The Thermionic and Photoelectric Work Functions of Molybdenum

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The photoelectric and thermionic emission from pure molybdenum was studied during a prolonged process of outgassing by heat treatment at temperatures up to 2100°K. In a sealed-off tube an equilibrium condition was reached which was not changed by further treatment extending up to 1600 hours. Photoelectric curves taken at room temperature and at 940°K and analyzed by Fowler's method yielded a true work function for the outgassed Mo of 4.15 ± 0.02 volts. Thermionic data for the same specimen also yielded a work function of 4.15 volts, and a value of the constant A close to the theoretical value of 60 amp./cm^2 deg.^{2}.

THE present investigation was undertaken as a part of a program of examining the photoelectric and thermionic properties of metals after a prolonged heat treatment in the highest attainable vacuum. Its aim was twofold: (1) to clear up if possible the discrepancies between the various published values for the surface work function of molybdenum, and (2) to obtain a further experimental test of Fowler's theory of photoelectric emission.

The thermionic work function of Mo has been determined under good vacuum conditions by Dushman and his co-workers[1] and by Zwikker.[2] The values obtained by these observers, 4.44 and 4.38 volts, respectively, are in good agreement with each other and undoubtedly represent the best values heretofore obtained for the outgassed metal. However, Dushman reported that great difficulty was encountered in eliminating the last traces of oxide from the molybdenum specimens so that completely consistent values of the thermionic emission were never obtained. The results of the present investigation indicate that it is possible to eliminate residual gas effects only by a very prolonged treatment and that the work function for the more thoroughly cleaned metal is slightly lower (4.15 volts) than the values obtained by the above observers.

Martin[3] studied the photoelectric properties of Mo during outgassing treatment and found that after about 150 hours of heating at temperatures up to 1700°K the work function reached an apparently stable value of about 3.2 volts, while the value of the thermionic work function for the same specimen was 3.48 volts. While these two values are in fair agreement, the large discrepancy between these values and those obtained by Dushman and Zwikker led Dushman[4] to suggest that the heat treatment had not been car-

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[1] Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25,** 338 (1925).
[2] C. Zwikker, Proc. Amst. Acad. Sci. **29,** 792 (1926).
[3] M. J. Martin, Phys. Rev. **33,** 991 (1929).
[4] S. Dushman, Rev. Mod. Phys. **2,** 395 (1930).

ried out in this case at high enough temperatures to eliminate all impurities. In any case it appeared worth while to examine again the photoelectric and thermionic emission from Mo after a very prolonged treatment at the highest possible temperatures, to see whether a more gas-free condition could be reached than had hitherto been obtained.

Apparatus and Procedure

With the few exceptions mentioned below the experimental technique was the same as that used by the authors in a recently reported study of palladium[5] and need not be described again. The specimens, in the form of ribbons, were cut from a piece of very pure Mo foil about 0.01 mm thick. Temperatures were obtained from optical pyrometer readings, using the temperature scale determined by Worthing, and also from the resistance of the filament using Worthing's data.[6]

After a thorough baking of the tube, the outgassing of the filament was begun at a temperature in the neighborhood of 1750°K, since it was found that prolonged heating at higher temperatures during the early stages caused a failure of the filament before complete outgassing was attained. As the outgassing progressed the specimen was heated for long periods at 1900°K and for shorter periods up to 2100°K, at which temperature it soon burned out. It was found that if the tube was left sealed to the pumps it never reached a condition where consistent values of the photoelectric and thermionic emission could be obtained, even though the treatment was continued for 1000 hours. By sealing the tube from the pumps and allowing the residual gas to clean up by the getter action,[7] it was found that a stable and apparently gas-free condition could be reached which was not changed by further heating. One specimen withstood continuous heating for about six weeks after being sealed from the pumps, during most of which time there was no change in the work function. Most of the data given below were obtained from this specimen, though other specimens which burned out more quickly showed a similar behavior.

The single-prism monochromator used in previous investigations was replaced by a Van Cittert double quartz-prism monochromator to obtain more nearly pure monochromatic light. The relative intensities of the spectral lines of the mercury arc source were measured with a Burt vacuum thermopile connected to a Zernicke galvanometer. A sodium-in-quartz photoelectric cell connected to an FP-54 tube amplifier[8] was used for checking the intensities from time to time, and for determining the intensities of lines too weak to be measured with the thermopile. As before, the photoelectric currents were measured with a sensitive Cambridge Compton electrometer. The thermionic currents at the lower temperatures were measured with a Type R galvanom-

[5] L. A. DuBridge and W. W. Roehr, Phys. Rev. **39,** 99 (1932).

