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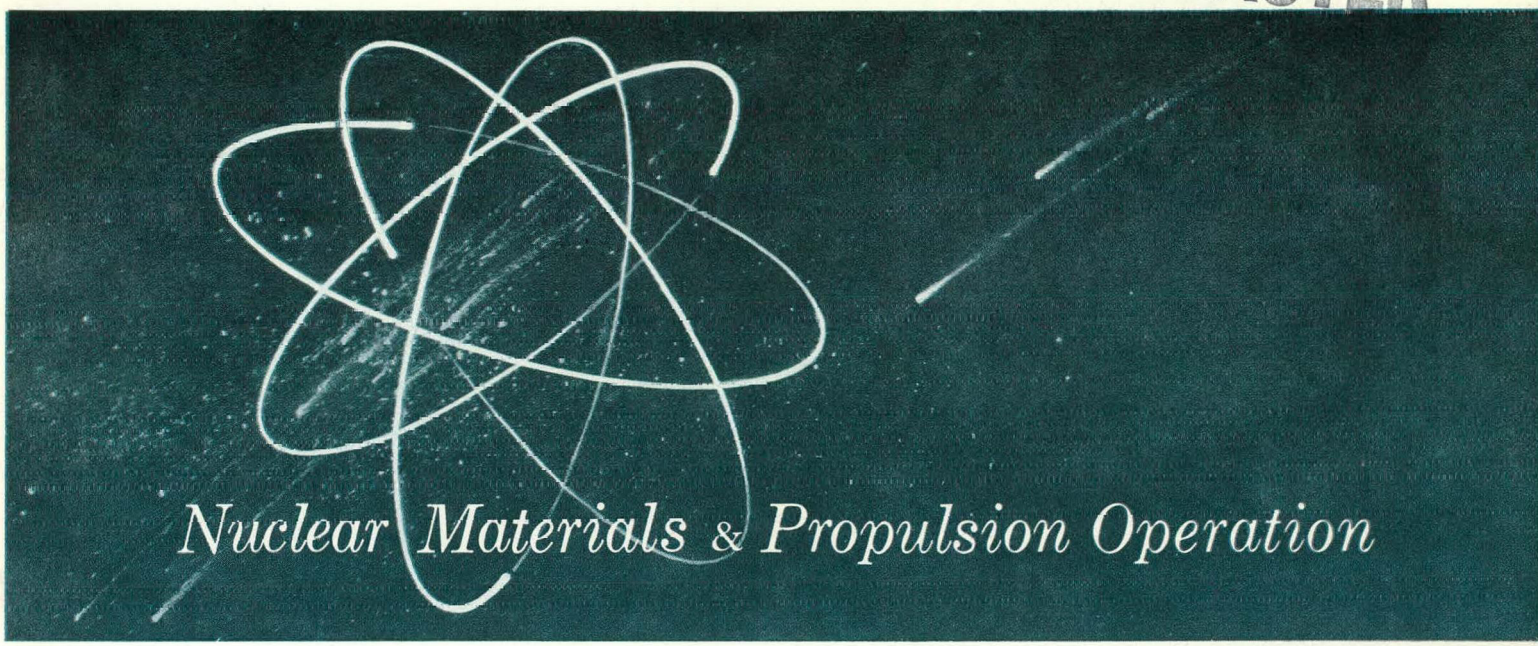

PROPERTIES OF SOME REFRACTORY METALS

III - Thermal Expansion Characteristics of Tungsten, Rhenium, Tantalum, Molybdenum, Niobium, W-25Re, Ta-10W, and Mo-50Re

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ABSTRACT

Previously published linear thermal expansion data for several refractory metals and refractory metal alloys are reviewed and compared. In addition, an optical technique is described which was employed to measure the expansion characteristics of several refractory metals and alloys to 2500°C. These most recent data are also compared to the existing data.

A refraction error has been identified which is inherent in the optical measurement of thermal expansion for certain experimental conditions. Tests in helium have been shown to yield results which are noticeably lower than those obtained in vacuum. Correction factors have been obtained for use with the helium tests to obtain accurate expansion values.

Linear thermal expansion data to 2500°C are reported for tungsten, rhenium, tantalum, molybdenum, niobium, tungsten - 25 rhenium, tantalum - 10 tungsten, and molybdenum - 50 rhenium. In the case of rhenium, tungsten - 25 rhenium, and molybdenum - 50 rhenium, these data are the first such measurements for these materials to high temperatures.

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PROPERTIES OF SOME REFRACTORY METALS
III. Thermal Expansion Characteristics

INTRODUCTION

The dimensional changes which take place during heating and cooling represent an important material characteristic. Many design considerations are influenced strongly by this property because of its relation to structural integrity, induced stresses, etc. In composite structures and cladding applications thermal expansion considerations become especially important. It seems advisable, therefore, to review and compare existing thermal expansion data for the refractory metals in view of the importance of this material characteristic to NMPO design and development activities. The existing data and the recent results obtained in the NMPO thermal expansion measurement program are presented to make all such information accessible in a single document.

In general, measurements of linear thermal expansion are based on a determination of the specimen length at various temperatures. The resulting length-temperature plot is then used to express the expansion characteristics in the desired form. For example, the instantaneous coefficient of linear thermal expansion, α_i, is obtained by evaluating the instantaneous slope, dL/dT, of such a curve and dividing this value by the instantaneous length. Thus:

$$\alpha_i = \frac{1}{L} \frac{dL}{dT} \tag{1}$$

This same plot can also yield the more commonly used average coefficient of linear thermal expansion:

$$\alpha_m = \frac{L_T - L_O}{L_O (T-T_O)} = \frac{\Delta L}{L_O (T-T_O)} \tag{2}$$

In this calculation the length, L_O, at the temperature T_O is subtracted from the length at temperature T and divided by L_O and the temperature difference between T and T_O. Since linear thermal expansion curves are usually concave upward the instantaneous coefficient is always higher than the average value.

In equation (2) if T_o is taken as 0^oC the expression becomes:

$$\alpha_m = \frac{\Delta L}{L_o T} \tag{3}$$

Furthermore, since then the length at any temperature can be expressed as:

$$L_T = L_o (1 + \alpha_m T) \tag{4}$$

the value of α_i becomes:

$$\alpha_i = \frac{(dL/dT)}{L_o (1 + \alpha_m T)} \tag{5}$$

From equation (4):

$$\frac{dL}{dT} = \left[\alpha_m + T\left(\frac{d\alpha_m}{dT}\right)\right] L_o \tag{6}$$

which when substituted into (5) gives:

$$\alpha_i = \frac{\alpha_m + T\left(\frac{d\alpha_m}{dT}\right)}{1 + \alpha_m T} \tag{7}$$

This is the relationship between α_i and α_m.

It is also common practice to express linear thermal expansion data by plotting the fractional or percentage increases in length as a function of temperature. Thus:

$$\frac{L - L_o}{L_o} = f(T) \tag{8}$$

or:

$$\frac{L - L_o}{L_o} \times 100 = f'(T) \tag{9}$$

Usually the temperature function is adequately expressed by a polynomial to yield:

$$\frac{L - L_o}{L_o} \times 100 = A + BT + CT^2 \tag{10}$$

Differentiation of this expression then gives:

$$\left(\frac{100}{L_o}\right) \frac{dL}{dT} = B + 2C T \tag{11}$$

which is not quite the instantaneous coefficient of linear expansion. However, since for refractory metals the linear expansion values are normally no more than 2 or 3 percent even at temperatures of 2500°C the difference between the coefficient calculated in (11) and the actual value of the instantaneous coefficient is quite small. The difference, however, should be recognized.

Another format employed in expressing linear thermal expansion data is similar to that in equation (10), but with the mean coefficient of thermal expansion replacing the percentage increase in length. Thus:

$$\alpha_m = \frac{(L - L_o)}{L_o\,(T-T_o)} = A + BT + CT^2 \qquad (12)$$

Percentage increase in length can be obtained quite simply from this expression by the proper substitution of temperature and then multiplying this result by $(T-T_o)$ and converting to percentages. This approach is the one employed by White[1] in dealing with several of the refractory metals.

While the measurement of linear thermal expansion characteristics seems quite straightforward certain experimental difficulties exist. This is particularly true in the case of refractory metals where data close to 3000°C are required. For such measurements an adequate high-temperature furnace is needed and it is necessary further to assure temperature uniformity over the entire specimen length in order to obtain the desired accuracy. Furthermore, the furnace atmosphere must be sufficiently free of impurities to prevent contamination of the specimens during the expansion measurements. It is also important that no changes in the specimen structure take place other than those associated with the standard and well identified phase transformations. For example, sintered materials tested at temperatures above the original sintering temperatures yield results which are not representative of true thermal expansion effects. And finally, a technique for accurately measuring the increase in specimen length with temperature must be available.

The factors just discussed are all equally important in obtaining accurate linear thermal expansion data at elevated temperatures. The failure to maintain proper control over any one of these important considerations can lead to erroneous results. It is in this light then that a review of available expansion data for several of the refractory metals is made and any discrepancies noted in measurements of the same material can in all probability be attributed to one of the above factors.

REVIEW OF LITERATURE DATA

Linear thermal expansion measurements for tungsten, tantalum, and molybdenum have been reviewed by White[1]. The data chosen from this study are shown in Figure 1 along with the rhenium data of Sims, Craighead, and Jaffee[2], the niobium data of Kearns, Clark, Young, and Jones[3], and the chromium data of Lucks and Deem[4]. These data have been considered to be representative of these materials even though disagreement between investigators has been reported in a few cases.

Molybdenum

Of all the data reported to date that for molybdenum probably exhibits the most consistency. Data from various investigators are found to be in fairly good agreement with the curve shown in Figure 1 for this material. The curve relating the expansion characteristics of molybdenum to 2900°K published by Goldsmith, Waterman, and Hirschhorn[5] is almost identical to that in Figure 1 for this material. Molybdenum data reported by Fieldhouse and co-workers[6] to 1600°C are also in excellent agreement with those of Figure 1. Additional agreement is found in the data of Edwards, Speiser, and Johnston[9] based on X-ray measurements of lattice constants. These data reported for temperatures of 850° to 1800°C are essentially identical to the Figure 1 data in the temperature range close to 1000°C but are about 3 percent higher than the Figure 1 data in the higher temperature range. Some older data obtained by Worthing[8] by the resistance heating of molybdenum wires in vacuum are some 5 percent higher than the data in Figure 1 below 1500°C. Above this temperature the agreement is within a few percent. More recent data published by Rasor and McClelland[7] identify a very interesting phenomenon. During the first heating of an arc-melted unalloyed molybdenum specimen the thermal expansion data obtained were identical to those given for molybdenum in Figure 1. However, during the second heating the obtained data were some 5 percent higher over the entire temperature range. No explanation for this behavior was given although chemical analyses before and after the initial heating were reported but failed to show any difference in impurity levels. It was noted, however, that the specimen suffered a small permanent elongation following the initial heating. No reason was given for this observation either. In general then the agreement between various investigators regarding the thermal expansion data for molybdenum is fairly good.

