL PYROMETER AS TEMPERATURE REFERENCE[b]		
	S mK/h	σ_s mK/h	σ_r K	S mK/h	σ_s mK/h	σ_r K
1	-0.7	0.1	0.5	-0.5	0.2	0.7
2	-0.8	0.1	0.6	-0.7	0.2	0.8
3	-0.5	0.1	0.5	-0.3	0.2	0.7
4	-0.8	0.1	0.5	-0.6	0.2	0.7

S = slope of straight line fit to drift data by method of least squares.

σ_s = standard deviation of slope.

σ_r = standard deviation of residuals.

[a]88 data points.

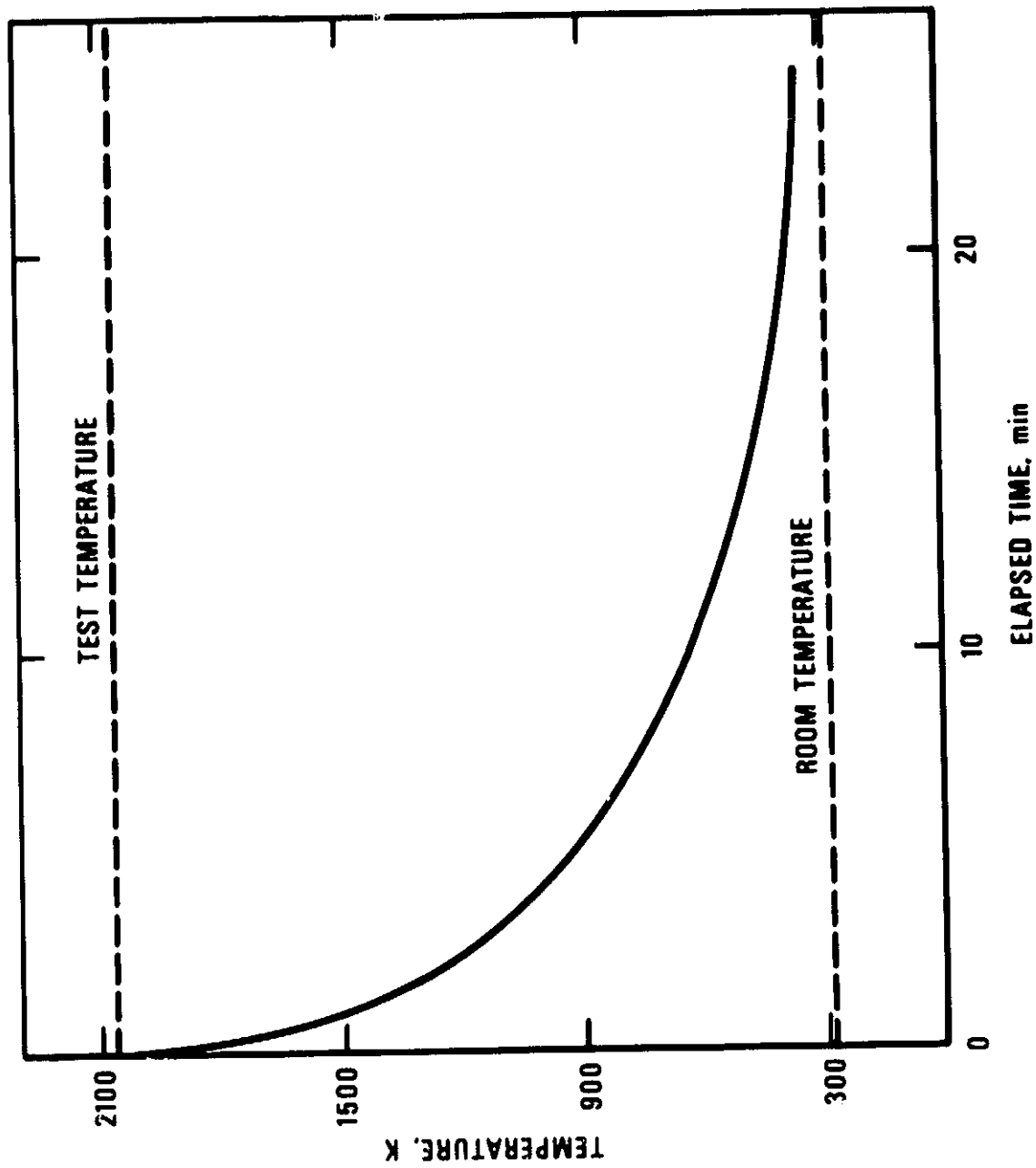[b]53 data points, includes data of two observers.

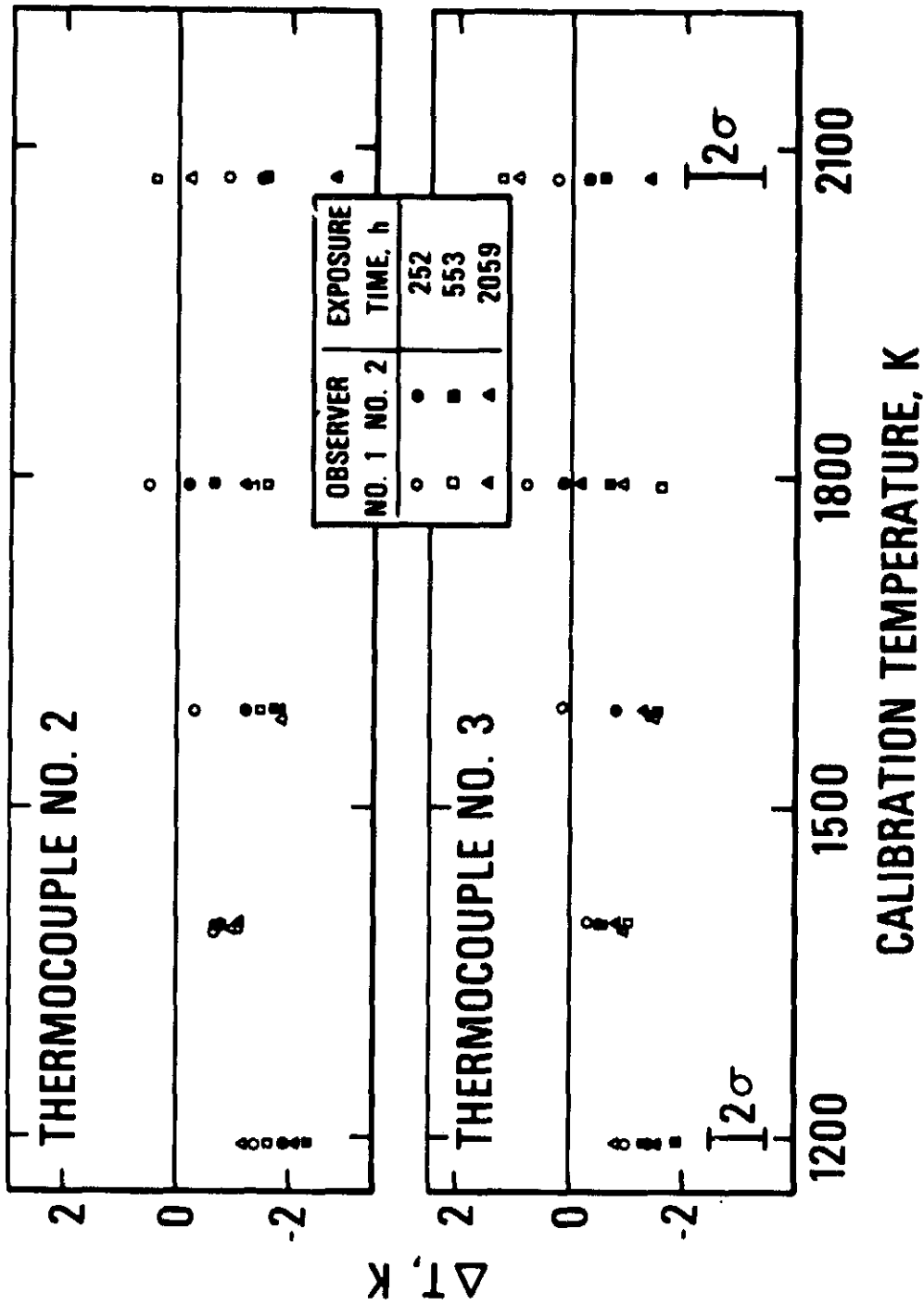Figure 4. Rate of cooling of sheathed thermocouple assemblies.

Figure 5. Change (ΔT) in the calibration of tantalum sheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple assemblies at various temperatures after exposure in helium at 2073 K for the indicated times. A positive value of ΔT indicates an increase in the emf. The thermocouple assemblies were installed in a tantalum blackbody enclosure that was heated in a high temperature furnace and the temperature was measured with a visual optical pyrometer (two observers made readings). The brackets indicate a change equivalent to two times the estimated observer precision (σ) at the indicated temperature.

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If the above allowances for systematic error are added, one gets 1.9 K for measure-
ments with the automatic photoelectric pyrometer and 2.4 K for measurements with the visual
optical pyrometer. When the imprecision of the experimental data is considered together
with possible systematic errors, the observed changes, which were less than 2 K during the
2059 hour test, are small by comparison and are therefore concluded to be insignificant.