[6] A. G. Worthing, Phys. Rev. **28,** 190 (1926).

[7] Aluminum was found to be a more satisfactory getter than magnesium since it did not distil throughout the tube during the baking process.

[8] See L. A. DuBridge, Phys. Rev. **37,** 392 (1931).

eter and at the high temperatures with a potentiometer and standard 1-ohm resistance.

Results

1. Photoelectric emission

During the early stages of the outgassing process both the photoelectric and thermionic readings showed great irregularities and large and irregular changes with temperature, typical of a metal which has not been freed of gas. The threshold shifted at first toward the red reaching a value in the neighborhood of 3500A (3.5 volts). As the heating progressed the limit shifted again to the violet, to a minimum value near 2800A (4.4 volts), and after still longer treatment, with the tube sealed from the pumps, the threshold finally reached a stable value of 2980A (4.15 volts) as determined by the Fowler curves. This value could not be changed by further treatment at the highest temperatures.

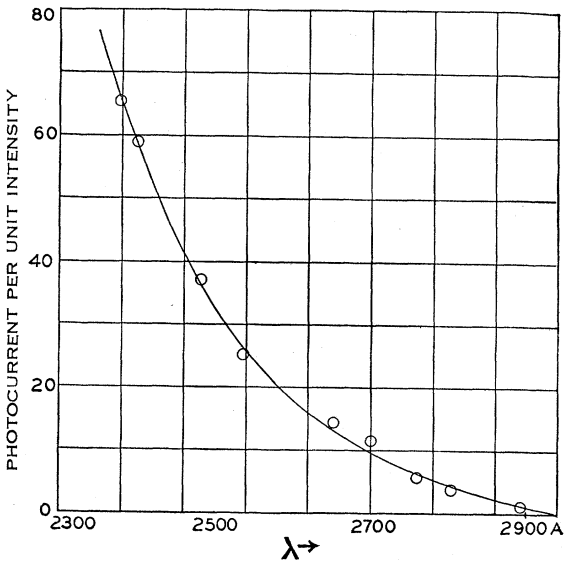

Fig. 1. Photoelectric threshold curve for outgassed Mo.

The ordinary threshold curve, taken at room temperature, for a specimen which had been outgassed for 1600 hours at temperatures up to 2100°K is shown in Fig. 1. This curve had remained practically unchanged by the last 800 hours of treatment, the tube having been sealed from the pumps after the first 400 hours. The pressure in the tube after sealing off, as read by an ionization gauge, was below 10^{-7} mm and showed a gradual decrease with time. During the last 800 hours of treatment both the photoelectric and thermionic measurements were entirely consistent and reproducible from day to day, indicating that the specimen was in a very gas-free state.

The Fowler curve for this specimen is shown in Fig. 2. The readings plotted were taken at room temperature (303°K) and at 940°K, the latter being

the temperature at which the thermionic currents just became appreciable. From the amount by which the observed points had to be shifted horizontally to fit the theoretical curve the following values of the threshold and work function were deduced:[9]

$$\text{for } T = 303°,\ \lambda_0 = 2992\text{A},\ \phi = 4.14 \text{ volts};$$
$$\text{for } T = 940°,\ \lambda_0 = 2983\text{A},\ \phi = 4.16 \text{ volts}.$$

These values are in excellent agreement, and their average, 4.15 volts, may therefore be taken as the best value of the photoelectric work function for clean molybdenum. There is a possible error of the order of 0.5 percent involved in fitting the Fowler curves.

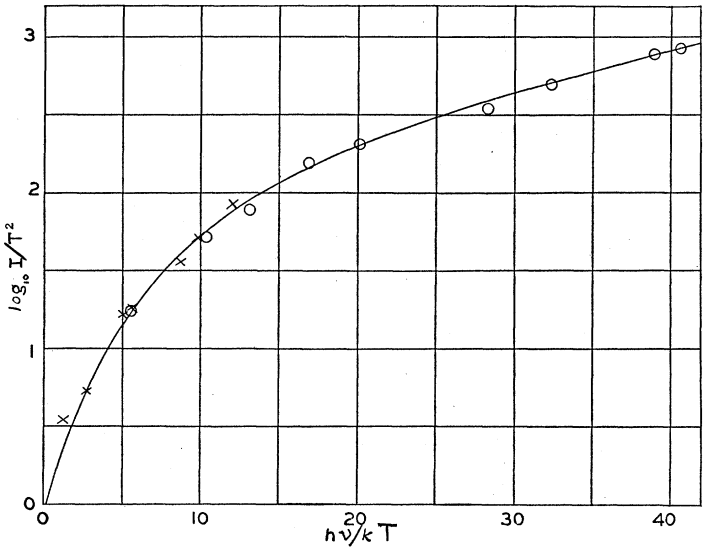

Fig. 2. Analysis of photoelectric data for Mo by Fowler's method. Circles, $T=303°$K; crosses, $T=940°$K.