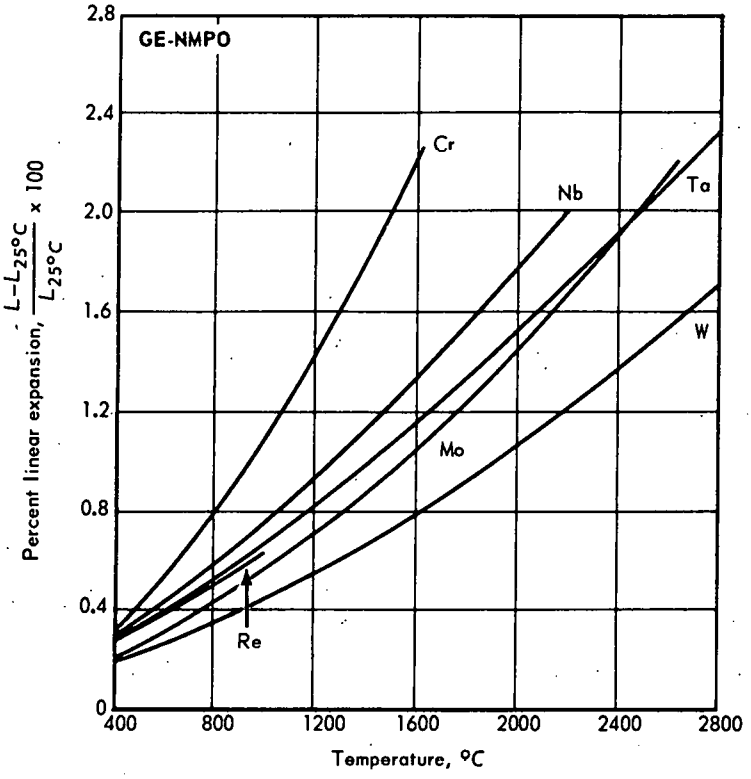

Fig. 1 – Linear thermal expansion of several refractory metals

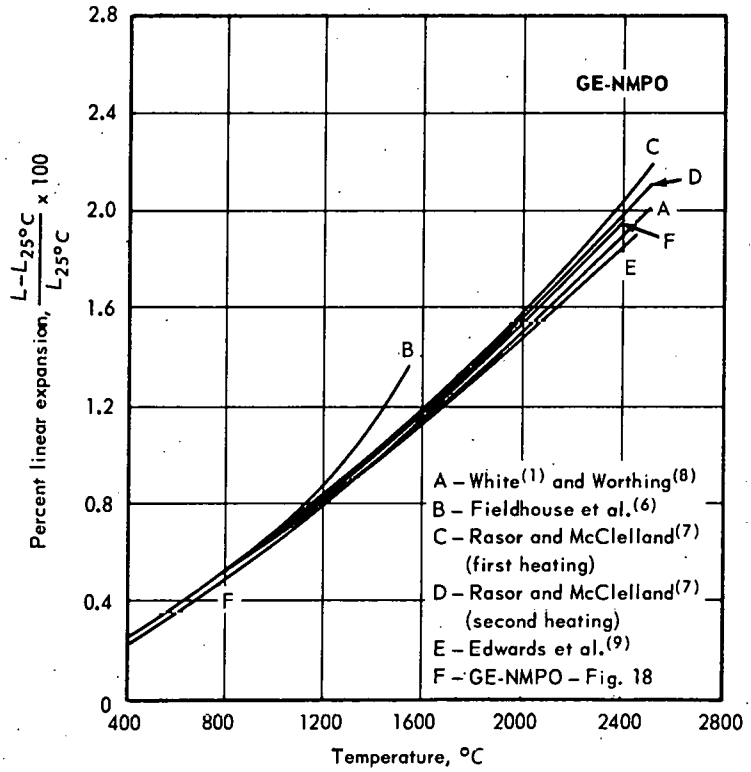

Fig. 2 – Linear thermal expansion of tantalum

Tantalum

This same measure of agreement is not observed in the thermal expansion data for tantalum. While a portion of this variation may be due to differences in experimental techniques, more of it is probably due to differences in material purity. It has long been known that tantalum absorbs trace impurities when tested in various cover gas atmospheres and it has also been shown that these impurities (O_2, N_2, H_2, etc.) when absorbed cause significant changes in the properties of tantalum. The differences which exist in the reported experimental data are best recognized by a study of the linear thermal expansion data shown in Figure 2. Reported data of Fieldhouse, et al[6] seem to be in good agreement with the Figure 1 data up to 1000°C, but then the data increase to higher values. In the data reported by Rasor and McClelland[7] different behavior was observed for tantalum after the initial heating. It was reported that after heating to close to 3000°C the impurity content of the tantalum decreased markedly. Chemical and spectroscopic analyses were reported which indicated decreased contents of Si, Cr, Cu, Al, Ca, Ni, Zr, Fe, Mn, Ti, and C after heating. For example, the Cu and Fe contents dropped from 7300 to 19 ppm and 2100 to zero ppm, respectively. The carbon content was reduced from 800 to 150 ppm by this heating. This increased purity following the initial heating was cited as the cause for the change in thermal expansion measurements. Tantalum data reported by Worthing[8] exhibit excellent agreement with the data reported by White[1]. However, this is due to the fact that the analysis by White of all existing thermal expansion data for tantalum was influenced quite strongly by the Worthing data. For this reason no degree of confirmation can be claimed in this instance and the lack of agreement cited above still persists. Perhaps the best agreement with the tantalum data of Figure 1 is provided by the lattice constant measurements reported by Edwards, Speiser, and Johnston[9]. These data agree within about 5 percent over the temperature range between 1000° and 2200°C. However, in general the linear thermal expansion data for tantalum are seen to be less than completely defined and some additional data appear in order to identify this system more precisely.

Tungsten

Only a few studies of the thermal expansion characteristics of tungsten have been reported at temperatures above 2000°C. In his analysis of existing tungsten data, White[1] relied on the values of Worthing[10] to 2400°C and those of Demarquay[11] to 2100°C. Both of these measurements exhibited fairly good

agreement and at 2100°C were within a few percent of being identical. The equation proposed by White[1] has been extrapolated into the higher temperature range to yield the curve shown in Figure 1. The data of Apblett and Pellini[12] were not given much consideration by White in view of the high expansion values reported. A comparison of these thermal expansion results is shown in Figure 3. Some recent data for tungsten have been reported by Glasier, Allen, and Saldinger[13], but these also seem much too high to be considered correct. As seen in Figure 3 these data are in fairly good agreement with the Apblett and Pellini data. Despite the good agreement between these two sets of data these values are still subject to doubt.

Niobium

Published thermal expansion data for niobium appear to exhibit agreement which is just slightly better than that observed in the case of tantalum. Differences of some 20 percent exist in the data from various investigators as compared to the differences of close to 30 percent observed in the tantalum data. Since these two metals are quite similar in regard to their gaseous impurity absorption characteristics, the factors affecting the reproducibility of the data are probably the same in each case. The niobium data shown in Figure 4 reveal that the fairly high values reported by Fieldhouse, Hedge, and Lang[17] actually result in the large deviations referred to above. The values reported by Tottle[16] to 1000°C are in excellent agreement with the data of Kearns, Clark, Young, and Jones[3]. Furthermore, the data from X-ray measurements of Edwards, Speiser, and Johnston[9] are in fairly good agreement with the data of Kearns, et al., especially at temperatures above 1200°C. Even though the agreement observed in the niobium data is much better than that exhibited by the tantalum data, some additional measurements appear warranted to attempt to resolve the existing discrepancies.

Chromium

The expansion data for chromium appear quite consistent and the agreement between various investigators is excellent.[5] Lucks and Deem[4] have reported data to about 1600°C which seem to be representative of this particular metal. These data are shown in Figure 1.

Rhenium

As pointed out in Figure 1 very few data have been reported for rhenium and these have covered the temperature range to 1000°C. No other higher temperature linear thermal expansion data for rhenium have been reported.