It is interesting to compare the results of this test with those reported recently by
Heckleman and Kozar (ref. 10) for an out-of-pile evaluation of some sheathed W-3% Re versus
W-25% Re thermocouples. Heckleman and Kozar measured the thermal emf drift of six
tantalum sheathed, BeO insulated, 0.157 cm diameter, grounded junction W-3% Re versus
W-25% Re thermocouples during exposure to temperatures in the 1900 to 2100 K range for in
excess of 8000 hours. The thermocouples were built commercially to rigorous specifications
and supposedly represented the current state of the art as far as fabrication techniques
were concerned. During the test they were inserted in a tantalum blackbody, which was
heated in a high purity helium gas environment. A negative drift of 55 to 60 K at 2073 K
occurred during the first 2000 hours of testing but little change occurred thereafter.
Post-test examinations of the thermocouples directed towards identifying the mechanisms
responsible for the drift were planned, but could not be reported, because of termination
of the reactor program. Heckleman and Kozar conjectured that the drift was probably caused
by chemical composition changes resulting from contamination by impurities that were pre-
sent in the insulator, sheath, or on the wires. They concluded that after about 2000 hours
the impurities had apparently been gettered or had diffused to some other location where
they were no longer effective in promoting further drift.

The thermocouples tested by Heckleman and Kozar used crushable insulators that were
compacted by swaging and had grounded junctions, while those tested in the present work
had hard, sintered double-bore insulators and ungrounded junctions. This might possibly
account for some difference in behavior. We attribute the highly stable behavior of the
thermocouple assemblies that were fabricated at NBS primarily to the careful selection,
preparation and assembly of the component materials. While the type of construction may
also be a factor, its importance is thought to be secondary. In any event, from the
results of these two experiments it is clear that highly reliable tantalum-sheathed W-Re
type thermocouple sensors can be fabricated. Satisfactory performance for periods in
excess of 8000 hours at temperatures to 2100 K without any appreciable emf drift is
possible with suitably fabricated sensors in environments that are not intrinsically
deleterious to the sensor materials.

Post-test examination of materials. At the conclusion of the 2059 h test, the
thermocouple assemblies and tantalum blackbody were removed from the furnace as a unit
and inspected. Some warpage of the tantalum sheaths was evident and each of the sheaths
was fused to the tantalum blackbody at the point where it entered the 3.2 cm diam. en-
closure (see Fig. 1). The sheath on thermocouple No. 2 was also fused to one of the
tantalum radiation shields at the top of the furnace hot-zone and it had a small crack
at this point. It was not clear whether the crack occurred during the test (probably on
thermal cycling) or whether it occurred when the assemblies were removed from the furnace.
In any event, the performance of thermocouple No. 2 was not significantly different from
that of the other three thermocouples. To check on gas tightness, the sheaths on the
other three thermocouple assemblies were evacuated and helium leak tested. No leaks were
detected in any of the sheaths. Visual inspection revealed no evidence of any serious
chemical attack of the tantalum sheaths or the tantalum blackbody enclosure.

The thermocouple assemblies were then removed from the blackbody enclosure and dis-
mantled. By making transverse cuts at several places along the thermocouple assemblies
the BeO insulators were easily removed from the tantalum sheaths. The thermocouple wires
were free within the bores of the insulators and were also easily removed for examination.
No gross chemical attack of the thermoelements, BeO insulators, or the tantalum sheaths
was apparent.

Photomicrographs of transverse cross-sections that were taken at about 2 cm and at
about 28 cm from the sheath tip of one thermocouple assembly are shown in Fig. 6. The
microstructures of the materials, as illustrated in the cross-section at 2 cm, are typical
of that exhibited by materials which were taken from locations up to 15 cm from the sheath

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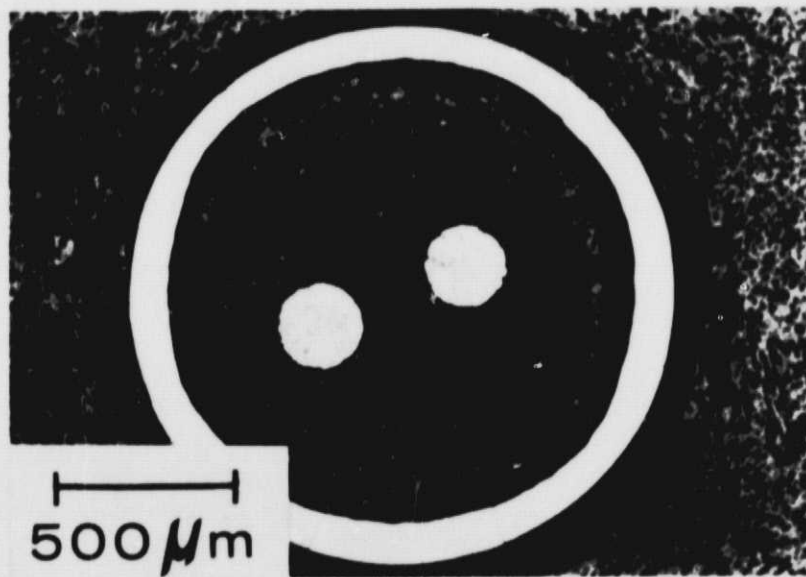
(a)
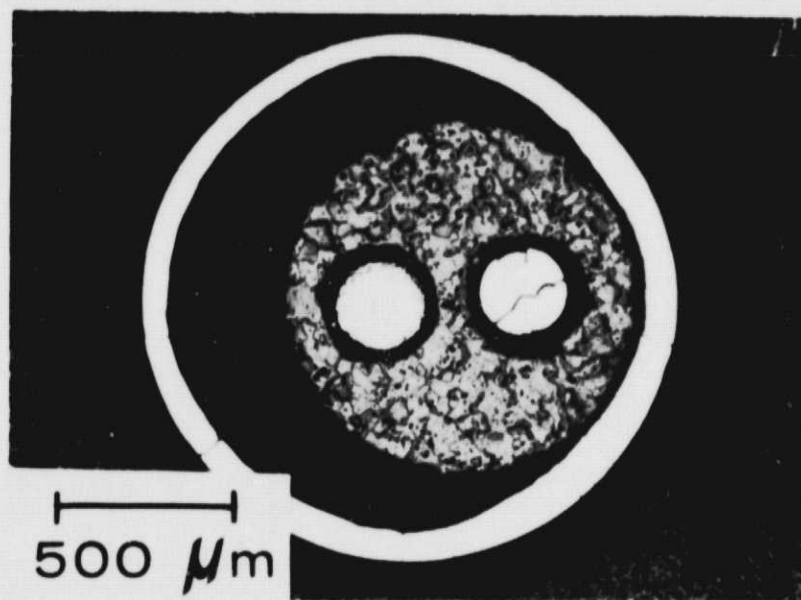
(b)

Figure 6. Photomicrographs showing transverse cross-sections of a 1.6 mm diameter tantalum sheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple (a) at 28 cm from the sheath tip where no high temperature exposure occurred, and (b) at 2 cm from the sheath tip where exposure for 2059 hours at 2073 K occurred.

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tip. The cross-section at 28 cm from sheath tip was taken at a location along the thermocouple assembly that was not heated. Therefore, the microstructures are typical of the materials prior to testing (and subsequent to the preparatory heat treatments and assembly). Those portions of the W-25% Re thermoelements that were in the hot-zone region of the furnace experienced substantial grain growth, with the wires exhibiting equiaxed grains roughly 50 µm up to one-half wire diameter in size. In contrast, the exposed portions of the W-3% Re thermoelements experienced virtually no grain-growth. They had a fine-grained structure similar to that of the aged "starting" material. These results are to be expected from material behavior observed in earlier work (refs. 1 and 4), where bare thermoelements were exposed at temperatures up to 2400 K for periods as long as 1000 hours.

As shown in Fig. 7, a temperature gradient of approximately 400 to 500 K/cm existed along the thermocouple assemblies during the test in the region between 15 and 18 cm from the sheath tips. Examination of the thermoelements in this region revealed that some chemical interactions had occurred at the wire surfaces. The appearance of the surfaces of both thermoelements is shown by the photomicrographs in Fig. 8. For purposes of comparison, photomicrographs showing the typical appearance of the surfaces of thermoelements in the high-temperature zone (extending from the sheath tip to 15 cm from tip) and in the unheated zone are included in Fig. 8. The interaction is more apparent in the W-25% Re thermoelement. The surface of the W-25% Re thermoelement is shown at higher magnification by the photomicrograph in Fig. 9. The formation of an apparent second phase at the grain boundaries can be seen. A longitudinal cross-section taken very near the surface of the W-25% Re thermoelement is given in Fig. 10 and it clearly shows the presence of a second phase at the grain boundaries. The second phase presumably resulted from some attack of the wire surface by chemical contaminants. While some diffusion from the wire surface along the grain boundaries is evident, it is limited to a depth of about 10 µm. Transverse cross-sections of the thermoelements in this region revealed no evidence of other phases at the interior of the wire. A positive identification of the chemical composition of the second phase has not been made. However, spectrochemical analyses of specimens that were taken from the thermoelements in this region indicated a small increase in the Mg and Ca impurity levels. No significant increases in the impurity levels of Aℓ, Be, Fe, Si, or Ta were detected.

The BeO tubing that was in the high temperature zone had a translucent appearance. As shown in Fig. 6 appreciable grain-growth and about a 10% reduction in the tubing diameter are evident. The grain size of the exposed BeO tubing ranges from about 30 to 90 µm. By comparison, the grain size of the "as received" BeO tubing was typically 1 to 5 µm and virtually no change in the grain size occurred as a result of the preparatory heat treatments (vacuum degassing). The diameter reduction is thought to be a result of densification. In other tests (see section on Studies of BeO-Ta Sheath Compatibility and also ref. 1) where tubing from the same lot was exposed at temperatures in the 2000 to 2250 K range for prolonged periods in the presence of tantalum similar behavior was noted. In addition, in earlier work (refs. 1 and 3) a substantial increase in the purity of the exposed insulators was observed; sizable reductions were detected in the impurity levels of principally Aℓ, C, Ca, Mg and Na. The residual impurities were suspected to have been gettered by the tantalum. The results of mass spectrographic analyses on exposed tantalum specimens from the present test further support this assumption. Typical chemical analyses are given in Table II for a specimen of the chemically cleaned, etched, and vacuum degassed tantalum tubing and for a specimen of tantalum tubing that was taken from one of the thermocouple assemblies at a point between 2 and 6 cm from the sheath tip.

