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THE THERMAL CONDUCTIVITY OF MOLYBDENUM OVER THE TEMPERATURE RANGE 1000-2100°F

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Engineering Experiment Station
Performed under Subcontract No. 362

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THE THERMAL CONDUCTIVITY OF MOLYBDENUM OVER THE TEMPERATURE RANGE 1000 TO 2100°F

E. P. Mikol

SUMMARY

The thermal conductivity of 99.9% pure molybdenum has been determined over the temperature range 1000 to 2100°F by means of a radial heat-flow apparatus. The data indicate that the variation with temperature is linear in this range. Values of the conductivity at uniform temperature intervals are given in Table 1. Extrapolation of these data to 32°F gives a value that agrees within 2% with the most probable value given in the International Critical Tables. These results agree with those of Osborn[1] within 8% over the temperature range.

TABLE 1

Conductivity Values

TEMPERATURE (°F)	THERMAL CONDUCTIVITY (Btu/hr-ft^2-°F/ft)
1000	70.3
1100	69.1
1200	67.9
1300	66.7
1400	65.4
1500	64.2
1600	62.9
1700	61.6
1800	60.4
1900	59.0
2000	57.7
2100	56.5

The individual data points for this determination agree within 5% with the values given in Table 1.

[1]R. H. Osborn, "Thermal Conductivities of Tungsten and Molybdenum at Incandescent Temperatures," *J. Optical Soc. Am.* 31, p. 428-432 (1941).

EXPERIMENTAL METHOD AND DESCRIPTION OF APPARATUS

The method used involved heat flow radially outward through a thick-walled cylinder. The apparatus was essentially that described by R. W. Powell[2] and used by him to determine the thermal conductivity of Armco iron up to 1000°C.

The radial heat-flow method was selected in preference to longitudinal or spherical methods because it appeared that the problem of guard-heater design and manipulation would be simpler than for the longitudinal heat-flow method, while fabrication difficulties would be considerably less than for the spherical heat-flow method. Experience with the apparatus has confirmed these views.

For true radial heat flow outward through a thick-walled cylinder, the heat transfer in the steady state is given by

$$Q = \frac{2\pi KL(t_1 - t_2)}{\ln \frac{r_2}{r_1}},$$

where Q = heat transferred radially, Btu/hr,

K = thermal conductivity (assumed to be constant over the temperature interval), Btu/hr-ft^2-°F/ft,

t_1, t_2 = temperature measured at two different radii, °F,

r_1, r_2 = the radii at which temperatures t_1 and t_2 are measured,

L = length of test section of cylinder, ft.

[2]R. W. Powell, "The Thermal and Electrical Conductivity of Iron at High Temperatures," *Proc. Phys. Soc.* 51, p. 407-418 (1939).

Solving algebraically for the thermal conductivity,

$$K = \frac{Q \ln \frac{r_2}{r_1}}{2\pi L(t_1 - t_2)} .$$

If the energy input is electrical heating of a resistance wire,

$$Q = 3.4128\ VI ,$$

where V = potential drop along heating element at test section, v,

I = current through heating element at test section, amp,

3.4128 = conversion factor, Btu/hr/w.

The molybdenum was purchased from the Fansteel Metallurgical Corporation. The material was prepared by powder-metallurgy techniques, and after pressing and sintering of the original ingot the material was rolled to finished size. Rolling was accomplished at temperatures just below the recrystallization temperature. The following is a typical analysis for Fansteel wrought-molybdenum products.

Molybdenum	99.9%
Iron	0.005% maximum
Carbon	0.003% maximum

Figure 1 shows the details of the apparatus used. The molybdenum sample consisted of a stack of 15 disks, each approximately 5 in. outside diameter, 0.75 in. inside diameter, and 0.50 in. thick. The five middle disks served as the test section while the five disks above and below the test section acted as end guards. The use of a series of disks stacked together rather than a single thick-walled cylinder was dictated by two practical considerations. The accurate machining of long holes that are small in diameter is an almost impossible task, and wrought molybdenum is difficult to obtain in large sized samples. As noted by Powell,[(2)] an advantage does accrue from the use of stacked disks in that the poor thermal contact between disks offers considerable resistance to longitudinal heat flow. Accordingly, the difficulty of guarding to prevent end losses is greatly reduced.