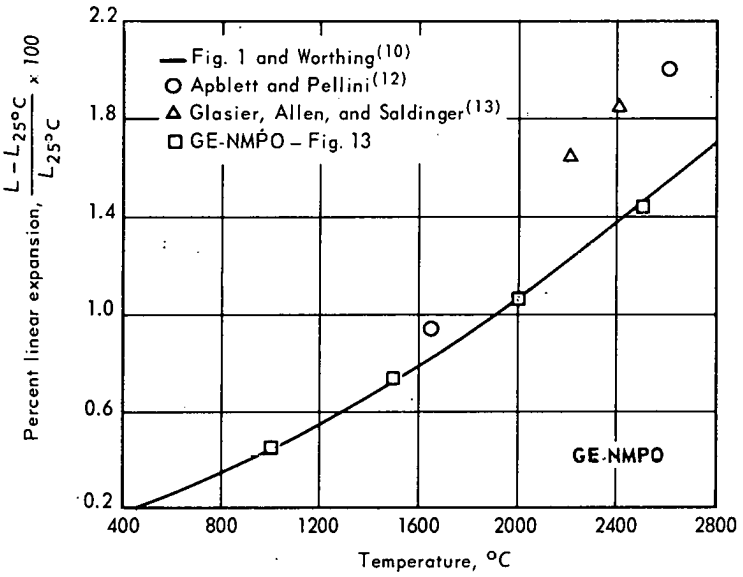

Fig. 3 – Linear thermal expansion of tungsten

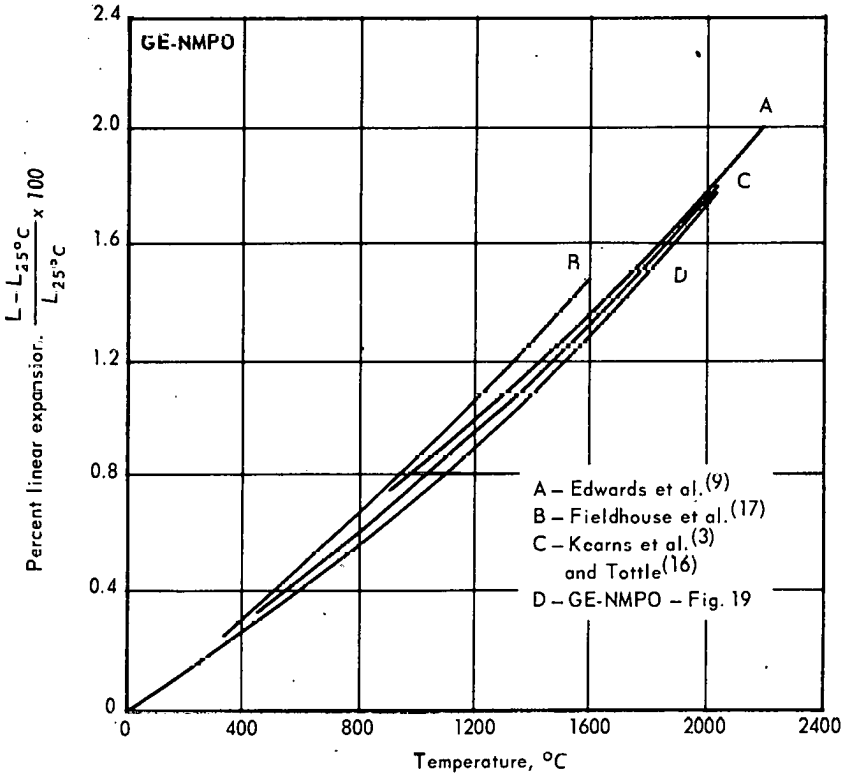

Fig. 4 – Linear thermal expansion of niobium

EXPERIMENTAL RESULTS

Linear thermal expansion measurements for several refractory metals and refractory metal alloys were made to 2500°C in helium using a resistively heated tungsten tube furnace. The furnace heating element consisted of a tungsten tube (riveted construction), 4 inches in diameter, 20 inches in length, and 20 mil in thickness (see Figure 5). The upper end of this heating element was inserted in a 0.25 inch wide annulus in the top water-cooled copper electrode and electrical contact was obtained by pressing a copper rope into the remaining void between the electrode and the outer surface of the heating element (see Figure 6). Another water-cooled electrode at the bottom of the furnace contained a similar annulus which housed the lower end of the heating element. This annulus contained a liquid (liquid at room temperature) gallium-indium - tin alloy to provide electrical contact and to allow for thermal expansion of the heating element with increasing temperature.

An outer tungsten muffle (6 inches O.D., 17 inches long with a 0.5 inch wall thickness) surrounded the heating element and served both as a radiation shield and as a barrier for the ceramic insulation positioned between it and the water-cooled furnace shell. For testing to about 2500°C zirconia insulation in this zone of the furnace is satisfactory while at higher temperatures thoria becomes necessary. In addition, a ceramic-free furnace construction is possible and has been employed on occasion by substituting a 12-layer refractory metal thermal radiation shield assembly for the ceramic insulation. Operation in this latter case has been demonstrated to 3000°C (5432°F).

Linear expansion measurements were made by sighting paired filar micrometer microscopes on fiducial marks located near the ends of the specimen. The specimen was positioned horizontally in a specially machined tungsten block supported within the hot zone of the furnace. Two specimen configurations were employed; the one was a rod 0.25 inch in diameter by 2.5 inches in length; the other, which was employed when rod material was not available, was made from 0.020 inch sheet material formed into a "U" shaped beam about 0.3 inch wide and 0.3 inch deep, by 2.5 inches in length.

The specially machined tungsten block which served as the specimen holder was about 2 inches square and about 3 inches in length. This specimen holder is shown in Figure 7 along with two typical specimens. In the U-shaped sheet

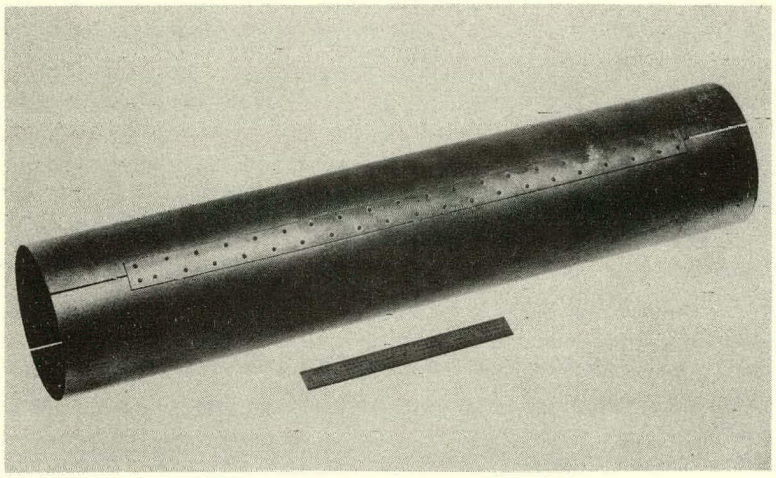

Fig. 5 – Riveted tungsten tube heater

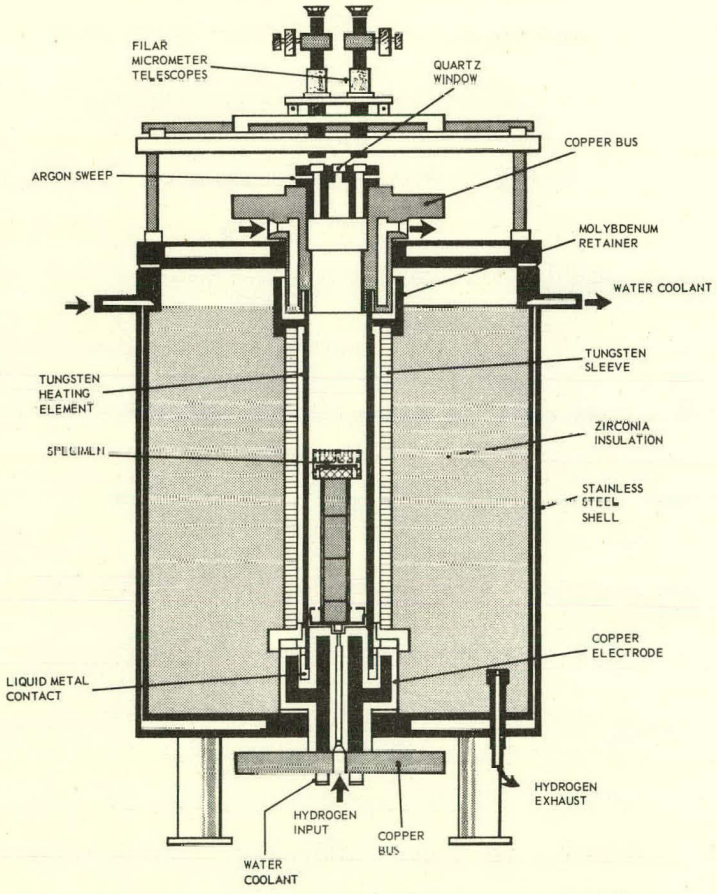

Fig. 6 – Schematic of thermal expansion apparatus

specimen two 0.010 inch holes, 2 inches apart, served as the fiducial marks. These were drilled about 0.25 inch in from each end of the specimen and were found to yield excellent results. In view of the success obtained with the small diameter holes as fiducial marks for the sheet specimen, this same approach was applied to the rod specimens. However, due to the difficulty of drilling such a small hole through the rod specimens, a special construction was employed. A 0.075 inch hole was drilled radially into the rod to within about 0.020 inch of penetrating a milled flat on the opposite surface. This flat was about 0.20 inch in width, 0.020 inch in depth, and was perpendicular to the large diameter hole. This gave the effect of a thin sheet in this area of the rod and then a 0.010 inch hole was drilled in the flat to penetrate through to the larger diameter hole. In essence, then the fiducial marks in the rod specimens were identical to those which were shown to be so effective in the sheet specimens.

The specimen holder, which was supported on a tungsten pedestal to position it at the longitudinal midpoint of the heating element, is shown in cross section in Figure 8 with the specimen in place. Both fiducial marks were placed in line with the two vertical holes to allow viewing from above and also to allow the fiducial marks to be viewed against a contrasting (low temperature) background formed by the lower end of the furnace. With this arrangement the fiducial marks were clearly visible during all portions of the measurement. A central hole in the specimen holder provided a clear view of the specimen and a black body hole (L/D equal to 6) at the midpoint of the specimen was thus readily accessible for temperature measurements. In most cases the conditions within the central cavity were such as to make it impossible to define the black body hole (i.e. black body conditions were obtained within the specimen holder) except during temperature transients.

As a final precautionary measure a radiation shield in the form of 5 mil tungsten sheet cut to the outer shape of the specimen holder and with holes to match those in the upper face of the tungsten block was dropped in place. This enhanced the temperature uniformity of the specimen rod for without it the heating element, which was of necessity at a slightly higher temperature than the specimen holder, would radiate to the ends of the specimen and cause a slight increase in rod temperature in this area. With the outer radiation shield in place temperature uniformity over the entire 2.5-inch specimen was within $\pm$ 10°C.

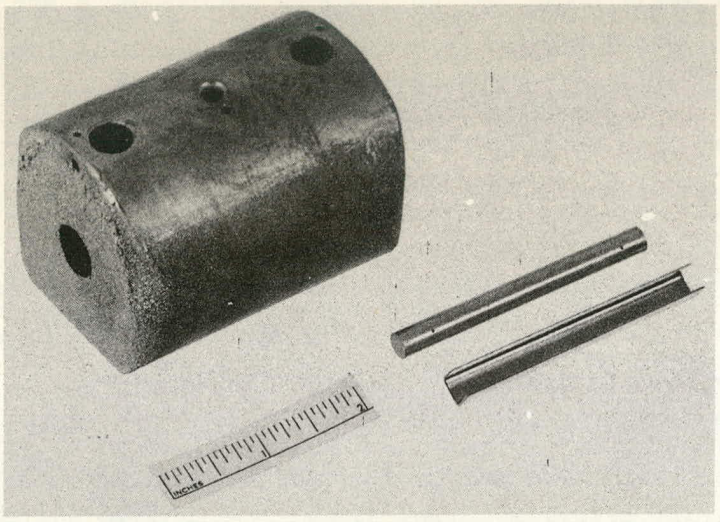

Fig. 7 – Specimen holder and specimens

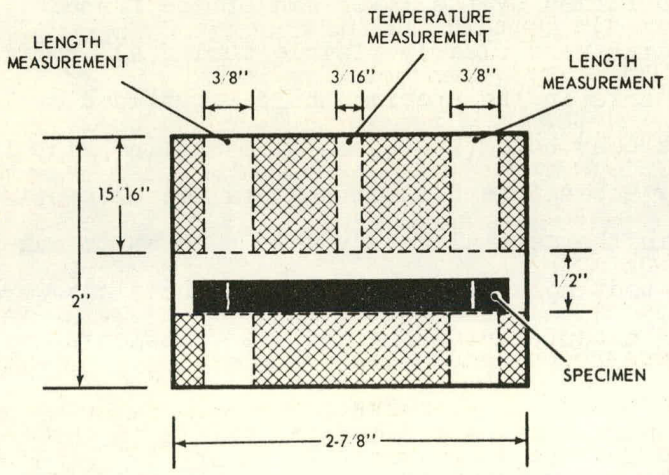

Fig. 8 – Cross section of specimen holders

Temperatures to 1000°C were measured by a platinum/platinum-10 percent rhodium thermocouple positioned in the small central hole in the specimen holder. Above 1000°C temperatures were measured by means of an optical pyrometer sighted through a quartz window in the top of the furnace into the black body hole either in the specimen or in the specimen holder midway between the two microscope sight holes. Optical pyrometer corrections for the quartz window were obtained in previous calibration tests.