Aℓ, Ca, Fe, Mg, Na, Si and Ti, which are residual impurities in the BeO tubing, are detectable in the exposed thermocouple sheath at a level at least ten-fold greater than in the unexposed tantalum tubing. The most notable increase is that for Aℓ. This is not surprising since Aℓ is the principal impurity in the BeO tubing, where it is detectable at the 200 to 300 ppm level (refs. 1 and 3). The BeO tubing is also the most probable source of the contaminants which were responsible for the attack noted at the surface of the thermoelements in the temperature gradient zone.
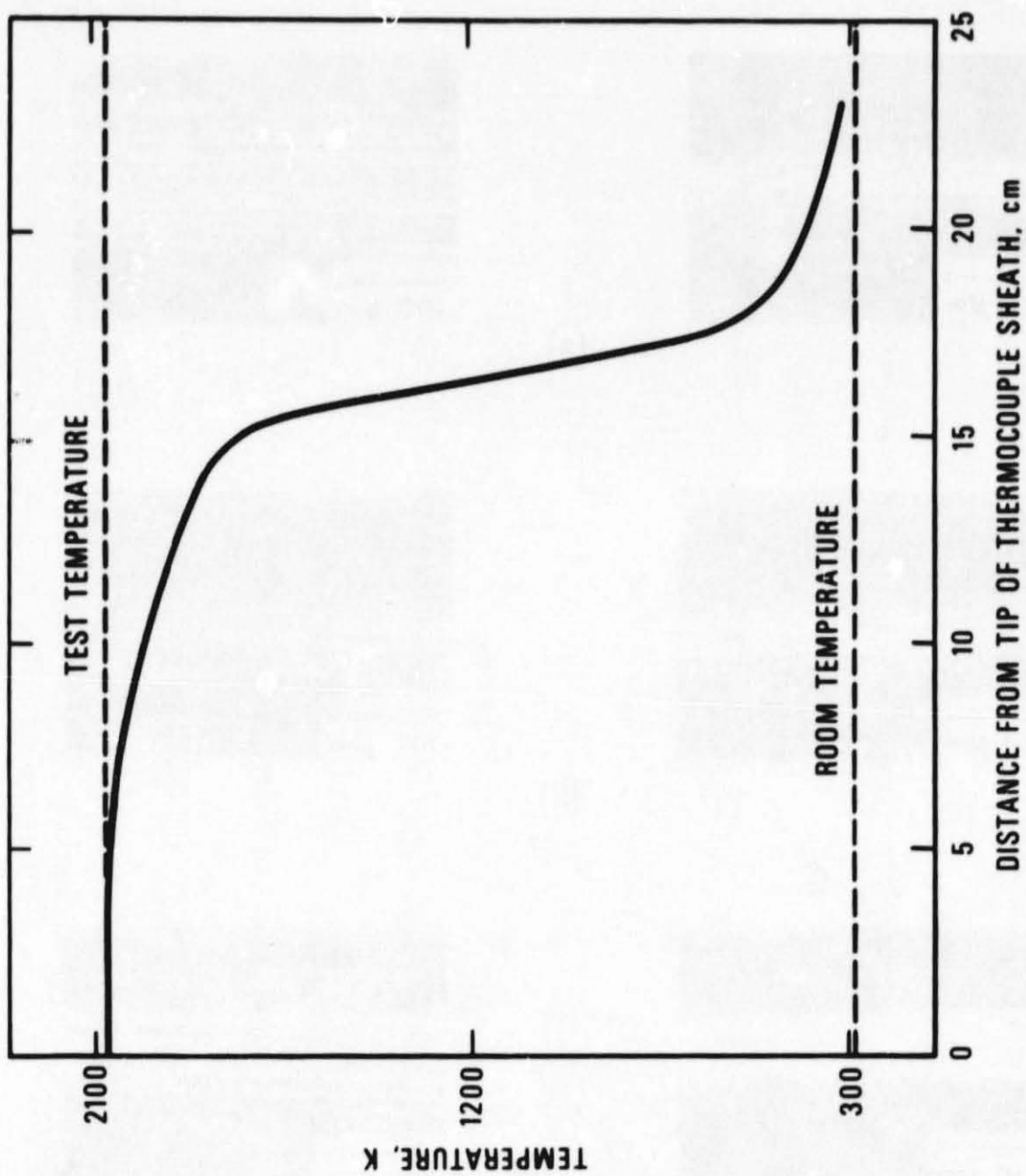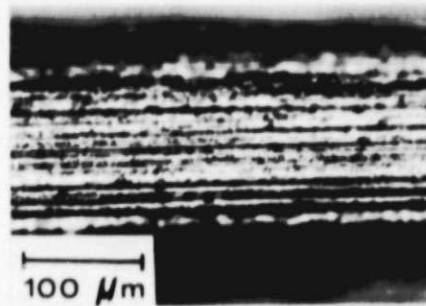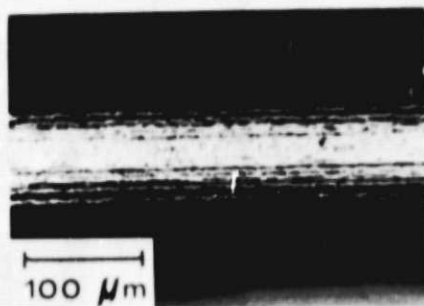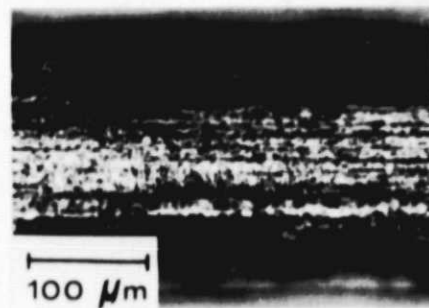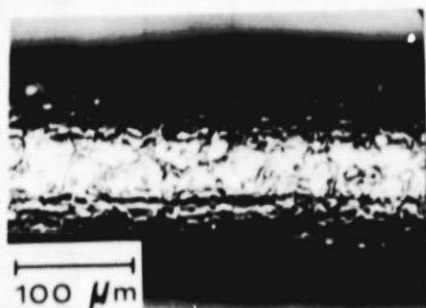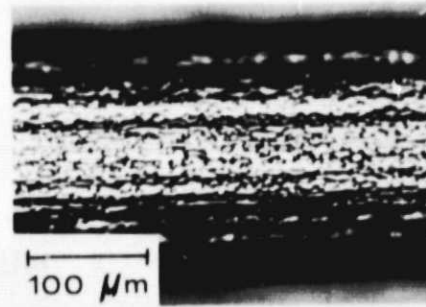
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Figure 7. Temperature distribution along the sheathed thermocouple assemblies during the drift test at 2073 K.
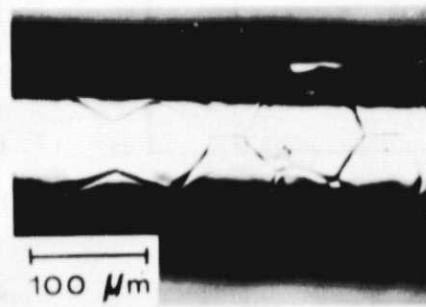
Figure 8. Photomicrographs showing the typical appearances of the surfaces of the thermo-elements in various regions along the tantalum sheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple assemblies that were exposed for 2059 hours at 2073 K: (a) in the unheated-zone greater than 25 cm from the sheath tip; (b) in the temperature-gradient zone between 15 and 18 cm from the sheath tip; and (c) in the high temperature zone extending from the sheath tip to 15 cm from the tip.

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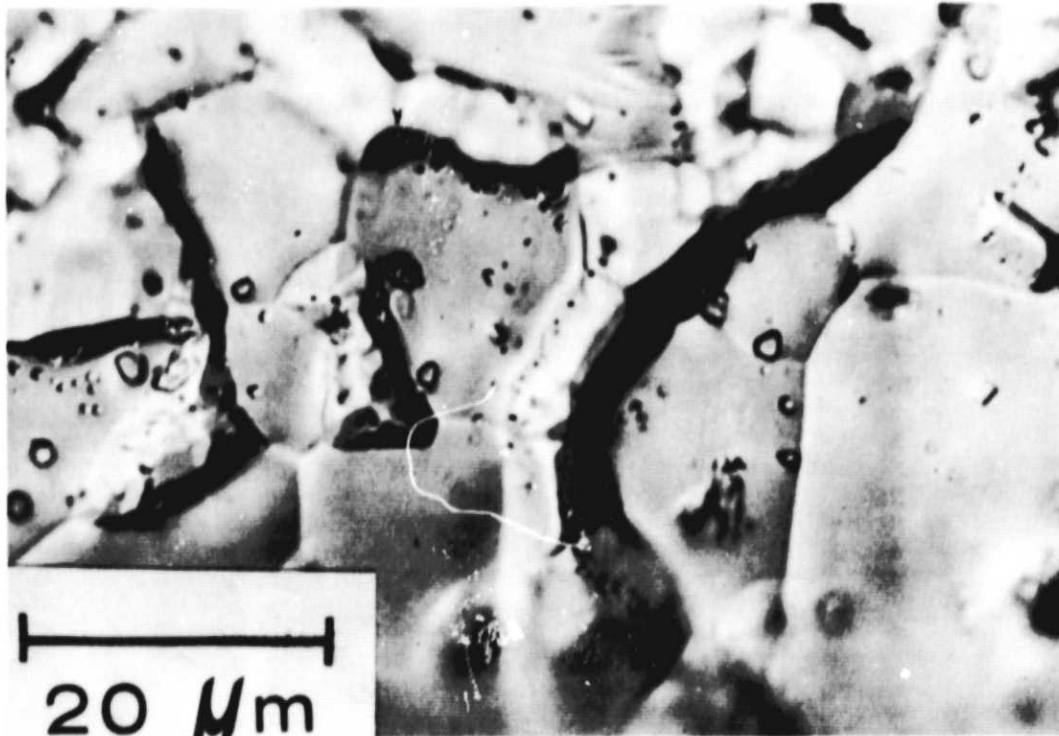20 μm