Additional protection against end losses was provided by end guard heaters which consisted of three Nichrome heating coils cemented into concentric grooves machined into steatite disks. These were placed above and below the molybdenum stack and each heater coil was supplied from a separately controllable alternating-current source.

Provision for rapid heating of the sample and assistance in attainment of the highest temperature levels was made by an outer guard heater operating on alternating current. The guard heater consisted of Kanthal wire on a threaded ceramic core.

The central heater consisted of Kanthal wire wound upon a 0.50-in.-diameter threaded ceramic core, which was mounted concentrically with the inner bore of the molybdenum stack. To facilitate accurate power measurements, direct current was supplied to the central heater. The energy flowing to the test section was derived from measurements of the current and the potential drop along a 2-in. length of the central heater adjacent to the test section. For this latter purpose, fine platinum potential leads were welded directly to the Kanthal windings. The platinum leads were so connected as to bring a series combination of 100-ohm and 10,000-ohm precision resistors into parallel with the resistance wire of the test section. From the measured potential drop across the 100-ohm resistance, the potential drop across the test section was determined. The current flow was obtained from the measurement of potential drop across a 0.01-ohm precision resistor in series with the central heater. A type K-2 potentiometer was used for the above potential-drop measurements.

Temperature measurements were made using a platinum-to-platinum, 10% rhodium thermocouple insulated by fine twin-bore ceramic tubing. Five thermocouple probe holes were provided, located as shown in Fig. 2. The holes in the test section were 0.070 in. in diameter whereas those in the upper five disks were made slightly larger (0.094 in.) to ease the problem of alignment. With this arrangement, it was possible to traverse the test