The paired filar micrometer microscopes were mounted vertically and in parallel on 2-inch centers on an Invar bar attached to a special fixture mounted on the top of the furnace. A pair of rotatable polaroid discs in each microscope provided the necessary control of light intensity for high temperature sightings.

Prior to each test a microscope calibration was performed by employing a standard linear scale etched on a glass slide. After removing the complete microscope system from the top of the furnace it was placed on a special table and the glass scale was then placed directly below the microcopes. At this time the vertical distance between this scale and the microscopes was set equal to that between the specimen and microscopes during furnace operation. The eyepiece cross hairs were then moved to be coincident with the extremities of the 2-inch scale and the two eyepiece micrometer readings were recorded. Following this measurement the microscope system was then repositioned atop the furnace and an electrically heated tungsten coil within the top of the furnace was then energized to illuminate the specimen. In this manner the room temperature value of the distance between the fiducial marks on the sample was measured by adjusting the eyepiece cross hairs until they were coincident with the fiducial marks. Readings taken from the eyepiece micrometers then enabled the cold length to be easily calculated based on the above calibration. Measurements made as the furnace temperature was increased were referred to this initial length in the usual manner to enable percent elongation to be calculated. At furnace temperatures below 900°C the resistively heated tungsten coil provided the necessary illumination of the fiducial marks for the elongation measurements. (Note: See Appendix A for the correction for refraction effects which must be applied to these measurements).

Employing the techniques described above, the linear thermal expansion characteristics of several of the refractory metals and of several refractory metal alloys (see Table 1 for analyses of materials employed in these studies) have been measured to 2500°C in helium. In these tests rod or sheet specimens were employed depending on material availability and in every case the runs were made in duplicate or triplicate to evaluate the reproducibility of these measurements. The data for a given specimen were then programmed to yield an expression of the form shown in equation (10). Equation constants for all the materials tested are presented in Table 2. The least squares curve resulting from this analysis is shown for each material in the figures to be discussed below.

Molybdenum

Expansion data for arc-cast molybdenum sheet are shown in Figure 9. The data presented for the two consecutive runs reveal the excellent reproducibility obtainable with this technique. Similar data for powder metallurgy sheet material are shown in Figure 10 and for a powder metallurgy rod specimen in Figure 11. As in the test of the sheet specimen the reproducibility of the data for the rod specimen was excellent. It was typical of all these tests that the heating and cooling curves were coincident (points obtained during cooling are not shown) and that successive heating and cooling curves were identical to those obtained in the first run. Curves representing the least squares polynomial expressions for these three specimens are shown in Figure 12 indicating quite graphically that the data for arc-cast sheet and sintered rod and sheet material are essentially identical. This comparison of arc-cast and sintered material was prompted by the differences in stress-rupture and creep behavior noted[14] for arc-cast and sintered molybdenum.

Several points from the molybdenum curve in Figure 1 have been included in Figure 12 for comparison purposes. The agreement is seen to be excellent (within 3 percent) at temperatures below 1500°C. At higher temperatures the data in Figure 12 are 5 to 8 percent above the Figure 1 values for molybdenum. It is noteworthy, however, that the data presented in Figure 12 are essentially identical to those of Rasor and McClelland[7] for the second heating of the arc-melted molybdenum specimen.

TABLE 1 - CHEMICAL ANALYSES OF MATERIALS USED IN THERMAL EXPANSION MEASUREMENTS

Material			Impurities, ppm																	
			C	H	O	N	W	Mo	Si	Fe	V	Al	Cu	Mn	Ca	Zr	Ti	Ni	Cr	Mg	K
Tungsten	(PM)	rod	53	0.6	2.0	3.0		< 100	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	N.D.
	(PM)	sheet	18	2.0	32.0	3.0		100 to 1000	< 100	< 100	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	(AC)	sheet	63	0.7	5.6	0.1		< 100	N.D.	50 to 500	N.D.	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	< 100	N.D.	N.D.
Rhenium	(PM)	sheet	20	1.0	25.0	2.0	N.D.	< 100	< 100	50 to 500	N.D.	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	N.D.	< 100	N.D.
Tantalum	(AC)	sheet	23	1.0	65.0	3.0	< 500	100	100	100	90	< 100	50	50	< 50		< 100				
Molybdenum	(PM)	rod	42	< 0.1	12.0	0.9	50 to 500		< 100	< 100	< 100	< 100	< 100	< 100	< 100	N.D.	< 100	< 100	< 100	< 100	< 100
	(PM)	sheet	42	8.0	237.0	11.0	< 400		< 100	< 100	< 100	< 100	< 100	< 100							
	(AC)	sheet	140	1.0	17.0	19.0	N.D.		< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100		
Niobium	(AC)	sheet	53	7.7	177.0	3.9	N.D.	N.D.	< 100	< 100	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	< 100	N.D.	N.D.	< 100	N.D.
W - 25Re	(PM)	sheet	46	2.0	7.0	1.0		N.D.	< 100	< 100	N.D.	< 100	< 100	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	N.D.
Mo - 50Re	(PM)	sheet	22	1.0	14.0	12.0	N.D.		< 100	50 to 500	N.D.	N.D.	< 100	N.D.	N.D.	N.D.	N.D.	< 100	N.D.	N.D.	N.D.
Ta - 10W	(AC)	sheet	34	1.3	98.0	28.0		< 100	< 100	50 to 500	N.D.	N.D.	N.D.	N.D.	< 100	N.D.	N.D.	< 100	N.D.	N.D.	N.D.

(PM) - Powder Metallurgy

(AC) - Arc-Cast

N.D. - Not Detected

TABLE 2 - Least Squares Equation Constants For Refractory Metal Linear Expansion Data

$$\frac{L - L_{25^oC}}{L_{25^oC}} \times 100 = A_o + A_1T + A_2T^2 \quad (T \text{ in } {}^oC; \text{ all tests in helium})$$

Material		A_o	A_1	A_2	Temperature Range, °C
Tungsten	(PM) rod	-8.69×10^{-3}	3.83×10^{-4}	7.92×10^{-8}	25 - 2500
	(PM) sheet	-4.58×10^{-3}	3.65×10^{-4}	9.81×10^{-8}	25 - 2500
	(AC) sheet	-6.76×10^{-3}	3.91×10^{-4}	8.98×10^{-8}	25 - 2500
Rhenium	(PM) sheet	-9.79×10^{-3}	5.89×10^{-4}	8.57×10^{-8}	25 - 2500
Tantalum	(AC) sheet	-6.69×10^{-3}	5.40×10^{-4}	1.18×10^{-7}	25 - 2400
Molybdenum	(PM) rod	-8.88×10^{-4}	3.94×10^{-4}	1.85×10^{-7}	25 - 2500
	(PM) sheet	-5.80×10^{-3}	4.59×10^{-4}	1.46×10^{-7}	25 - 2250
	(AC) sheet	-4.84×10^{-3}	4.25×10^{-4}	1.71×10^{-7}	25 - 2250
Niobium	(AC) sheet	-4.10×10^{-3}	5.96×10^{-4}	1.34×10^{-7}	25 - 2100
W-25Re	(PM) sheet	-8.46×10^{-4}	3.91×10^{-4}	1.14×10^{-7}	25 - 2500
Mo-50Re	(PM) sheet	-1.08×10^{-2}	5.30×10^{-4}	1.26×10^{-7}	25 - 2250
Ta-10W	(AC) sheet	-7.34×10^{-3}	5.36×10^{-4}	1.26×10^{-7}	25 - 2350

(PM) Powder Metallurgy

(AC) Arc-Cast

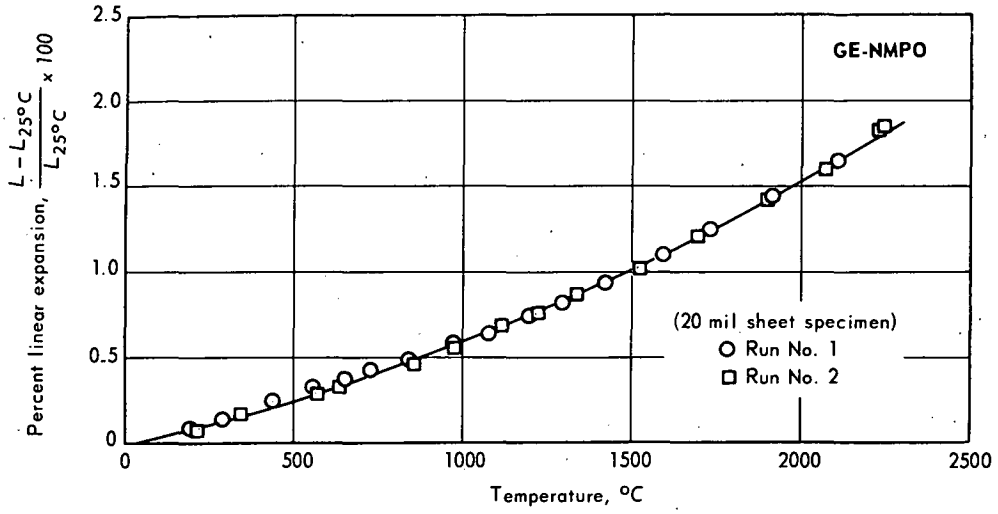

Fig. 9 – Linear thermal expansion of arc-cast molybdenum sheet in helium

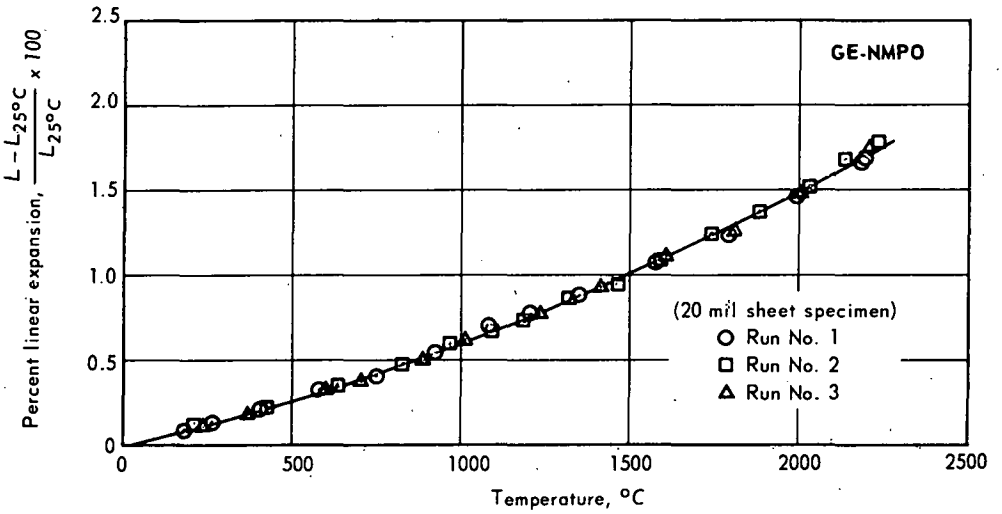

Fig. 10 – Linear thermal expansion of powder metallurgy molybdenum sheet in helium

