THE PHOTOELECTRIC AND THERMIONIC PROPERTIES OF MOLYBDENUM

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Abstract

The variation of the photoelectric sensitivity of a molybdenum surface during prolonged heat treatment has been studied over a period of 300 hours of intense heating. Thin ribbons of molybdenum were heated to a temperature of 1325°C in a high vacuum and the photocurrents produced by the light from a quartz mercury arc were measured with a quadrant electrometer. The photoelectric sensitivity was found to increase as the heating progressed, finally reaching a limiting value. The increase in sensitivity was accompanied by a shift in the wave-length limit from approximately 2600 A. U. to approximately 3800 A. U.

The photoelectric work function of molybdenum was determined from the characteristic wave-length limit of the heat treated surface after a condition of stability had been attained. The value of the work function so determined was $3.22\pm.16$ volts.

The thermionic work function of molybdenum was determined for the same specimens. The thermionic emission as a function of temperature was plotted logarithmically according to Richardson's equation. The value of the thermionic work function determined from the slopes of these curves was $3.48\pm.07$ volts. The photoelectric and thermionic work functions were thus found to agree within 0.26 volts.

The variation of photoelectric sensitivity of molybdenum with temperature was observed. The sensitivity was found to increase with temperature, the variation amounting to approximately 30 percent between room temperature and 1000°C.

Introduction

THIS paper is a brief report of one of a number of experiments now under way in this laboratory upon the general problem of the photoelectric and thermionic characteristics of metals which have been subjected to rigorous heat treatment under extreme vacuum conditions. DuBridge[1] has reported a thorough investigation of the photoelectric and thermionic properties of platinum and Cardwell[2] has recently published an account of the work upon iron. This report deals with the following investigations:

(1) The variation of the photoelectric sensitivity of a molybdenum surface while undergoing prolonged heat treatment.

(2) The determination of the photoelectric work function of the metal from the characteristic long wave-length limit of the heat treated surface.

(3) The determination of the thermionic work function from the slope of the logarithmic graph of Richardson's thermionic equation.

(4) The variation of the photoelectric sensitivity with the temperature of the specimen.

Apparatus

The apparatus was essentially the same as that used by DuBridge[1] and Cardwell.[2] The specimens were prepared from samples of molybdenum

[1] DuBridge, Proc. Nat. Acad. Sci. **12**, 162 (1926; Phys. Rev. **29**, 451 (1927).

[2] Cardwell, Proc. Nat. Acad. Sci. **14**, 439 (1928).

obtained from two different sources.* They were rolled into ribbons 13 cm long by 0.5 cm wide by 0.03 mm thick. After cleaning with alcohol the ribbon was suspended in the form of a loop from two tungsten leads inside a Pyrex tube, thus forming a filament which could be heated to any desired temperature by an electric current. Surrounding the filament was a nickel cylinder in which holes were provided for illuminating the specimen and for viewing with the pyrometer, and which served as a collecting electrode. This nickel cylinder was carefully washed alternately in nitric acid and warm water and then baked in a separate vacuum system before being introduced into the tube. The specimen was illuminated through a quartz window which was attached to the tube by means of a graded quartz-Pyrex joint. The source of ultra-violet light was a Cooper-Hewitt quartz-mercury arc of the vertical type which was enclosed in an asbestos housing. It was operated at a current of 3.5 amperes with 65 volts drop in potential across the arc. This gave a very intense illumination and reduced the maximum variation of light intensity to approximately 3 per cent. Light was focussed upon the specimen by means of a crystalline quartz lens. Pressures in the earlier stages of the process were measured with a McLeod gauge and in later stages with an ionization gauge of the type described by Dushman and Found.[3] The photoelectric currents were measured with a Compton electrometer shunted by a resistance of 10^9 ohms, thus permitting the use of the steady deflection method. In observing the photo-currents produced by the full radiation of the arc a sensitivity of 700 mm per volt was used, while in making determinations of the wave-length limit a sensitivity of 20,000 to 60,000 mm per volt was used. Temperatures in the thermionic work were measured with an optical pyrometer of the disappearing filament type, which had been previously calibrated by observations upon the gold point and the palladium point, intermediate points being determined by sectoring down from the palladium point. Black body temperatures were corrected for the emissivity of molybdenum according to the data of Mendenhall and Forsythe.[4]

Procedure

The entire tube and the ionization gauge were encased in electric furnaces and baked at a temperature of 550°C for over 200 hours. Towards the end of this baking interval the pressure was 10^{-6} mm of Hg with the furnaces hot. Immediately after baking the long wave-length limit and the initial sensitivity of the specimen were observed. The specimen was then heated by a current continuously day and night, frequent observations of the sensitivity being taken as the out-gassing progressed. Finally a stage was reached at which further heat treatment did not change the sensitivity. Observations were then made of the long wave-length limit from which the photoelectric work function was computed. Curves of the thermionic

* Fansteel Products Company and the Elkon Company.