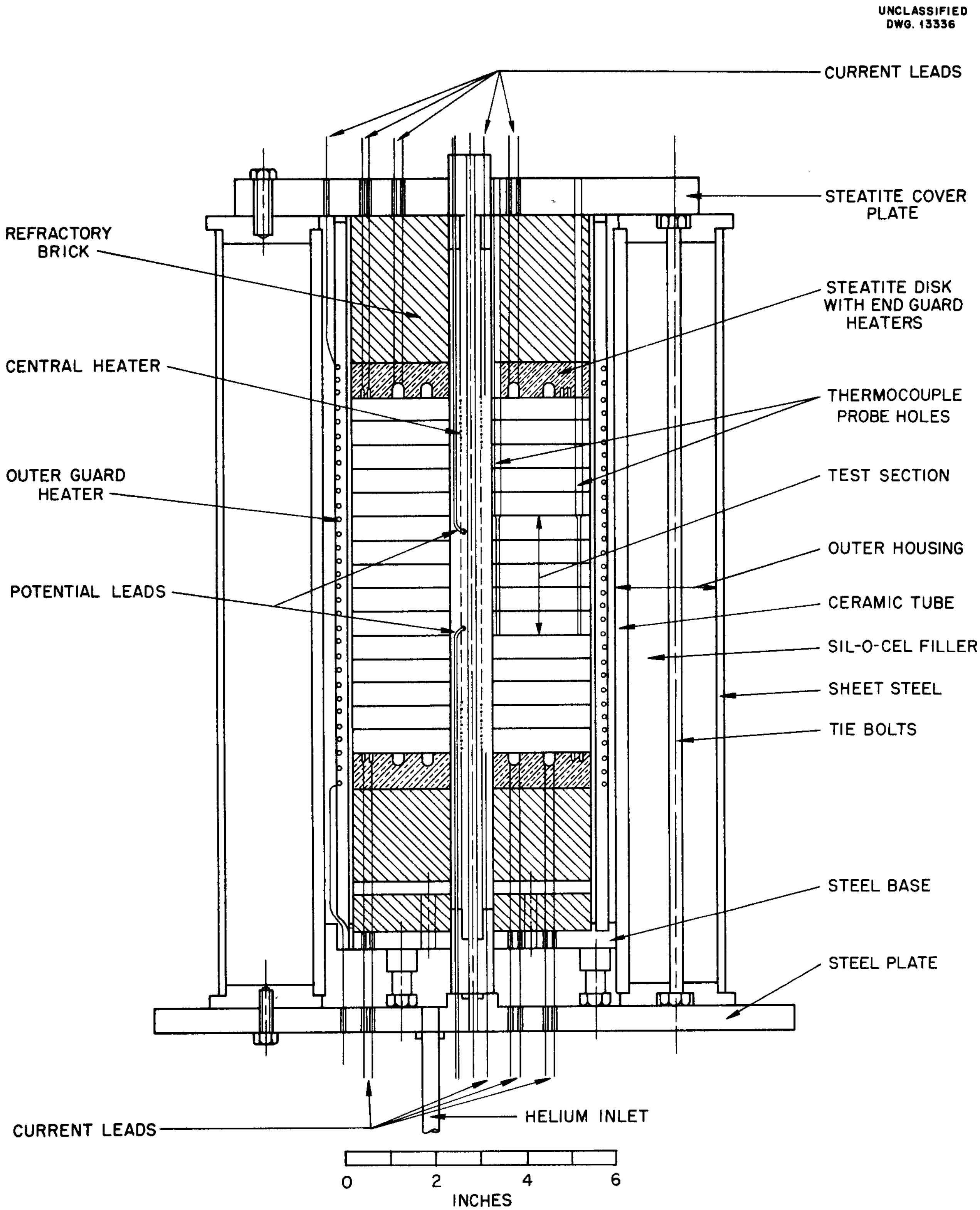

Fig. 1. General arrangement of apparatus for measurement of thermal conductivity by the radial heat-flow method.

section longitudinally to determine whether any appreciable temperature gradient existed. The same thermocouple was used to traverse each of the five holes, thereby assuring good accuracy in the determination of the temperature differences required for calculation of the thermal conductivity. For temperatures below 1900°F, a Leeds & Northrup White potentiometer (range 0 to 10,000 μv) was used for measurement of the thermal emf. Above 1900°F, a type K-2 potentiometer was used.

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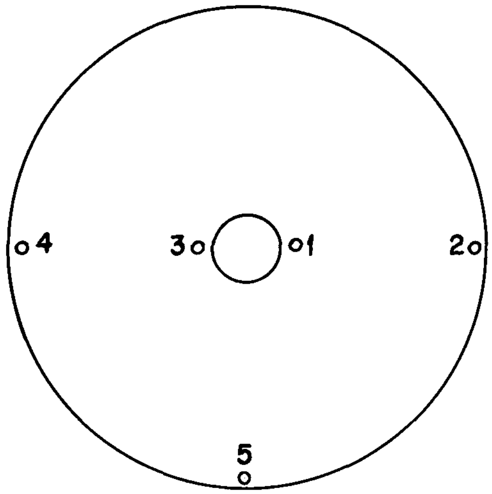

Fig. 2. Plan view of molybdenum test section disk. ID, 0.75 in.; OD, 5 in.; thickness, 0.50 in.; inner probe hole radius, 0.500 in.; outer probe hole radius, 2.375 in.; probe hole diameter, 0.070 in.

Since molybdenum is known to oxidize very rapidly at temperatures above 900°F, it was necessary to provide a neutral atmosphere. Helium was used for this purpose. The furnace was carefully sealed with cement at every possible leakage point and a positive pressure of helium of about 0.2 in. of water was maintained at all times. When any of the thermocouple holes were not in use, the opening through the top of the furnace was plugged. Even with these precautions, appreciable oxidation of the sample occurred.

PROCEDURE

The furnace was brought to the desired temperature level using both the central heater and the outer guard heater. Helium flow was started when the indicated central-heater temperature reached 600°F. As the desired temperature level was approached, the current to the outer guard heater was reduced to hasten the attainment of steady state. A traverse of one inner and one outer thermocouple hole served to indicate how the end guard heaters should be controlled to improve the distribution. This procedure was continued until the best possible distribution in the test section was obtained. Since the d-c battery was not of sufficient amp-hr capacity to supply central-heater power during the warm-up period, a d-c motor-generator set was used until the observed rate of temperature change within the test section was as low as 0.04°F/min (about 0.2 μv/min with platinum-to-platinum, 10% rhodium thermocouples). At this point, the central heater was switched to a battery power supply. The current was then held constant to closer than 0.1% by manual control of slide-wire resistances in series with the central heater. Once operation on the battery supply had stabilized, steady state was hastened by minor adjustments of the central-heater current until the observed rate of change was less than 0.02°F/min. A traverse of the thermocouple holes was made in the order of the numbering shown in Fig. 2, and the traverse was repeated immediately to assure that steady state had been attained. Change of conditions was accomplished by first switching back to d-c motor-generator operation and adjustment of either the central-heater current or the outer guard heater. Operating in this manner, it was seldom necessary to run on batteries for more than $1\frac{1}{2}$ hr.