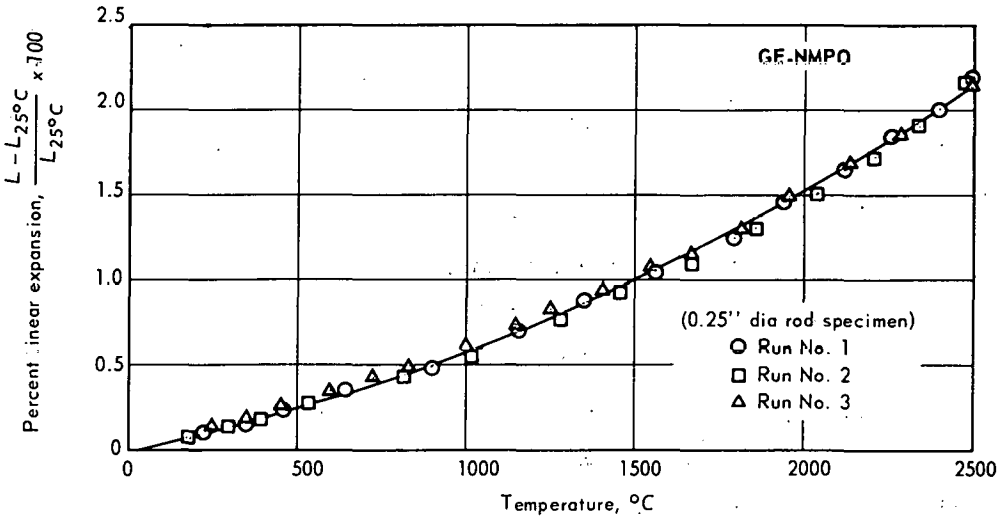

Fig. 11 – Linear thermal expansion of powder metallurgy molybdenum rod in helium

Tungsten

The data for sintered tungsten rod and sheet material are presented in Figures 13 and 14. Once again the excellent reproducibility obtained in duplicate tests is evident. Also as in the molybdenum tests the heating and cooling curves were coincident. The smooth curves (least squares) for the rod and sheet specimens are shown in Figure 15 along with some recent data for arc-cast tungsten sheet. These data are considered identical. Also several points from the tungsten curve in Figure 1 are plotted for comparison. The agreement is excellent and it can be noted that the data for powder metallurgy tungsten rod are identical to the Figure 1 data for tungsten. The Figure 13 data are also presented in Figure 3 to yield a more direct comparison with other data.

Tantalum

Tantalum absorbs impurities so readily that specimen contamination presents a serious problem in high temperature thermal expansion measurements. As a matter of fact this single factor is probably the principal cause of the discrepancies which now exist in the expansion data discussed previously. This contamination is reflected not only in a distorted thermal expansion versus temperature relationship, but also in different heating and cooling curves. Following measurements at temperatures to 2400°C (actually this effect would be noticed after testing to 1400°C) the cooling curve is positioned distinctly above the heating curve. For a given temperature the percent linear expansion value might be 1.0 on heating and 1.4 at this same temperature during the cooling cycle. This suggests that a permanent deformation has taken place in the specimen upon exposure to impurities in the cover gas atmosphere at the high temperature. This suggestion of an apparent permanent deformation is confirmed by an inability to rezero the paired microscope system after the specimen returns to room temperature. In every case the micrometer readings indicate a length which is between 0.5 and 1.0 percent (5 to 10 mils in 1 inch) greater than the specimen length prior to test. This increase in length is not removed upon aging for the specimen fails to regain its original pre-test length even after standing at room temperature for long periods of time. Subsequent testing in the same atmosphere will also fail to yield the original pre-test specimen length and as a matter of fact this subsequent testing will lead to further contamination and further deformation. The actual

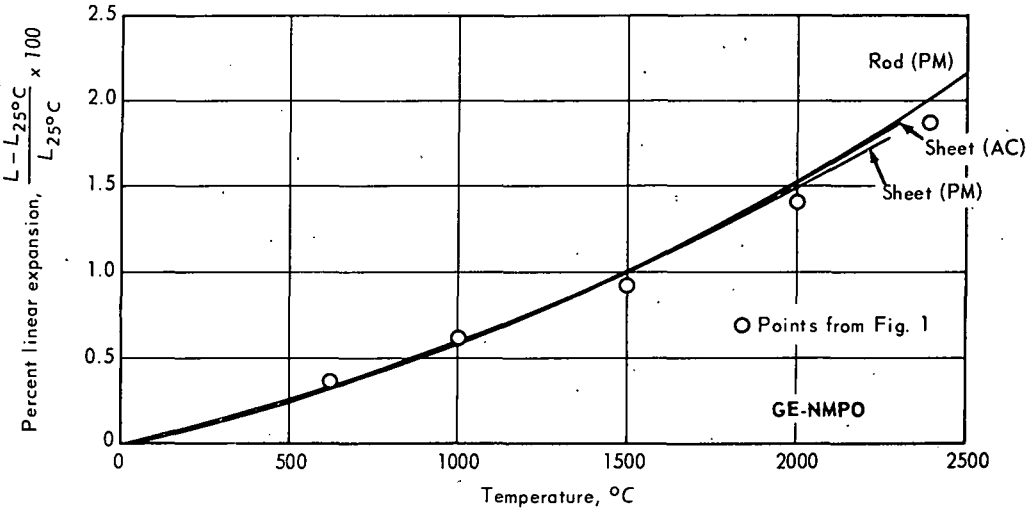

Fig. 12 – Linear thermal expansion of molybdenum in helium

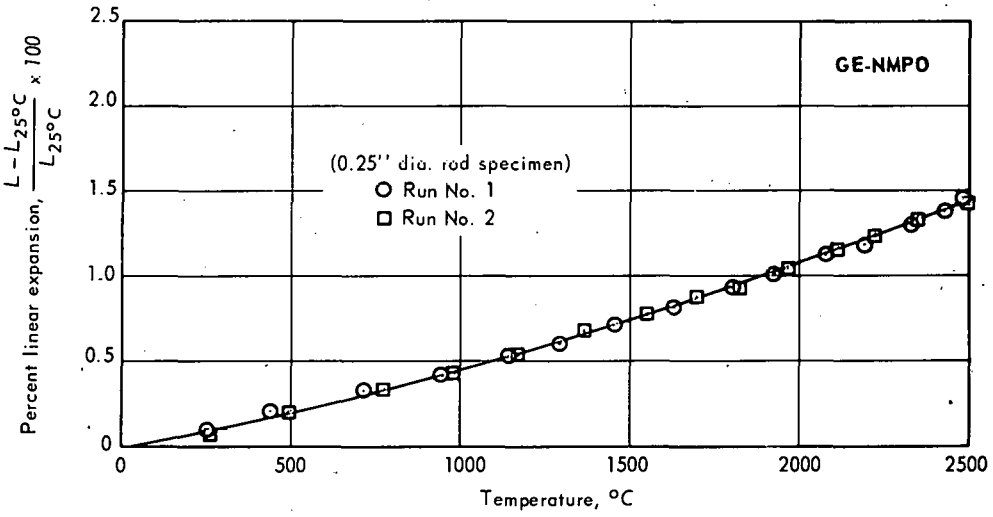

Fig. 13 – Linear thermal expansion of powder metallurgy tungsten rod in helium

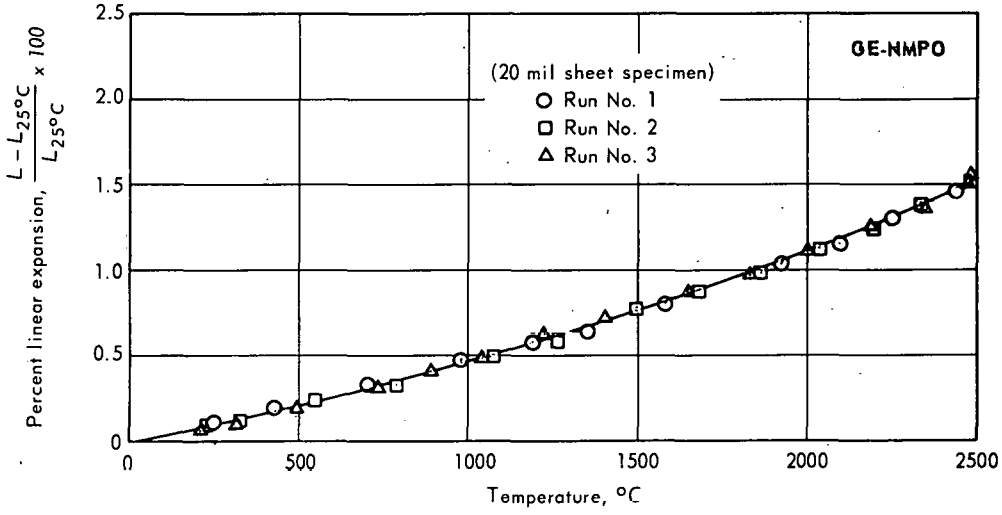

Fig. 14 – Linear thermal expansion of powder metallurgy tungsten sheet in helium

length after a second heating will be still greater than the original pre-test length. However, heating at 2300°C in vacuum for 3 hours will result in the specimen returning to its original length. Apparently the dissolved gases distort the metal lattice[18,19] as long as they remain in solution leading to what appears to be permanent deformation. Such deformation as described above is therefore not really permanent for the type of degassing procedure just described will result in the removal of essentially all the dissolved impurity gases and a return to original specimen dimensions.

A typical thermal expansion curve for tantalum in helium is shown in Figure 16 for the case where no attempt is made to remove all the impurities from the cover gas atmosphere. The initial heating curve appears smooth and has a shape characteristic of all metals. However, it is known that the sample begins absorbing impurities at temperatures above 1000°C which are sufficient to distort the lattice and lead to specimen lengths which are somewhat larger than would be obtained in the absence of contamination. During the cooling cycle the expansion curve is seen to be significantly different from the heating curve. This is due to the impurity content causing a semi-permanent (i.e., permanent until the impurities are removed by vacuum degassing) deformation which will not allow the specimen to return to its original length. The fact that the slope of the cooling curve is smaller than that of the heating curve in the higher temperature regions suggests that impurity absorption along with its associated lengthening effect is continuing. At temperatures close to 1200°C the slopes of the heating and cooling curves become quite similar and then the cooling curve exhibits a steeper slope in the lower temperature region. This is perhaps due to a loss of some of the dissolved impurities as the temperature is reduced. The specimen shrinkage due to this impurity loss leads, therefore, to a larger slope in this region of the cooling curve.