Figure 9. Photomicrograph showing the surface of the W–25% Re thermoelement in Fig. 8(b) at higher magnification.
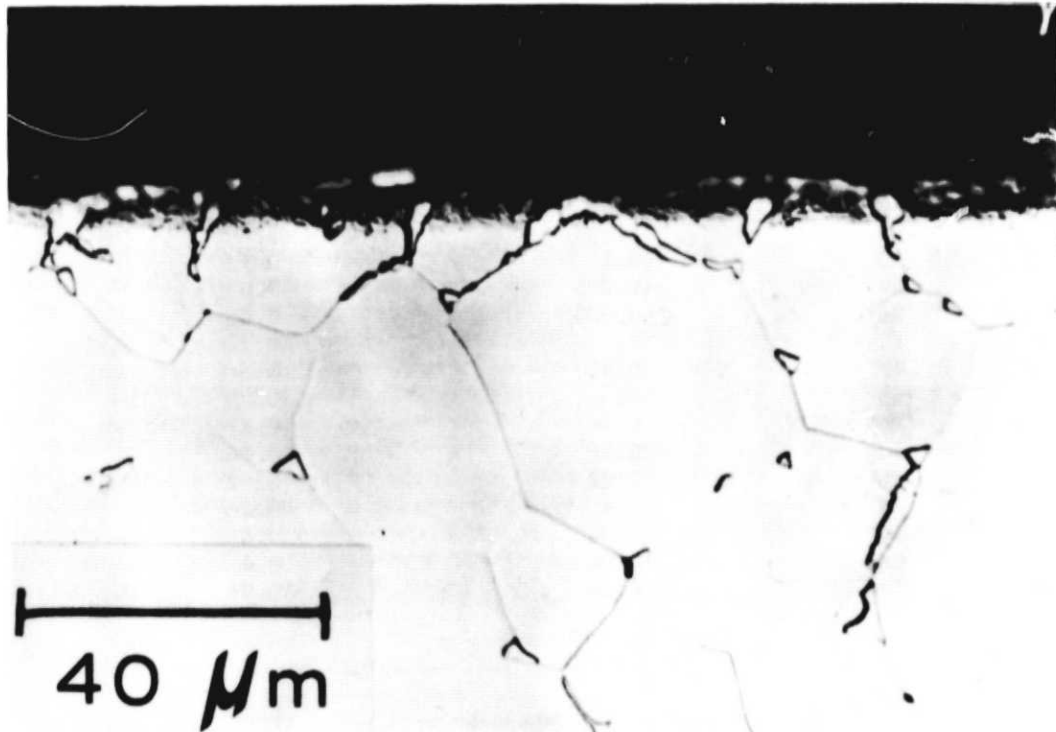

40 μm

Figure 10. Photomicrograph exhibiting a longitudinal cross-section just below the surface of the W–25% Re thermoelement, whose surface is shown in Figs. 8(b) and 9.

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TABLE II. MASS SPECTROGRAPHIC ANALYSES OF TANTALUM THERMOCOUPLE SHEATHS

(composition in ppm by weight)

Element	Chemically cleaned, etched, and vacuum degassed specimen[a]	Specimen[b] from sheathed thermocouple assembly after 2059 h at 2073 K
Li	0.001	0.002
Be	0.005	0.2
B	0.01	0.03
F	2.	30.
Na	0.4	6.
Mg	0.1	5.
Al	0.1	150.
Si	0.2	6.
P	0.05	3.
S	0.3	10.
Cl	0.4	2.
K	2.	5.
Ca	0.2	2.
Sc	<0.03	0.03
Ti	0.03	7.
V	0.05	1.
Cr	0.1	0.5
Mn	0.03	0.2
Fe	0.7	7.
Co	<0.02	0.2
Ni	<0.1	0.3
Cu	3.	2.
Zn	3.	5.
Ga	<0.01	<0.01
Ge	≤0.02	≤0.04
As	<0.04	<0.04
Se	<3.	<3.
Br	<0.1	0.1
Rb	<0.005	0.03
Sr	<0.005	0.05
Y	≤1.	≤0.2
Zr	<0.3	0.5
Nb	50.	50.
Mo	0.1	0.2
Ru	<0.06	<0.06
Rh	<0.02	<0.02
Pd	<0.2	<0.2
Ag	≤0.04	0.4
Cd	<0.04	0.4
In	<0.06	<0.06

(composition in ppm by weight)

Element	Chemically cleaned, etched, and vacuum degassed specimen[a]	Specimen[b] from sheathed thermocouple assembly after 2059 h at 2073 K
Sn	<0.03	0.3
Sb	<0.02	≤0.03
Te	<0.04	<0.04
I	<0.02	≤0.02
Cs	<0.02	<0.02
Ba	<0.01	0.4
La	<0.01	<0.01
Ce	<0.01	<0.02
Pr	<0.01	<0.01
Nd	<0.03	<0.03
Sm	<0.03	<0.03
Eu	<0.02	<0.02
Gd	<0.03	<0.03
Tb	<0.01	<0.01
Dy	<0.04	<0.04
Ho	<0.01	<0.01
Er	<0.03	<0.03
Tm	<0.01	<0.01
Yb	<0.03	<0.03
Lu	<0.01	<0.01
Hf	<0.1	<0.1
W	10.	20.
Re	<0.05	0.1
Os	<0.1	<0.1
Ir	<0.1	<0.1
Pt	<1.	<1.
Au	<2.	<2.
Hg	<0.03	<0.03
Tl	<0.03	<0.03
Pb	<0.1	0.4
Bi	<0.03	<0.03
Th	<0.2	<0.2
U	<0.3	<0.2
Ta	Balance	Balance

[a]See section on Experimental Procedures and Apparatus for details of specimen preparation.

[b]Taken from between 2 and 6 cm from the tip of sheathed thermocouple assembly.

TESTS OF UNSHEATHED BeO-INSULATED THERMOCOUPLES

Drift tests with BeO-insulated W-3% Re versus W-25% Re thermocouples were performed in argon at 2250 K for 1100 hours and at 2400 K for 307 hours. Newly constructed thermocouples were used in each test. The test results were as follows:

Thermal emf drift. The value of the thermal emf at 2250 K as a function of the time of exposure was typically that illustrated in Fig. 11. The data illustrated used the photoelectric pyrometer as a reference. For each thermocouple, the experimental data were fit by the method of least squares to either a quadratic or cubic equation. The results for all four thermocouples are summarized in Table III.

For three of the thermocouples (Nos. 2, 3 and 4) the largest change after 1100 hours was equivalent to only about +3 K. The other thermocouple (No. 1) exhibited a change equivalent to about +11 K. The changes computed for the same thermocouple from measurements with the photoelectric and the visual pyrometers differed slightly, but agreed to within the combined precision of the measurements (the standard deviation of the residuals was equivalent to about 0.4 K for the photoelectric pyrometer data and to about 1 K for the visual pyrometer data). The calibrations of both pyrometers were checked[8] before and after the drift test and these checks indicated that no appreciable change occurred in the calibration of either instrument (< 1 K for the photoelectric pyrometer and < 1.5 K for the visual optical pyrometer). A check of the furnace window before and after the test indicated no significant change (equivalent to < 0.5 K) occurred in its transmittance.

Considering the possibility of changes in the calibration of the pyrometers and in the transmittance of the furnace window, together with the scatter in the measurements and the nature of the drift results, it is perhaps better to describe the thermal emf of thermocouples 2, 3 and 4 as being stable during the 1100 hour test period to within the equivalent of about ±2 K at 2250 K.

The value of the thermal emf at 2400 K as a function of time was typically that illustrated in Fig. 12. Again, the data illustrated were obtained with the photoelectric pyrometer as a reference. Because of a gradual sagging of the Ta blackbody enclosure (about 6 mm in 307 hours), the test was terminated at 307 hours rather than risk failure of the enclosure and damage to the furnace. The results for four of the thermocouples in the test are summarized in Table IV. The values of the drift were obtained from curves (either linear or quadratic) that were fit to the experimental data by the method of least squares. The drift in the four thermocouples varied from about +3 K to about +11 K at 2400 K after 307 hours of exposure. A fifth thermocouple in the test behaved erratically after approximately 100 hours of exposure, and the results are not included in the summary. Post-test examination revealed a region of gross erosion of the BeO insulators that bared the thermoelements (as described in more detail in the next section). It is likely that electrical shorting of the thermoelements occurred, thus accounting for the erratic behavior of the fifth thermocouple.

Material behavior. Exposure of the insulated thermocouples at 2250 and 2400 K resulted in some undesirable material degradation and interaction effects that were not observed in previous tests at 2073 K (refs. 1 and 3). In both the 2250 K and the 2400 K test, material loss or erosion of the BeO occurred in the hot zone. At 2400 K, the erosion was substantial and bared the thermoelements; for a typical thermocouple, this occurred near the measuring junction of the thermocouple (see Fig. 13) and also in a region 4 to 7 cm above the measuring junction. At 2250 K, erosion of the BeO insulator in comparable sections of the thermocouples was also evident, but the loss of the BeO was not sufficient to bare the thermoelements.