The agreement between the observed points and the theoretical curve shown in Fig. 2 is within the limits of error involved in measuring the currents and the relative intensities of the spectral lines. These data for Mo thus constitute a further experimental verification of Fowler's theory.

2. Thermionic emission

During the early stages of outgassing the thermionic data did not at all fit the Richardson equation. When the observations were plotted in the usual form of log I/T^2 against $1/T$, a curve, usually concave toward the origin, instead of a straight line resulted. Hence no definite work function could be deduced. In general, however, the thermionic data ran parallel to the photoelectric data during the outgassing process. After equilibrium was reached

[9] See R. H. Fowler, Phys. Rev. **38**, 45 (1931); L. A. DuBridge, Phys. Rev. **39**, 103 (1932); also reference 5. A discussion of Fowler's theory will also be found in Hughes and DuBridge, *Photoelectric Phenomena* pp. 241–248 (McGraw-Hill, 1932).

the thermionic emission showed a very consistent and reproducible behavior, again showing evidence that the specimen was quite gas-free. In Fig. 3 is shown a thermionic curve, taken after 1600 hours of treatment on the same specimen for which the photoelectric data of Figs. 1 and 2 were obtained. The value of the work function computed from the slope of this curve is 4.15 volts ($b=48{,}100$). Three other curves taken for this specimen at intervals over a period of about six weeks yielded the following values: 4.15, 4.17 and 4.14 volts. The average value is thus close to 4.15 volts and is in excellent agreement with the photoelectric value.

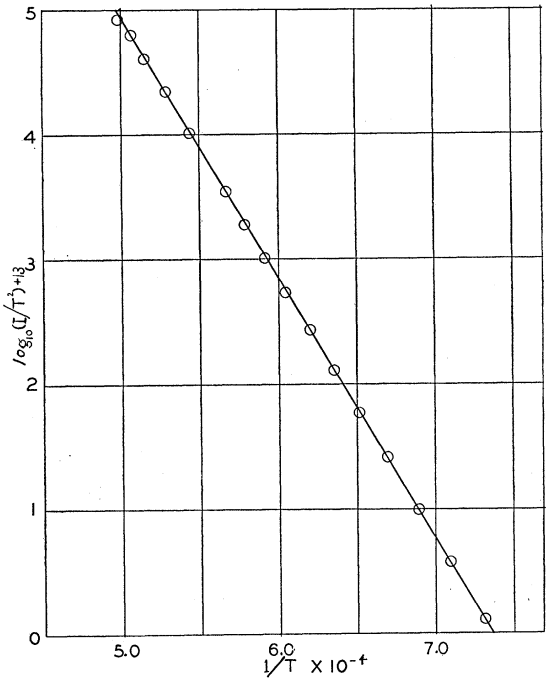

Fig. 3. Thermionic data for outgassed Mo. $\phi=4.15$ volts.

The average value of the thermionic constant A calculated from the data plotted in Fig. 3 is approximately 55 amp./cm^2 deg.^{2}, in good agreement with the theoretical value of 60.

Discussion

The results of these experiments seem to confirm the suggestion that the low value of the work function for Mo reported by Martin is to be attributed to the fact that in his experiments the heat treatment was not carried out for a sufficiently long time or at sufficiently high temperatures to eliminate all impurities. Values of the same order as those reported by Martin were observed in the present investigation only during the early stages of heating. More prolonged heating at high temperatures always caused an increase in the work function. Our failure to check exactly the values of 4.38 and 4.44

volts reported by Zwikker and Dushman was somewhat more puzzling. Apparently the value 4.4 volts is characteristic of a specimen which has been given a reasonably thorough outgassing treatment, but a very prolonged treatment results in the slightly lower value of 4.15 volts. Many of our specimens did show work functions of the order of 4.4 volts during the treatment, but those which withstood the longer heating gave the lower value, which we believe to be characteristic of a very gas-free state. It is possible, of course, that the prolonged heating also causes a microscopic recrystallization of the surface which results in a slight reduction in the work function.