At room temperature the length of the specimen (see Figure 16) is seen to be about 0.75 percent larger than the original pre-test length. A second heating in which all elongations are referred to the original pre-test length is also shown in Figure 16. This curve is again smooth and quite characteristic; as a matter of fact, it is essentially parallel to the initial heating curve. Once again, however, the cooling curve is displaced from the heating

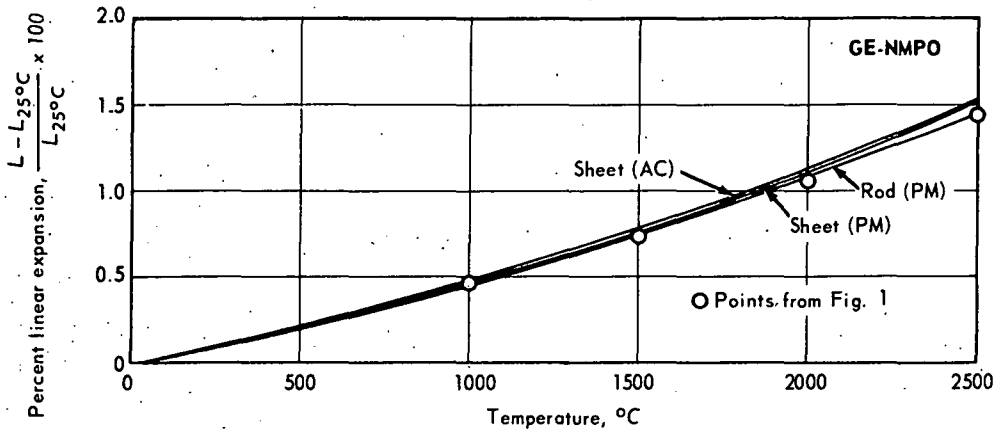

Fig. 15 – Linear thermal expansion of arc-cast and powder metallurgy tungsten in helium

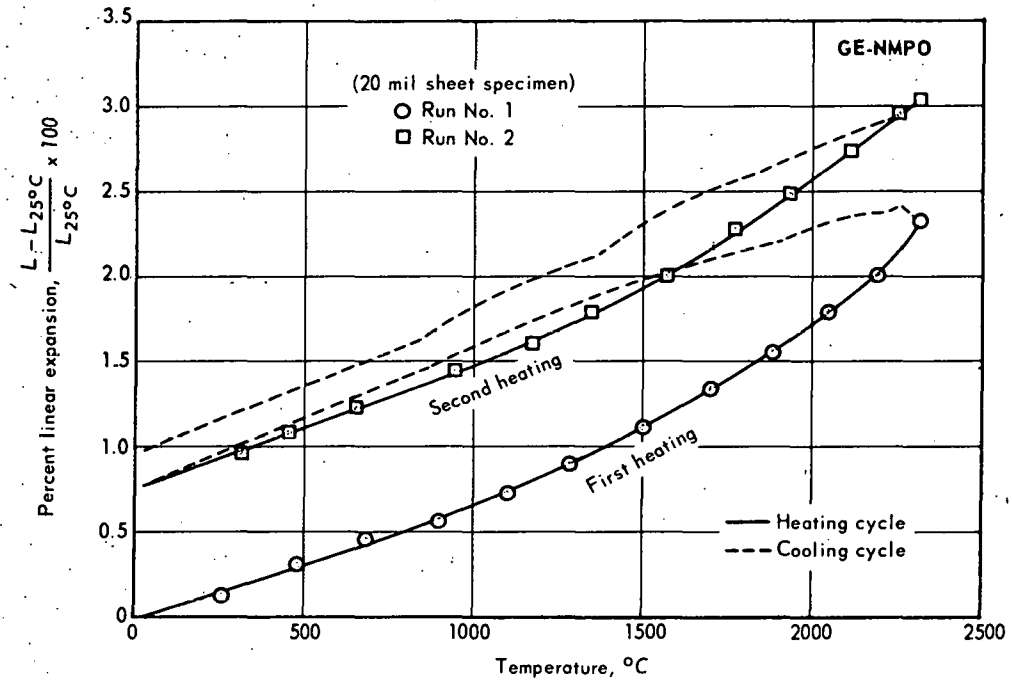

Fig. 16 – Effect of impurity absorption on linear thermal expansion of arc-cast tantalum in helium

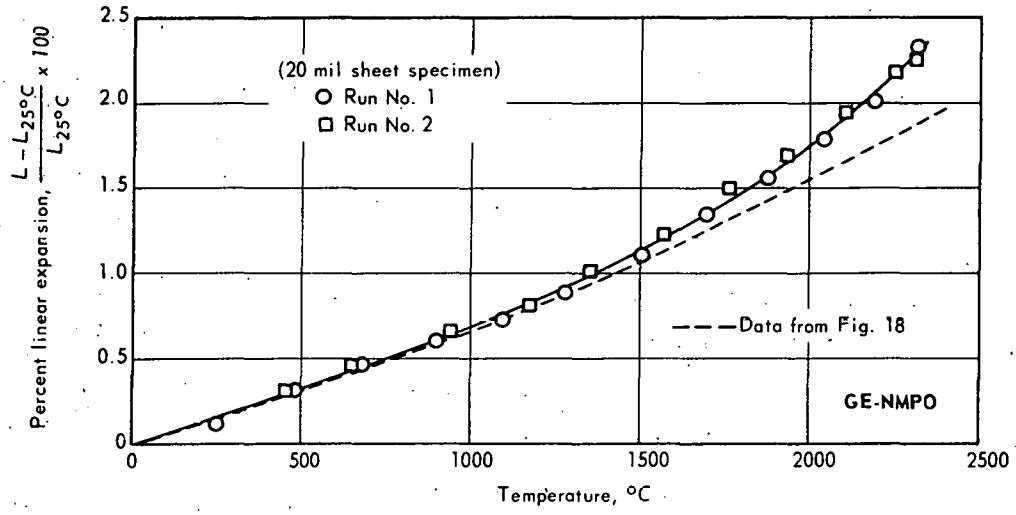

Fig. 17 – Recalculated linear expansion data for arc-cast tantalum referred to specimen length at start of heating cycle

curve and upon cooling to room temperature the specimen is found to suffer a further semi-permanent elongation. Even though the semi-permanent elongation associated with the second heating and cooling is much smaller than that observed after the first heating, the effect nonetheless is fairly pronounced. This phenomenon will continue until contamination is so extensive that it will lead to specimen bowing thus making further thermal expansion measurements meaningless. While not confirmed this bowing of the specimen is probably associated with compound formation at the higher levels of contamination.

The thermal expansion data shown in Figure 16 may be recalculated by referring all measured elongations to the length of specimen at the start of the heating cycle. In this way the original length of the specimen will be different for each heating curve and the observed elongations at the various temperatures will be calculated as differences from this length. Such calculations lead to the results shown in Figure 17. Within a few percent the heating curves are identical suggesting that the percent linear expansion and the average coefficient of linear expansion are the same for each specimen independent of the level of impurity content. Now this conclusion must apply only to conditions above a certain level of contamination for tantalum tested in such a way as to minimize contamination by cover gas impurities exhibits an expansion curve noticeably lower than that shown in Figure 17. It is noteworthy that this difference appears only at temperatures above 1200°C suggesting firstly that no specimen deformation due to impurity contamination occurs at temperatures below 1200°C. Secondly the essentially identical data at lower temperatures for the contaminated as well as the uncontaminated tantalum suggests no effect of impurity content on expansion characteristics in this range or at least an effect too small to be identified by the present measurements.

The linear expansion data for tantalum obtained under conditions designed to minimize specimen contamination are shown in Figure 18. In these measurements the specimen holding fixture was surrounded by several layers of tantalum to act as a "getter" for the cover gas impurities. The effectiveness of this technique was established by noting that the cooling curve was essentially identical to the heating curve. Further, the microscope micrometer readings at room temperature were found to rezero within 0.06 percent indicating that

the permanent deformation suffered by the specimen was negligible. Subsequent heatings and coolings, therefore, were found to yield expansion curves identical to that obtained in the first measurement. This agreement is apparent in the data shown in Figure 18.

It can also be noted in Figure 18 that the thermal expansion curve is identical to that shown in Figure 17 at temperatures to about 1200°C. At higher temperatures the Figure 18 data are some 20 percent lower than the data for the contaminated specimens. From these data then the effect of dissolved gases is quite obvious and the temperature at which these gases begin to exert an effect on the thermal expansion measurements of tantalum is seen to be about 1200°C.

The thermal expansion data presented in Figure 18 have been included in Figure 2 and are seen to be lower than any of the other data shown at temperatures to about 1500°C. Above this temperature the Figure 18 data gradually rise above the Edwards, Speiser, and Johnston[9] data and then above the Figure 1 data for tantalum at about 1700°C. Except for the Fieldhouse, et al[6] data, which appear much too high, the agreement between all tantalum data is well within a band of about ± 10 percent. Therefore, with the exception just mentioned all the thermal expansion data reported for tantalum must be considered to exhibit very good agreement. It is also to be noted that the data from Figure 18 are seen to fall midway between the first heating data of Rasor and McClelland[7] and the data of Edwards, et al. (Note: While the curves published by Rasor and McClelland[7] were widely spaced, it is obvious that the curve representing the second heating was not based on the correct specimen length prior to heating. All data points appear much too high suggesting that the elongation values were based on the specimen length existing prior to the initial heating. Since some permanent deformation was observed after the first heating, such a calculation procedure would lead to results which are too high. Such data were recalculated for use in Figure 2 and are seen to fall slightly lower than the data obtained in the initial heating. In this case the agreement between those data and those