Further, those sections of BeO insulator that were located just outside of the high temperature zone of the furnace exhibited a metallic deposit on the outer surface of the BeO (see Fig. 14). The deposit could be observed as a thin metal film on the BeO insulator and as beads of metal varying from 5 μm diameter to 400 μm in length. Samples from

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[8] Performed by the Optical Radiation Section of the NBS.
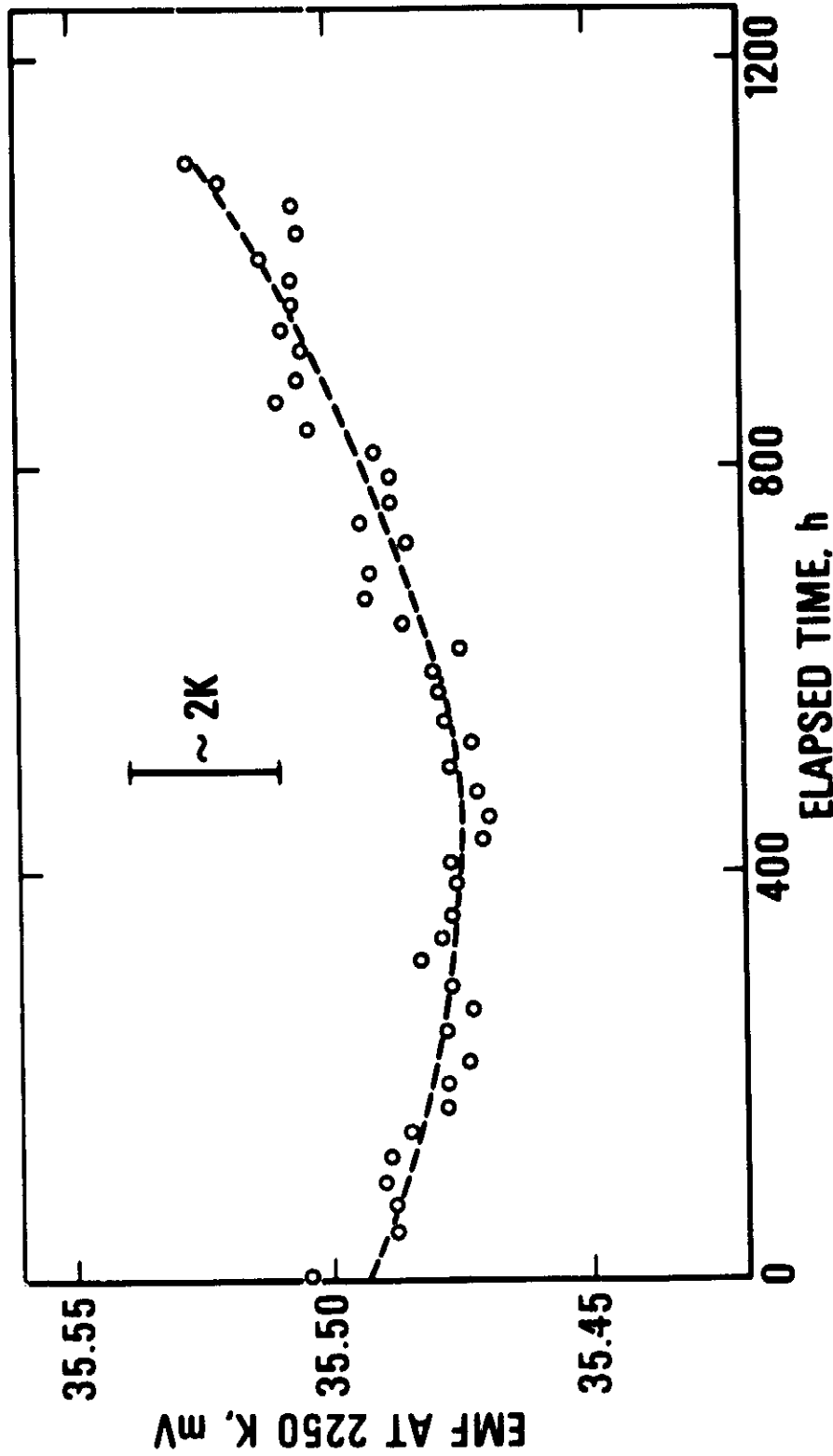
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Figure 11. Drift in the thermal emf of an unsheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple during exposure in argon for 1100 hours at 2250 K. The thermocouple was installed in a tantalum black-body enclosure that was heated in a high temperature furnace and the temperature was measured with an automatic photoelectric optical pyrometer. The reference junctions of the thermocouple were maintained at 273.15 K. The curve through the data points is a quadratic equation fit to the data by the method of least squares.

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TABLE III. SUMMARY OF THE RESULTS OF THE 1100 HOUR DRIFT TEST AT 2250 K
WITH U.SHEATHED, BeO INSULATED, W-3% Re VERSUS W-25% Re THERMOCOUPLES

RESULTS EXPRESSED IN TEMPERATURE EQUIVALENTS

Thermocouple No.	Automatic Photoelectric Optical Pyrometer as Temperature Reference[a]		Visual Optical Pyrometer as Temperature Reference[b]		Approximate Relative Position of Thermocouple Measuring Junction in the Tantalum Blackbody Enclosure
	ΔT K	σ_r K	ΔT K	σ_r K	
1	+10.4	0.6	+11.5	1.1	1.5 cm above center
2	+ 2.1	0.4	+ 0.4	0.9	center
3	+ 0.4	0.4	- 1.0	0.9	2.2 cm below center
4	+ 3.1	0.4	+ 2.2	1.0	1.5 cm below center

ΔT = apparent change after 1100 hours, where a positive value indicates an increase in emf.

σ_r = standard deviation of residuals, where the values of ΔT and σ_r were obtained from least squares fits of polynomial functions (cubic for thermocouple No. 1 and quadratic for the other thermocouples) to the experimental data.

[a] 46 data points.

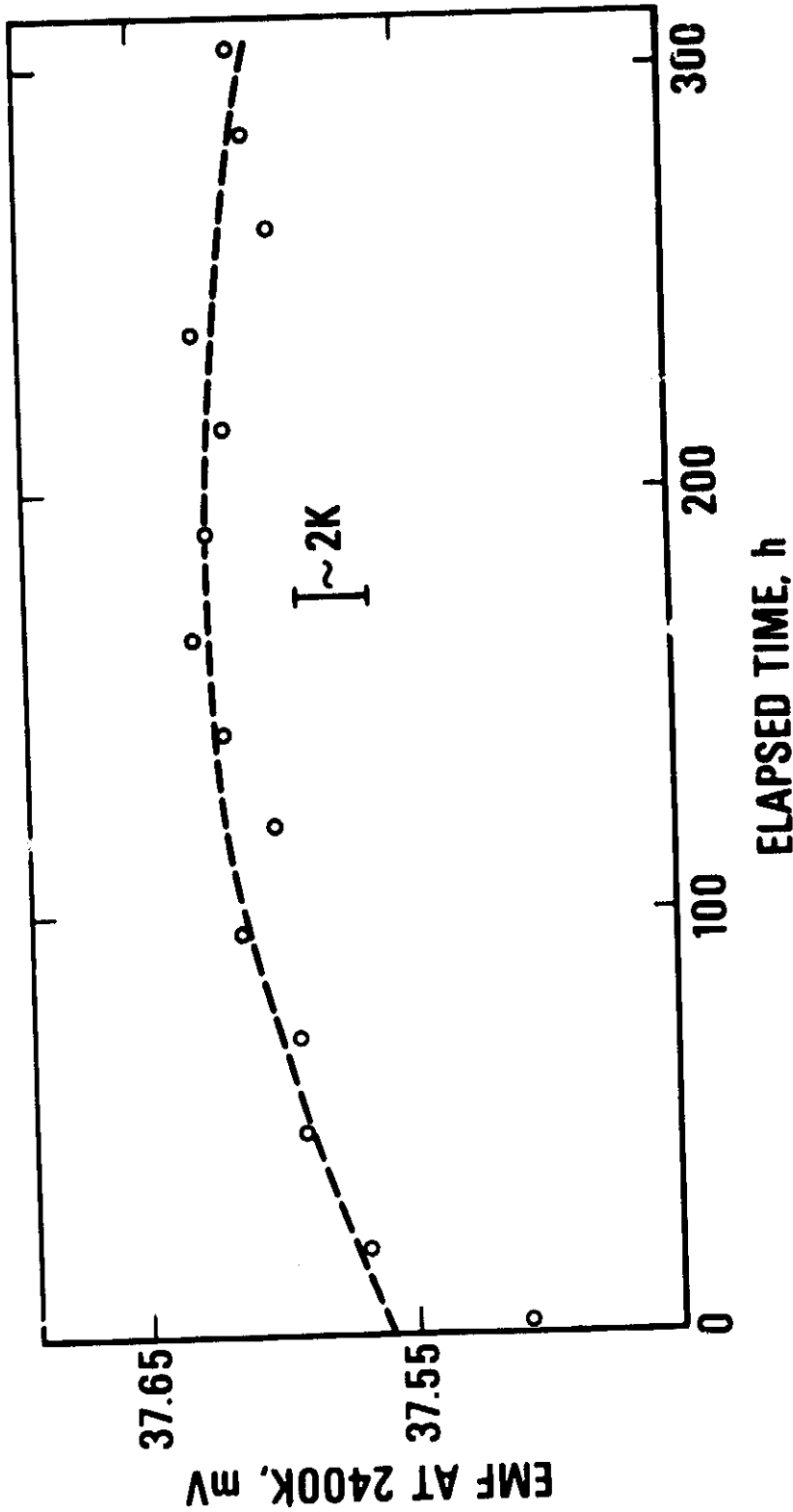[b] 30 data points, includes data of two observers.

Figure 12. Drift in the thermal emf of an unsheathed, BeO-insulated, W-3% Re/W-25% Re thermocouple during exposure in argon for 207 hours at 2400 K. The thermocouple was installed in a tantalum black-body enclosure that was heated in a high temperature furnace and the temperature was measured with an automatic photoelectric optical pyrometer. The reference junctions of the thermocouple were maintained at 273.15 K. The curve through the data points is a quadratic equation fit to the data by the method of least squares.