A typical set of data is given in Table 2. A sample calculation with these data gives

$$K_{1350^\circ F} = 66.3 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F/ft} .$$

RESULTS

The data obtained in the present investigation, and the best curve from which the values in Table 1 were taken are shown in Fig. 3. The spread of the data points at the lower temperatures was caused in large measure by the relatively small temperature interval obtainable (6.5 to 8.5°F). A reduction in insulation or provision for water cooling would be necessary to obtain larger temperature differences at these and lower temperature levels.

TABLE 2

Data for Thermal Conductivity Calculation

Mean sample temperature	1350°F
Mean temperature difference	10.75°F
Potential lead spacing, L	0.168 ft
Mean inner radius, r_1	0.499 in.
Mean outer radius, r_2	2.373 in.
Central heater current, I	10.57 amp
Potential drop, V	13.34 v
Electrical heating effect, VI	141.0 w

LOCATION OF THERMOCOUPLE JUNCTION ABOVE BOTTOM OF TEST SECTION (in.)	THERMOCOUPLE EMF (μv)						
	t_1	t_2	$(t_1 - t_2)$	t_3	t_4	$(t_3 - t_4)$	t_5
0.25	6600.8	6535.8	65.0	6596.3	6534.6	61.7	6538.8
0.75	6603.0	6539.0	64.0	6600.0	6538.0	62.0	6541.1
1.25	6604.0	6540.1	63.9	6602.5	6539.7	62.8	6542.2
1.75	6604.0	6538.5	65.5	6600.6	6538.8	59.7	6540.9
2.25	6600.5	6534.4	66.1	6597.1	6535.1	60.6	6536.5
MEAN VALUES	6602.5	6537.6	64.9	6599.3	6537.2	62.1	6539.9
MEAN TEMPERATURE, °F	1355.2	1344.2	11.0	1354.6	1344.1	10.5	1344.6

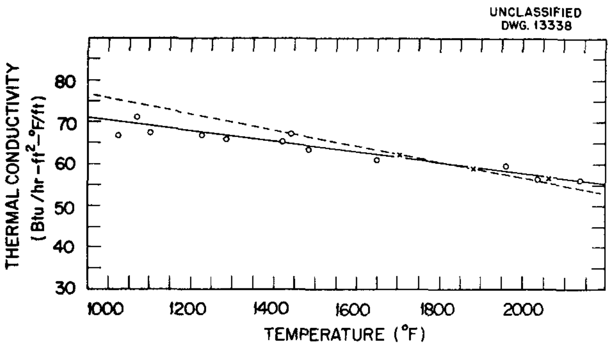

Fig. 3. Variation of thermal conductivity of molybdenum with temperature. ——— X, Osborn's results; ——— o, results using radial heat-flow method.

These data were obtained with *five different* assemblies of central heaters, and as may be noted, the agreement with the best curve is within 5% over the entire range. Additional evidence of the reliability of the data is afforded by the results of Osborn[1] in the same temperature range. The broken line, which is an extrapolation of Osborn's data to lower temperatures, is shown for reference in Fig. 3. Agreement between the two curves is within 8% over the entire range. At the higher temperatures the results are almost identical.

Extrapolation of the present results to 32°F yields a value for conductivity (1.43 w/cm^2-°K/cm or 82.7 Btu/hr-ft^2-°F/ft) which agrees within about 2% with the most probable value at this temperature as reported in the International Critical Tables (1.46 w/cm^2-°K/cm). Osborn noted in his report that extrapolation of his data gave a value of 1.6 w/cm^2-°K/cm at 32°F. This value is about 9.5% higher than the International Critical Tables value.