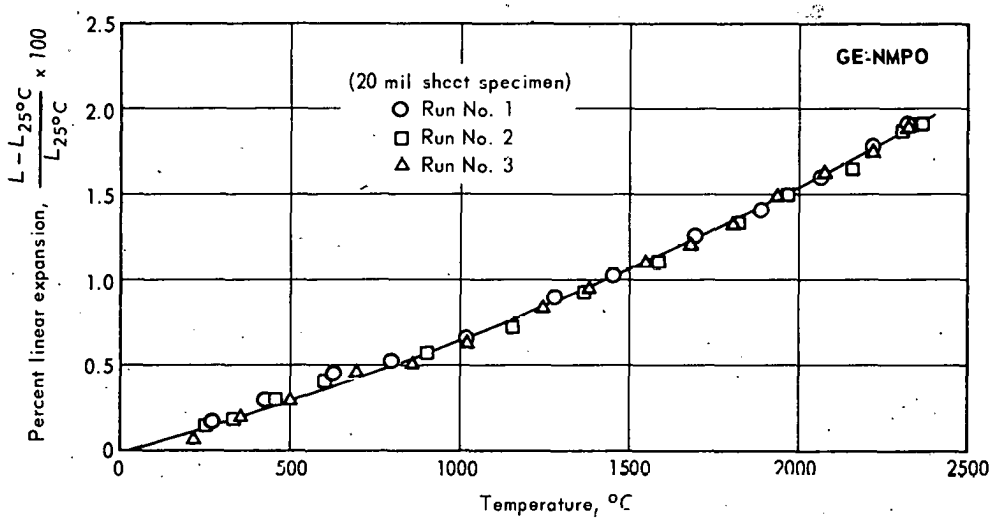

Fig. 18 – Linear thermal expansion of arc-cast tantalum sheet in helium

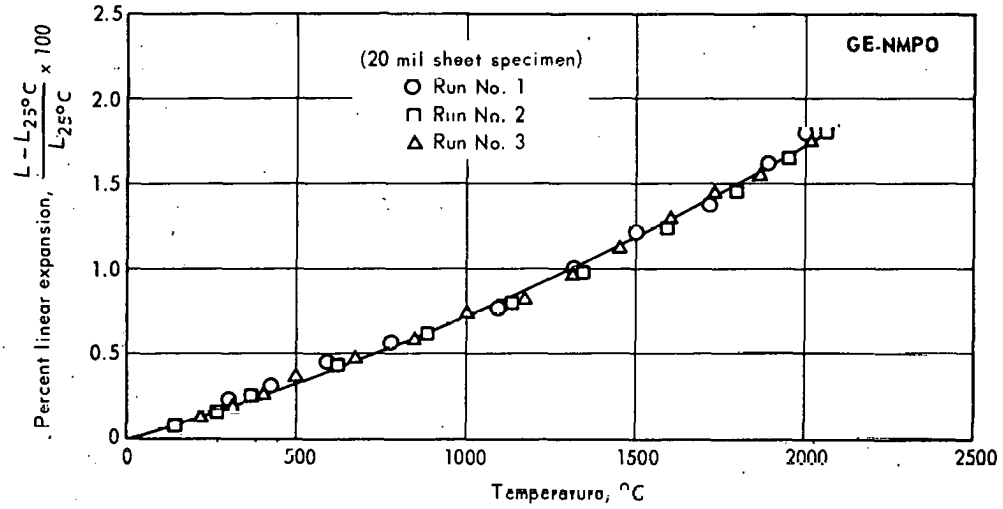

Fig. 19 – Linear thermal expansion of arc-cast niobium sheet in helium

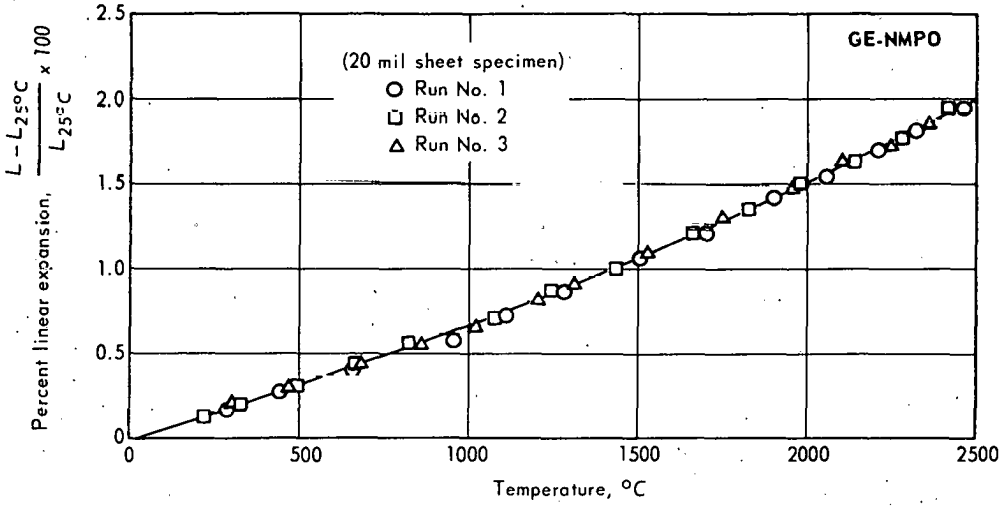

Fig. 20 – Linear thermal expansion of powder metallurgy rhenium sheet in helium

of Figure 18 is excellent and appears to be well within 5 percent over the entire temperature range.)

Niobium

Data for niobium obtained in this study are shown in Figure 19. The same difficulties with respect to contamination as observed with tantalum were also observed with niobium. When the greatest precautions were not taken, specimen contamination by cover gas impurities was observed which resulted in cooling curves which were different from the heating curves (one niobium specimen was analyzed after two heating and cooling cycles between room temperature and 2200°C and found to contain 20, 1650, and 5320 ppm of hydrogen, oxygen, and nitrogen compared to pre-test values of 8, 180, and 4). Furthermore, semi-permanent specimen elongations were noted by a failure of the specimen to return to its original length after heating. These difficulties were solved by adopting the same techniques as employed with tantalum. Several layers of niobium sheet material were placed around the specimen support block to serve as a "getter" for the impurities. This resulted in cooling curves which were coincident with the heating curves. In addition, the specimen was always found to return to its original length after heating and cooling.

When the data from Figure 19 are compared with data obtained under conditions for which no getter material was employed, the same differences in expansion curves are noted as observed in the case of tantalum. Above 1100°C the absorption of impurities by the niobium leads to higher expansion values than obtained in the uncontaminated specimens. Below 1100°C the expansion data are identical for both the contaminated and uncontaminated specimens. It is interesting that the temperature above which impurity contamination has a noticeable effect is almost the same (actually about 100°C different) for both tantalum and niobium.

The niobium data in Figure 19 are presented in Figure 4 and are seen to be lower than any of the previously reported values for this metal. This persists over the entire range of investigation to 2000°C. The comparison afforded by Figure 4 reveals that the Fieldhouse, Hedge, and Lang[17] data for niobium fall 20 percent higher than the current measurements at 1000°C and remain considerably higher even to the highest temperatures. Other data

while slightly higher than these present measurements in the low temperature range reveal a gradual merger at temperatures close to 2000°C. At 2000°C the present data, those of Edwards, Speiser, and Johnston[9], and those of Kearns, Clark, Young, and Jones[3] are all identical within about 3 percent.

Rhenium

Linear thermal expansion data for rhenium are shown in Figure 20 and represent the first such measurements for this material to these temperatures. Heating and cooling curves for rhenium were found to be identical and the reproducibility obtained by duplicate measurements is seen to be excellent. Also no difficulty at all was encountered with specimen contamination. In every case the microscope micrometers indicated an exact rezero corresponding to a complete return to the original dimensions.

Refractory Metal Alloys

Thermal expansion data for the refractory metal alloys W-25Re, Ta-10W, and Mo-50Re are shown in Figures 21, 22, and 23. In the case of W-25Re and Mo-50Re these data represent the first measurements for these materials to high temperatures.

No measurement difficulties were encountered with W-25Re or Mo-50Re. However, the Ta-10W alloy was sensitive to impurity absorption and the same precautions employed with tantalum and niobium were observed. When this was not done, the heating and cooling curves were not coincident, and the specimens exhibited an increase in length upon cooling to room temperature. Some expansion data for Ta-10W presented by Emmons and Allen[15] are plotted in Figure 22. Their data are seen to be 20 percent lower than the GE-NMPO data at 1000°C and about 5 percent lower at 2000°C. The cause of this difference is not known at this time.

Other data for Ta-10W published by Hedge, Kostenko, and Lang[20] are in excellent agreement with the Figure 22 data. Over the entire temperature range the agreement is within a few percent. Such agreement would seem to confirm the accuracy of the Figure 22 data for this alloy and suggest that the Emmons and Allen data are subject to doubt.