TABLE IV. SUMMARY OF THE RESULTS OF THE 307 HOUR DRIFT TEST AT 2400 K
WITH UNSHEATHED, BeO INSULATED, W-3% Re VERSUS W-25% Re THERMOCOUPLES

RESULTS EXPRESSED IN TEMPERATURE EQUIVALENTS

Thermocouple No.	Automatic Photoelectric Optical Pyrometer as Temperature Reference[a]		Approximate Relative Position of Thermocouple Measuring Junction in the Tantalum Blackbody Enclosure
	ΔT K	σ_r K	
1	+ 2.8	0.7	2 cm above center
2	+10.8	1.0	2 cm above center
3	+ 3.3	0.8	center
4	+ 4.3	1.0	2 cm below center

ΔT = apparent change after 307 hours, where a positive value indicates an increase in emf.

σ_r = standard deviation of residuals, where the values of ΔT and σ_r were obtained from least squares fits of polynomial functions (linear for thermocouple Nos. 2 and 4 and quadratic for thermocouple Nos. 1 and 3) to the experimental data.
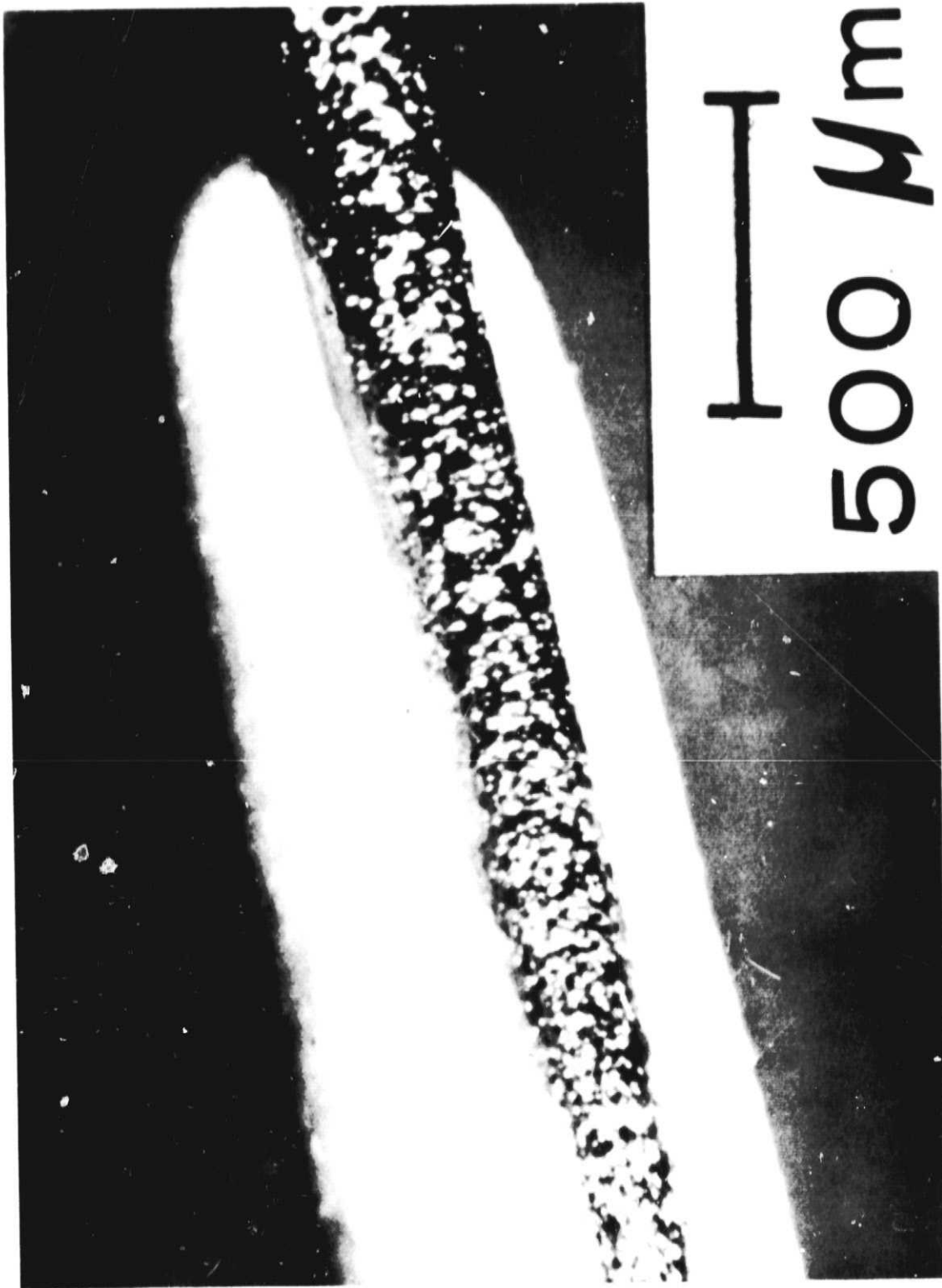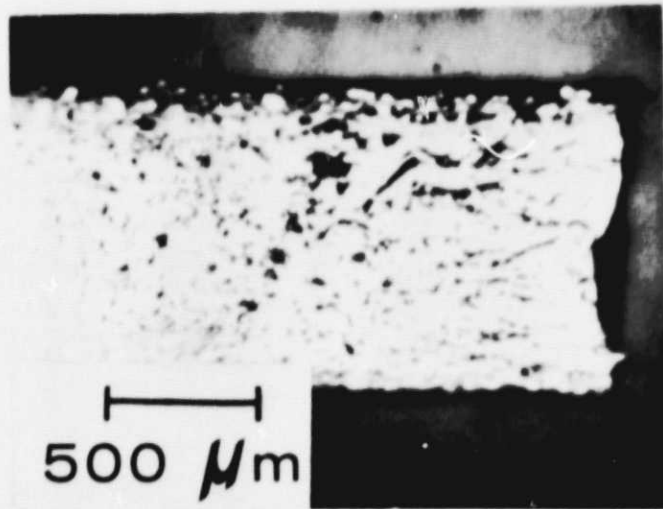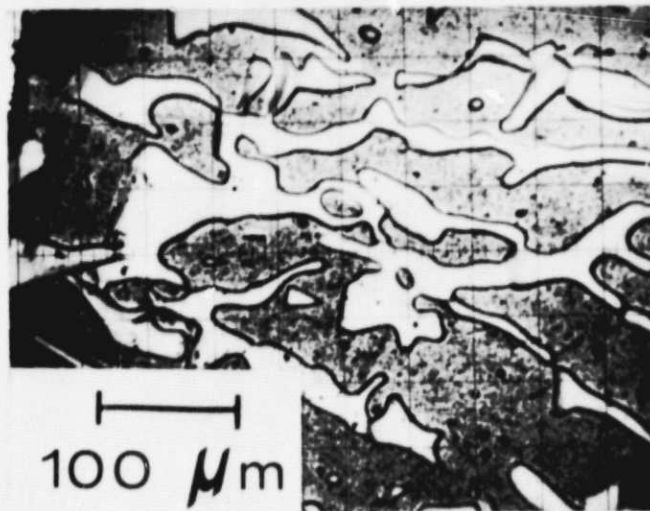
[a] 14 data points.

Figure 13. Photomicrograph showing the erosion of the BeO insulator near the measuring junction of an unsheathed thermocouple that was exposed within a tantalum blackbody enclosure for 307 hours at 2400 K in argon.

27

500 μm

(a)

100 μm

(b)

Figure 14. Deposit of beryllium on the BeO insulator in a region about 18 cm above the measuring junction of an unsheathed thermocouple that was exposed within a tantalum blackbody enclosure for 307 hours at 2400 K in argon, as seen by (a) reflected light microscope, and (b) scanning electron microscope.

both the 2400 K and the 2250 K test were examined using electron and ion probe micro-analysis. The deposit was identified as Be. No evidence of metallic Be in the interior of the BeO insulator could be observed under the microscope. The bore of the BeO insulator was free of any visible deposit throughout the total length of the insulator.

In addition, in the 2250 K test the Be deposit that was found on thermocouple No. 1 happened to occur in a section where there was about a 3 mm gap between adjacent lengths of the BeO insulating tubing. Coarse examination did not reveal a metallic deposit on the exposed thermoelements. Nevertheless, thermocouple No. 1 experienced a relatively large change (+11 K) in its thermal emf. The possibility that the metallic deposit at the gap in the insulators resulted in electrical shunting between the thermoelements is discounted because the emf of the thermocouple increased during the test.

Besides these effects, other undesirable material effects were also observed in the 2400 K test. On one thermocouple, the erosion of the BeO insulators in the hot zone was sufficient to bare several centimeters of the W-3% Re thermoelement. A formation of large equiaxed grains could be observed on the thermoelement in place of the usual elongated fine-grained structure. Conventional photomicroscopy of a transverse cross-section revealed an irregular metallic coating of up to 50 μm thickness on the wire (see Fig. 15). Electron and ion probe microanalysis revealed this to be Ta. In the region of the coating, the W-3% Re thermoelement did not retain its usual ductility.

In addition to the material loss of the BeO, those portions of the BeO that were at a temperature higher than the phase transformation temperature of approximately 2320 K (ref. 11) exhibited micro-cracks and were opaque. Those sections of the BeO that were below the phase transformation temperature exhibited the normal translucence, large grain size and shrinkage (densification) of approximately 10% in the diameter. Microcracking of BeO at temperatures above the phase transformation temperature is often observed (ref. 11) and for this reason the material is probably not well suited for use above that temperature.