Since careful consideration was given to all phases of the instrumentation, it is believed that the total error attributable to the measurements alone does not exceed 1%. However, random error, produced in part by slight misalignment of the central heater, nonuniformity of resistance wire, nonuniformity of sample, imperfect end guarding, inaccuracies in machining, and similar causes, accounts for the largest part of the spread in data.

With the foregoing considerations in mind, it is believed that the present data are reliable to within the 5% indicated by the spread in data points.

EXPERIMENTAL DIFFICULTIES ENCOUNTERED

Early in the investigation, erratic results were encountered of such magnitude as to suggest that serious inhomogenieties existed in the sample. The equipment was dismantled, the order of stacking of molybdenum disks was changed, and thermocouple hole No. 5 was provided, in order to sample the temperature at a location perpendicular to the four probe holes lying along a single diameter. Subsequently, the cause of the erratic results was traced to severe local overheating of the chromel-alumel thermocouples then being used. The overheating occurred where, for a short distance above the sample, the couple was exposed to direct radiation from the central heater. A change to platinum-to-platinum, 10% rhodium thermocouples solved the problem. Traverse of all five holes then indicated excellent uniformity of temperature. It was noted that for any one assembly of the central heater, the relative distribution of temperatures among the five holes remained very closely the same for different runs. A change in central heater usually resulted in a slight change in temperature distribution, these again remaining consistent for that assembly. This serves as evidence that the molybdenum is not inhomogeneous to any perceptible extent.

The temperature data obtained from a traverse of thermocouple hole No. 5 was not used in the calculation of the temperature differences. An attempt to do this always resulted in a spread of the data because the temperature differences along any one radius were in general more uniform than the temperature distribution circumferentially at a given radius. If a hole had been provided at the inner probe radius and along the same diameter as No. 5, it is believed that the temperature differences thus obtained would corroborate the present results. The substantiation of this comes from a study of the data which show that if t_1 is higher than t_3, t_2 is always higher than t_4 and vice versa. The data obtained from a traverse of probe hole No. 5 were used merely as a check for reasonable uniformity of temperature distribution and in the calculation of the mean temperature of the sample.

The initial design of the central heater had windings extending at each end about 2 in. beyond the molybdenum sample. In the later designs, these end windings were eliminated. The data obtained with each assembly agree within 3%, but the latter design gave consistently higher values for conductivity. This close agreement in results occurred only if the wire had not been raised too much above 2000°F for an appreciable time during use. It appears that deterioration of the end portions of the wire, when used at high temperatures, resulted in a marked increase in wire resistance along the end portions. For those data runs made after this had occurred, the end portions of wire probably operated at very much higher temperatures than the sections adjacent to the molybdenum. Under such circumstances, it is believed that an appreciable energy transfer occurred inwardly, thereby giving rise to an unmeasured energy transfer through the test section. Accordingly, the temperature differences noted were greater than those corresponding to the measured power input, and low values of conductivity were obtained. One entire series of data apparently indicated an increase in conductivity with increase in temperature. A study of the data revealed that the central portion of the heater wire had been operating at 2300°F. In addition, energy input to the end guard heaters had been very much higher for these data runs than had been previously necessary. With the above reasoning in mind, a new central heater was installed with the end windings eliminated. The data subsequently obtained agreed with the original data within 3%, which can be considered quite satisfactory. Although the evidence is not conclusive that the line of thinking given above is the complete explanation as to what had occurred, yet the corrective measures suggested by this reasoning gave results to corroborate the original data.

One minor practical point may well be mentioned here. The appearance of the Kanthal wire upon removal from the furnace suggests that it is in some way attacked or its deterioration is hastened by the presence of molybdenum oxide. The outer guard heater had to be replaced after burn-out of the winding. Upon removal it was found that excessive cracking of the ceramic had occurred, and where the ceramic cracked and exposed the Kanthal to the atmosphere from the region of the molybdenum stack, the wires were badly deteriorated. The appearance was as if acid attack had occurred. The wire in these regions was covered with a purple deposit resembling molybdenum oxide. Similar occurrences were noted with the last two central heaters used. The wire was apparently still in excellent condition except where burn-out occurred. Here again, the wire was badly deteriorated and a purple deposit covered the region.