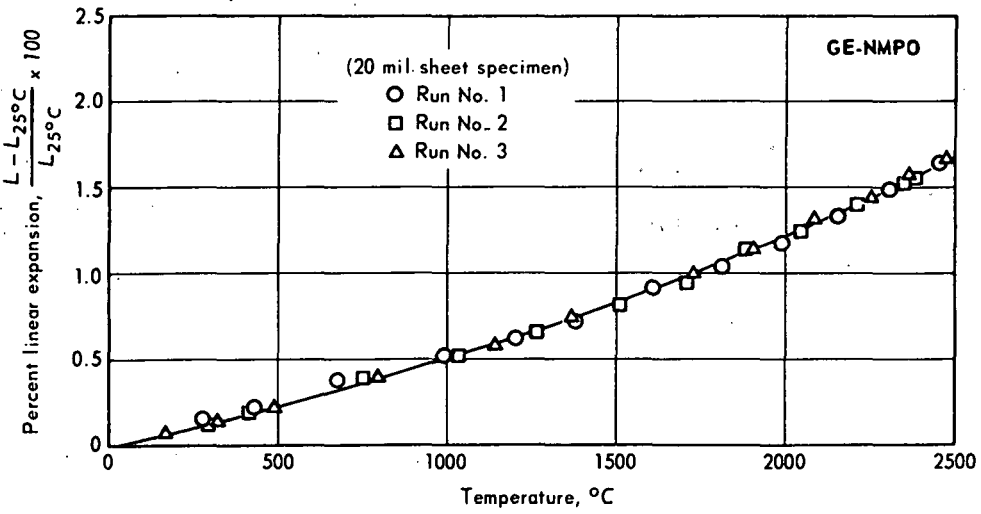

Fig. 21 – Linear thermal expansion of powder metallurgy W – 25Re sheet in helium

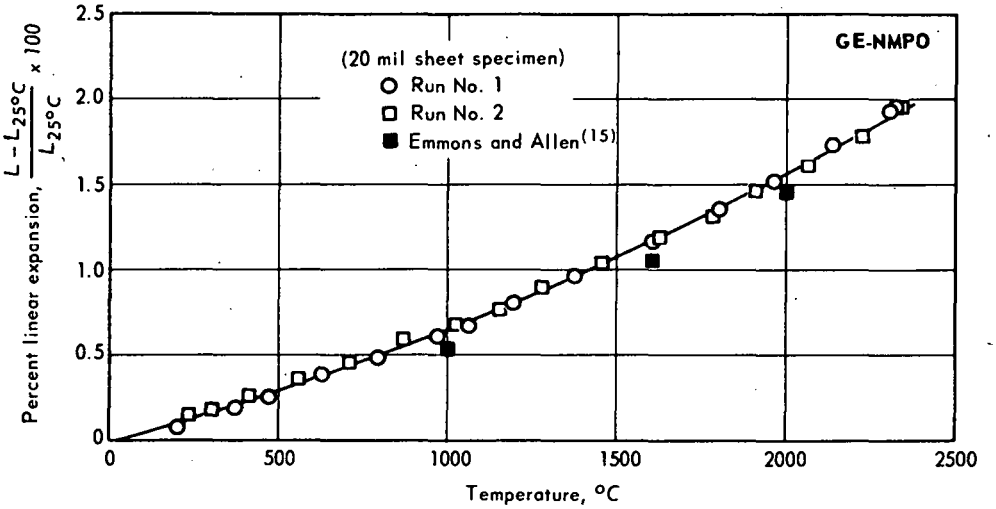

Fig. 22 – Linear thermal expansion of arc-cast Ta – 10W sheet in helium

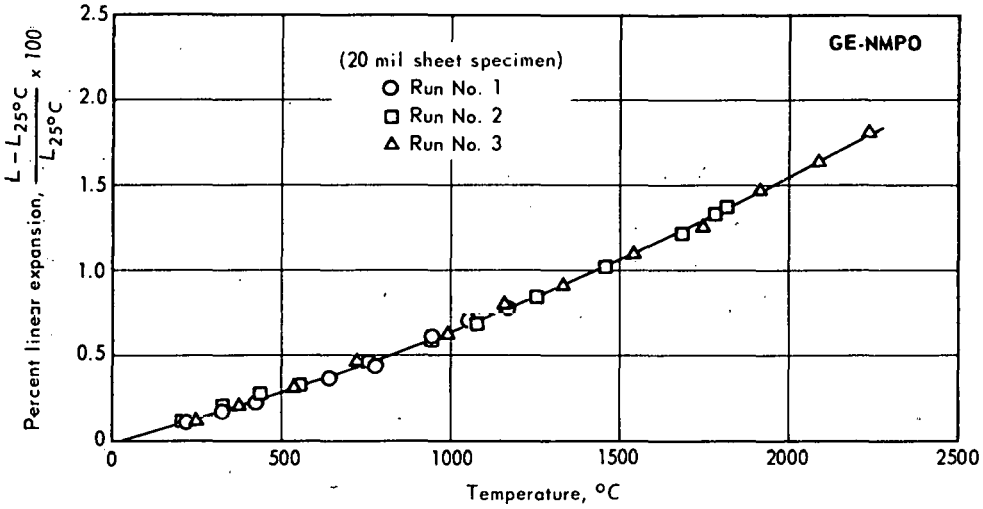

Fig. 23 – Linear thermal expansion of powder metallurgy Mo – 50Re sheet in helium

APPENDIX A

Correction For Refraction Effects

Although linear thermal expansion measurements made with the paired micrometer microscope system are fairly straightforward and rather routine, they are subject to noticeable error unless made in vacuum or in a furnace in which thermal gradients in the direction perpendicular to the optical path are eliminated. Recent measurements at GE-NMPO were the first to identify this phenomenon when tests of a sapphire specimen in vacuum and helium were found to yield different expansion results. This same behavior was also noted with 310 stainless steel and niobium specimens. In each case the specimen length as measured in helium was smaller than that measured in vacuum. Length measurements obtained at room temperature with the paired microscopes were, however, identical for both atmospheres. It has now been found that these differences are the result of refraction and arise because the optical path employed by the paired micrometer microscopes traverses a zone of non-uniform temperature gradient. With the specimen positioned horizontally in a resistively heated vertical tube furnace the sighting path employed was vertical, and hence passed through a rising temperature profile. In the absence of a simultaneous radial gradient in the 4-inch diameter tube furnace no refraction error of this type would be encountered. However, because of the existence of a typical radial gradient for this type of furnace (minimum temperature at centerline of furnace) optical paths intersect a given temperature isotherm at a slight angle and the resulting refraction makes the specimen appear shorter than it actually is. In vacuum where such refraction effects are absent no such behavior is observed and a true length indication is obtained.

Similar behavior was observed in hydrogen and argon when all elevated temperature specimen lengths appeared smaller than those measured in vacuum. As a matter of fact, in the argon tests the conditions were so extreme at one furnace temperature that the specimen appeared to be shorter than it was at room temperature. In other words this anomaly offered the observation that the specimen shortened on heating. Behavior identical to that observed in argon was also observed in air. Such behavior was actually predicted since

the properties (density, thermal conductivity, and index of refraction) of air and argon are quite similar.

Thermal expansion data obtained in these tests are shown in Figure 24. It is noted that in all atmospheres the specimen lengths are shorter than those observed in vacuum. In the argon tests the specimen at 200°C actually appears to have a length smaller than its room temperature value.

In certain expansion measurements in which optical techniques are employed it is possible that this behavior would not be noticed. For example, in some techniques small wires suspended from the specimen act as fiducial marks, and since these penetrate the furnace wall and the distance between wires is measured external to the furnace, the above consideration might not apply. Also some techniques employ specimens which are about 10 inches in length. In these cases the refraction error which is usually about 1 mil would be a very small fraction of the total elongation (about 40 mils in 10 inches at 800°C for most refractory metals), and hence would not be very noticeable. However, in those measurements where specimen lengths are on the order of 2 to 3 inches and where actual fiducial marks on the specimen are being monitored, specimens appear shorter in gaseous atmospheres and linear expansion results which do not acknowledge this will be subject to appreciable error. In helium this error was found to be at a maximum at temperatures close to 600°C in the apparatus being employed. Of course, at temperatures close to 2000°C specimen elongations are quite large, and hence this refraction error amounts to only 2 or 3 percent for specimens 2 inches in length. Such errors are, therefore, difficult to detect at these high temperatures.

Corrections for these refraction effects for use with the current thermal expansion data are shown in Figure 25. Measurements were made with a sapphire specimen in vacuum and in helium to 2000°C. Then the vacuum data were considered correct since they were identical to the NBS data for this material. Differences between these data and the helium data at various temperatures were then calculated to yield the graph shown in Figure 25. Similar measurements with tungsten, molybdenum, and stainless steel gave identical data for the correction curve. In making a measurement in helium, therefore, the correction to be added to each observed expansion value can be obtained from Figure 25. When the correction is properly applied, the data then correspond to data which would be obtained in vacuum tests.

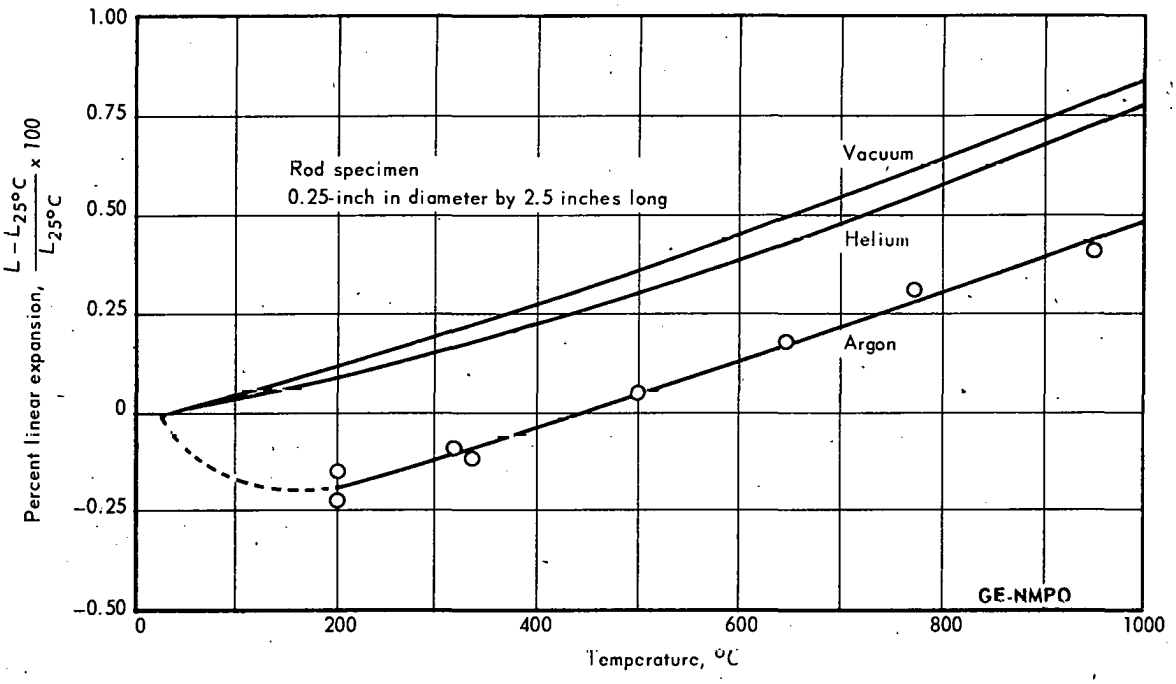

Fig. 24 – Thermal expansion data for sapphire obtained in various atmospheres (experimental points are shown for the argon tests only; curves for vacuum and helium tests have been faired through experimental points)

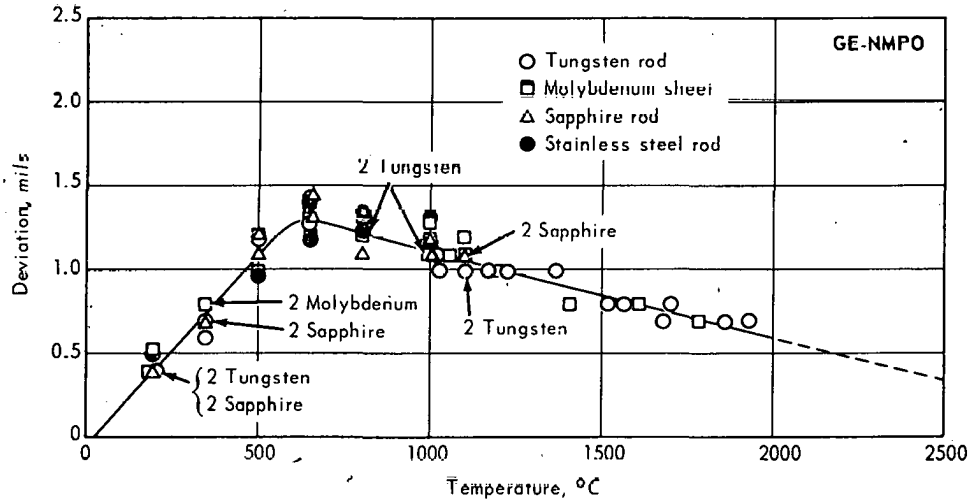

Fig. 25 – Refraction corrections applied to linear thermal expansion measurements obtained in helium. These corrections must be added to measured values of length.

It should be noted that the corrections exhibit a maximum value at a temperature close to 600°C. No reason for this maximum can be given at this time, but it appears related to changes in the radial temperature gradient which exists at various temperature levels. Obviously, as the temperature increases convection currents exert more and more influence in decreasing radial temperature gradients. This factor is thought to explain the gradual decrease in the refraction correction seen in Figure 25 as the temperature increases.

Another consideration deserving special notice is that the refraction corrections given in Figure 25 are definitely atmosphere sensitive, and hence are only applicable to measurements in helium. In addition, they are probably also geometry sensitive, and hence apply only to the furnace and measuring system employed in their determination. Changes in heating element diameter or length will no doubt require a different correction curve from that given in Figure 25.

ACKNOWLEDGMENTS

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