STUDIES OF BeO-Ta SHEATH COMPATIBILITY

Samples of BeO contained in the open-ended Ta sheaths were exposed for 50 hours, at 2073 K, 2250 K and 2400 K in argon. Tests were also performed for 307 hours at 2400 K and for 1100 hours at 2250 K. The exposed Ta sheaths exhibited no gross differences in behavior from those samples of Ta sheaths, also exposed in these tests, that did not contain BeO. Typically, large grains of the order of 200 to 500 μm formed in the tantalum with degassing, and little change in the microstructure occurred thereafter. In some regions, the Ta sheath exhibited pores along the inner surface of the sheath. The pores were observed also in the degassed assembly (see Fig. 16), and are thought to be the result of the sheath fabrication process, when the sheath was shrunk over a mandrel. The observations suggest that with high temperature exposure a pore breaks into several smaller pores.

After exposure of the Ta-BeO assemblies, the BeO insulators could be removed from the sheaths if the sheath was first cut with a diamond saw a few millimeters above the closed end of the tube. The BeO from the assemblies exposed for 50 hours at 2073 K and 2250 K exhibited similar behavior. The grain size was typically 15 to 60 μm, as compared to 1 to 5 μm for the degassed BeO. In addition, the originally opaque BeO had attained a trans-lucent appearance, which undoubtedly occurred as a result of the increase in the grain size. A transverse cross-section of a Ta-BeO assembly before and after exposure is shown in Fig. 17. The BeO insulators were reduced in diameter by about 10% as a result of the high temperature exposure. The reduction in diameter is essentially the same as that observed, in an earlier BeO-insulated thermocouple test (ref. 1) which exposed BeO in the presence of tantalum for 1029 hours at 2073 K (the BeO was contained in a tantalum blackbody enclosure for this test). In the test of the sheathed thermocouple assemblies, which is described in a previous section, similar behavior was also noted. Essentially no evidence of erosion or other material loss of BeO has been observed in any of the tests at 2073 K. It is therefore concluded that the reduction in diameter is merely shrinkage resulting from further densification of the BeO.
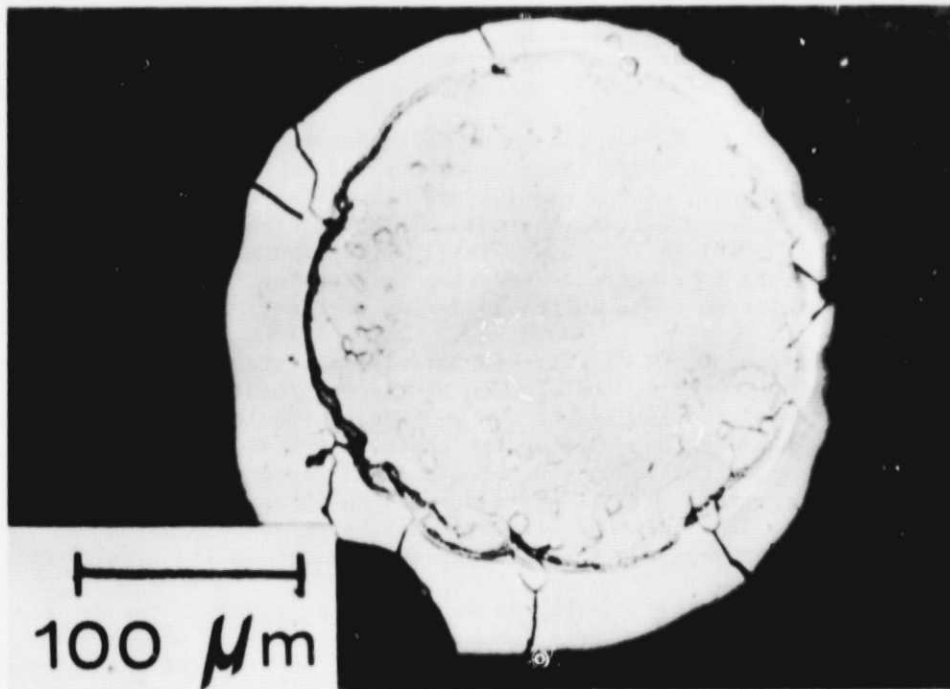
Figure 15. Photomicrograph showing a transverse cross-section of a W-3% Re thermoelement from an unsheathed thermocouple that was exposed within a tantalum blackbody enclosure for 307 hours at 2400 K in argon. The cross-section was taken at about 6 cm above the measuring junction of the thermocouple where the BeO insulator had eroded away and bared the thermoelement. The irregular outer coating of up to 50 µm thickness was identified as tantalum by electron probe microanalysis.
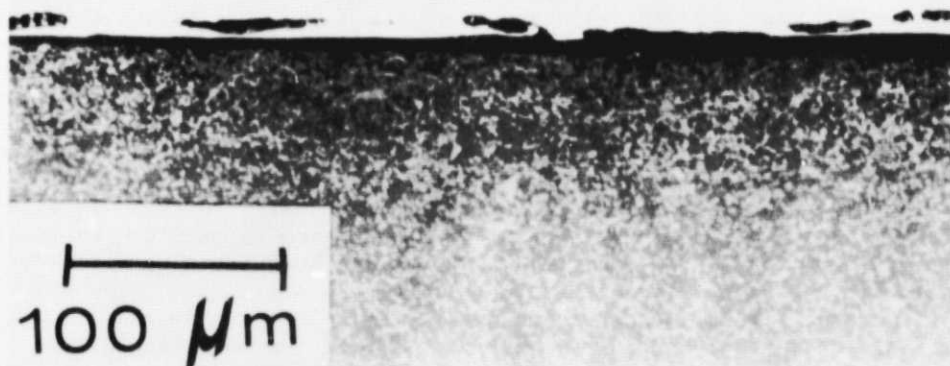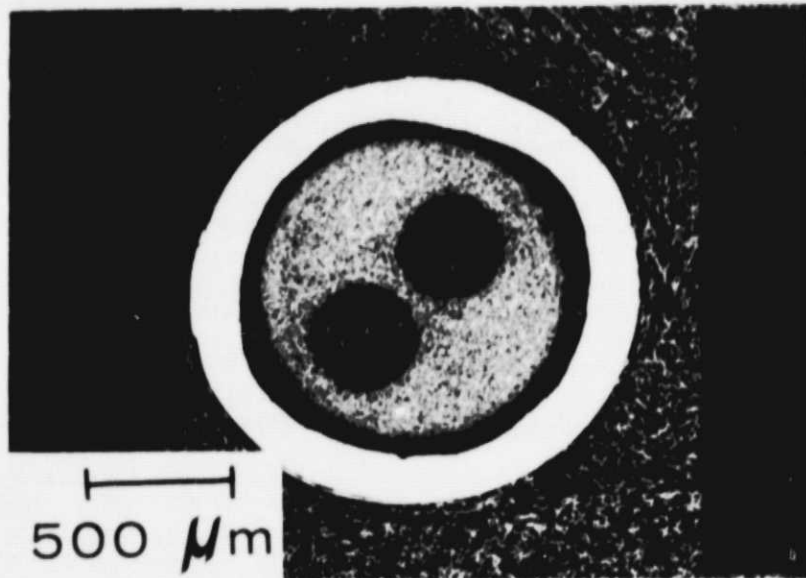

Figure 16. Photomicrograph showing a longitudinal cross-section of a BeO-Ta sheath assembly after vacuum degassing at temperatures to 1300 K. Note the pores along the inner surface of the Ta sheath.
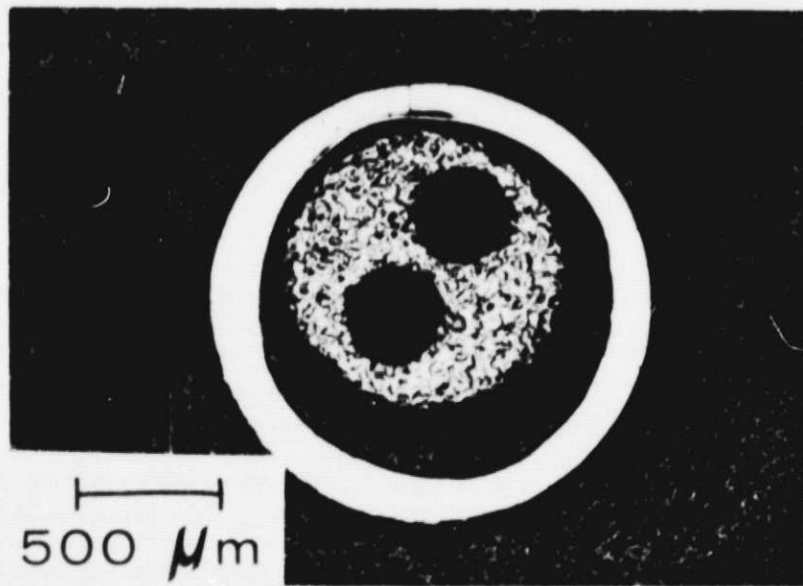
30

(a)

(b)

Figure 17. Photomicrographs showing transverse cross-sections of BeO-Ta sheath assemblies (a) after vacuum degassing at temperatures to 1300 K, and (b) after exposure for 50 hours at 2073 K in argon. The cross-sections were taken at about 4 cm below the open end of the sheath.

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In contrast, the BeO exposed at 2400 K exhibited a number of gross, detrimental effects. At the open end of the sheath, substantial erosion of the BeO insulators occurred. In assemblies exposed for 50 hours, a 50% reduction in the insulator diameter in the region where it exited from the sheath was typical. This reduction was confined to a region a few millimeters in length. One sample of BeO insulator removed from the sheath also exhibited a longitudinal channel approximately 0.08 mm deep by 0.15 mm wide that extended the entire length of the insulator. A black deposit with a metallic appearance could be observed on both sides of the channel. In Ta-BeO assemblies exposed for 307 hours at 2400 K, the BeO insulator was eroded away completely at the open end of the sheath and the end of the insulator had a conical shape. Gross erosion of the insulator was apparent at depths of 1 to 2 cm inside the sheath. A typical photomicrograph of one of the Ta sheath-BeO assemblies exhibiting a transverse cross-section 4 cm below the open end of the sheath is shown in Fig. 18. Large cracks in the BeO insulator and erosion of the BeO are evident. While very little erosion of the BeO insulator was detected in assemblies exposed for 50 hours at 2250 K, assemblies exposed for 1100 hours at this temperature showed substantial erosion of the insulator in the region where it exited from the sheath. A 70 to 80% reduction in the diameter of the insulator was observed in this region.

The tests at 2400 K were above the BeO phase transformation temperature of 2320 K (ref. 11). With the phase change, a large anomalous thermal expansion occurs, and the cracking of the dense, polycrystalline BeO in these tests is not surprising. The loss of BeO in the tests at 2250 and 2400 K might be explained by a number of different circumstances. However, if we assume that the observed material transport results only from reactions between Ta and BeO, the conclusions as to what is happening are entirely reasonable, as taken from a discussion by Droege, et al., (ref. 12). They employed thermodynamic considerations to deduce the chemical compatibility of high temperature ceramic oxides with several refractory metals. If the reaction products of BeO with Ta are confined including the diffusion of oxygen through the Ta sheath, the system is stable and very little reaction will take place. Near the open end of the sheath, the gaseous reaction products experience very little confinement, so that rapid loss of gaseous Be, gaseous tantalum oxides and perhaps some oxygen occurs. Using the data of Droege et al., at 2400 K the partial pressure of Be (g) under equilibrium conditions of BeO with Ta is 8×10^{-5} atm (6×10^{-2} torr). Thus the rapid loss of BeO is not surprising, even under a cover gas of 1 atm of argon. Well inside the sheath, the reaction products are relatively confined, so that quasi-equilibrium conditions are partially established, and thus the rate of loss of BeO is greatly reduced.

CONCLUDING REMARKS

This report has presented studies of the effects of high temperature exposure on the component materials and on the completed assemblies of Ta-sheathed, BeO-insulated W-3% Re/W-25% Re thermocouples. The exposures were in a high purity argon or helium environment. Some of the principal results follow.

1. BeO-Ta COMPATIBILITY TESTS.

Tests were performed at 2073, 2250 and 2400 K for 50 hours, for 1100 hours at 2250 K and for 307 hours at 2400 K. No gross physical changes in the tantalum sheaths were observed after the exposures (no tests were performed to detect changes in chemical purity). In the BeO, gross deleterious effects were observed in those samples exposed at 2400 K. Erosion of the BeO insulators was substantial. Typically greater than 50% of the BeO insulator was eroded at the top of the sheath. Erosion was markedly less inside of the sheath, where the gaseous reaction products were partially confined. With exposure at 2400 K, micro-cracking of the BeO occurred since the phase transformation temperature was exceeded. Serious problems with the BeO were not apparent at 2073 and 2250 K after 50 hours of exposure. At these temperatures the BeO insulators exhibited essentially only shrinkage (about 10% in diameter) that resulted from the further densification of the sintered BeO. Longer exposure (1100 hours) at 2250 K resulted in erosion of the BeO at the open end of the sheath. It was clear from these tests that BeO cannot be used reliably for long times in the presence of tantalum at temperatures above about 2100 K,

Figure 18. Photomicrograph showing a transverse cross-section of a BeO-Ta sheath assembly after exposure for 50 hours at 2400 K in argon. The cross-section was taken at about 4 cm below the open end of the sheath.

500 μm

33

if the gaseous reaction products are not well confined.

II. TESTS WITH UNSHEATHED, BeO-INSULATED THERMOCOUPLES

Drift tests with BeO-insulated W-3% Re/W-25% Re thermocouples were performed in argon at 2250 K for 1100 hours and at 2400 K for 307 hours. The thermocouples in both tests exhibited a positive change in the thermal emf that was small, typically ranging from the equivalent of a few degrees K up to +11 K. Nevertheless, undesirable material degradation and interaction effects were observed in both tests, with the effects much greater at 2400 K. In the hot zone of the furnace, the BeO insulators were eroded and reduced by the Ta; a deposit that was later identified as Be coated the outside of the BeO insulators in the region of the furnace temperature gradient. At 2400 K, the erosion was sufficient to bare the W-3% Re thermoelement and the thermoelement exhibited a 50 μm thick coating of Ta. In addition, those portions of the insulator above the phase transformation temperature exhibited microcracking. Comparison with the results of the Ta-BeO compatability tests suggest that somewhat better material performance may be expected at these temperatures if the insulated thermocouples are encased and sealed hermetically within a Ta sheath.

III. TESTS WITH SHEATHED THERMOCOUPLE ASSEMBLIES

Four 1.6 mm diameter Ta sheathed, BeO insulated, W-3% Re versus W-25% Re thermocouple assemblies were constructed from aged thermoelements, heat-treated BeO insulators, and cleaned and etched Ta sheaths. The assemblies were checked to be gas tight (no indication of a leak when tested with a partial pressure analyzer) and were filled with high purity argon gas (1 atm at test temperature) for the test. The test exposed the thermocouple assemblies for 2059 h at 2073 K in helium (1 atm).

The four thermocouple assemblies exhibited virtually identical behavior during the test. The drift in the thermal emf was small and linear, varying from the equivalent of -0.3 to -0.8 K per 1000 h of exposure at 2073 K. The thermocouples were rapidly cooled to room temperature four times during the test (the cooling rate was about 400 K/min for the first two minutes). The thermal cycling had no appreciable effect on the thermal emf at 2073 K. After these coolings, calibrations of the thermocouples on reheating to the test temperature indicated that the drift in the thermal emf was also less than the equivalent of -1 K per 1000 hours of exposure for calibration temperatures below 2073 K. The changes in the thermal emf during the test (equivalent to less than 2 K) were no larger than the systematic errors (estimated to be 1.9 K for measurements with the automatic photoelectric pyrometer).

At the conclusion of the test, the thermocouple assemblies were removed and dismantled. No gross chemical attack of the thermoelements, BeO insulators or the tantalum sheaths was apparent. Photomicrographs revealed the usual changes in structure observed in other tests (this report and refs. 1 and 4). Very large equiaxed grains (50 μm to one-half wire diameter in size) formed in the W-25% Re thermoelement. Densification of the BeO insulators that were exposed to high temperatures resulted in a 10% reduction in their diameter. This was accompanied by the formation of BeO grains of 30 to 90 μm in size (compared to 1 to 5 μm grain size in the starting material). In the region of the thermocouple assembly where the temperature rapidly fell towards ambient, a second phase at the grain boundaries of the W-25% Re thermoelement was observed, and was confined to the surface of the thermoelement (< 10 μm depth). Spectrochemical analyses of sections of both W-3% Re and W-25% Re thermoelements taken from this region indicated a small increase in the Mg and Ca impurity levels. In earlier work (ref. 1), sizeable reductions in the impurity levels of the BeO insulator were noted after exposure to high temperatures in the presence of tantalum. Chemical analyses of sections of tantalum sheath in this test indicated at least a ten-fold increase in Aℓ, Ca, Fe, Mg, Na, Si, and Ti, which were major residual impurities in the BeO tubing.

These tests results indicate that reliable, long term performance of Ta sheathed, BeO-insulated W-3% Re versus W-25% Re thermocouple assemblies can be obtained for thousands of hours with exposure at temperatures of 2000 to 2100 K in high purity gaseous environ-

ments. Careful selection, heat treatment, and handling of materials were employed in these investigations. It is possible that the material specifications and construction techniques that were used may be more stringent than that which is required. Nevertheless, those who would desire to obtain thermocouple assemblies that perform reliably at these temperatures can be furnished with guidelines for their construction.

The W-3% Re and W-25% Re thermoelements used in this investigation are available commercially. The thermoelements were given a special surface cleaning treatment by the supplier in order to more thoroughly remove surface contaminants introduced during the wire manufacturing process. The cleaning treatment included ultrasonic degreasing, abrading, and electro-etching. At NBS, the thermoelements were given an additional cleaning with ether. All materials were handled using clean plastic gloves and specially cleaned tools. Tests were performed on samples taken from the thermoelement wire lots to confirm that the emf-temperature relationship of the "as received" thermocouples from the matched lot complied with the suppliers calibration table to within the equivalent of ±1% of the temperature. The thermoelements were degassed in vacuum (< 5 x 10^{-6} torr) for about 1 hour at 1570 K, and then aged in argon at 2400 K for 1 hour (W-3% Re) or 10 minutes (W-25% Re) in order to essentially remove the initial emf shift. Recently obtained thermoelements may exhibit only minimal shifts (ref. 8), and aging of these thermoelements may not be required.

The sintered double-bore BeO insulators were in excess of 99.8% purity. They were given a preparatory vacuum (< 5 x 10^{-7} torr) degassing at temperatures up to 1700 K over a 24 hour period. The degassing removed sorbed gases and also was effective in reducing some of the metallic impurity levels (ref. i).

Tantalum tubing of greater than 99.97% purity was employed for the sheath. Degreasing and then etching was performed in order to remove surface contaminants, which are particularly difficult to remove on the inner wall of the tubing. The tubing was then degassed in vacuum (< 5 x 10^{-7} torr) at temperatures up to 2175 K.

Fabrication of the thermocouple assemblies was performed in air. The assemblies were evacuated (< 1 x 10^{-8} torr) and tested for leaks with a partial pressure analyzer. The evacuated assemblies were then degassed at temperatures up to 1325 K to remove residual gas impurities, and back-filled with high purity argon gas (less than 10 ppm total impurities).

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