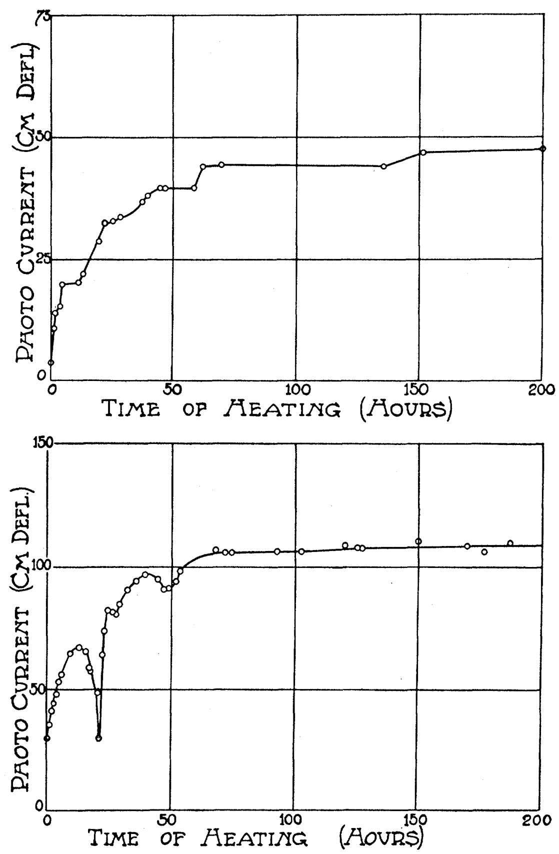
[3] Dushman and Found, Phys. Rev. **23,** 734 (1924).

[4] Mendenhall and Forsythe, Astrophys. Jour. **37,** 380 (1913).

emission were plotted from which the thermionic work function was computed. The variation of photoelectric sensitivity of the out-gassed metal with change of temperature was investigated. A description of the results of these investigations follows.

Results

(1) *The variation of the photoelectric sensitivity with prolonged heat treatment.* Figures 1 and 2 show the results of heat treatment upon two different specimens. Both curves are seen to be of the same general form and bear a strong similarity to the latter part of the curve that Cardwell[2] gives for



Figs. 1 and 2. Effect of heat treatment on two samples.

iron. The intervals between the observations on the curve of Figure 2 were so short as to indicate variations that would not show up on Figure 1. DuBridge's curve for platinum, although decreasing with time of heating, shows the same sort of variations. He has pointed out the fact that these variations are due to irregularities of pressure that are certain to occur in the initial stages of out-gassing. The curves for molybdenum indicate that the increase in sensitivity takes place in steps, which conforms with Cardwell's[2] findings for iron, and his hypothesis that these steps indicate the effect of additional lines of the spectrum becoming active seems reasonable.

The heating of the molybdenum specimens was begun at a temperature of 850°C and gradually increased to 1325°C at the end of 20 hours. Some of the irregularities of the curve of Figure 2 are due to increases of temperature. The marked decrease in photocurrent at 21 hours (Figure 2) occurred when the temperature was raised and was accompanied by a very great increase of pressure. The temporary decrease in photocurrent was obviously due to the evolution of a large amount of gas, and as the pressure was speedily reduced the photocurrent recovered quickly. At the end of 290 hours (in the case of the specimen represented by Figure 2) which was long after stability of pressure and constancy of photoelectric sensitivity had been reached, the temperature was raised to 1500°C. No appreciable change in sensitivity was observed and the long wave-length limit was the same as it had been found to be previous to this last increase of temperature. This was regarded as evidence that a thorough state of out-gassing had been attained.

At the beginning of this period of heat treatment the pressure was of the order of 10^{-7} mm of Hg as indicated by the ionization gauge. During the first few minutes of heating the pressure went up to about 10^{-5} mm of Hg but was rapidly reduced by subsequent heating. As the out-gassing progressed the pressure with the specimen hot approached the value of the pressure with the specimen cold. The equality of the pressure hot and the pressure cold was adopted as one criterion of complete out-gassing. Final observations were always made at pressures of from 1.0×10^{-8} to 2.0×10^{-8} mm of Hg.

During the out-gassing process "rest tests" were taken at intervals. An observation of the sensitivity was taken as quickly as possible after cutting off the heating current (approximately 30 seconds) and the specimen was allowed to stand without heating while observations of the change of sensitivity with time were taken. It was found that in the earlier stages the sensitivity changed rapidly with time, in some cases falling to half its value in 15 minutes. In the later stages the sensitivity was more stable and fell off much more slowly. Molybdenum was found to be very sensitive to small amounts of gas and a condition was never reached in which several hours standing did not produce a decrease in the sensitivity even though no change could be noted in the first hour or so. In all cases, however, one or two minutes of heating were sufficient to return the specimen to its former sensitivity at the beginning of the rest interval, which indicates that the change in sensitivity is due to a slight surface layer of gas which is readily removed. Figure 3 shows a series of these "rest tests" covering an interval of 15 minutes taken at various stages in the out-gassing process. In this graph the ordinates are merely electrometer deflections. The curves do not therefore appear in sequence, due to changes in sensitivity of the electrometer. The slopes of the curves only are of significance.

(2) *The determination of the photoelectric work function from the characteristic long wave-length limit.* In this work the method employed in determining the long wave-length limit was that used by DuBridge[1] and Cardwell[2] in which filters were used to cut out certain portions of the spectrum of the irradiating light. The filters consisted of organic solutions prepared according to the specifications given by Dahm,[5] and of certain glass screens obtained from Corning Glass Company. Immediately after a filter was used its transmission was photographed with a quartz prism spectograph. The long wave-length limit of the specimen taken after the baking but before heating the specimen itself was found to lie between 2536 A.U. and 2652 A.U. Observations upon the wave-length limit were not made in the earlier stages of the out-gassing due to the fact that the characteristics of the specimen would undergo a change in the time required for a set of observations. After the specimen had reached a stable condition, frequent determinations

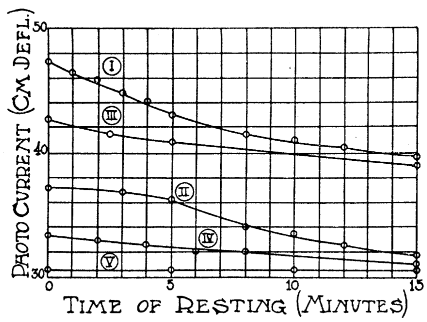


Fig. 3. Decrease of photoelectric sensitivity with time.
Curve I, taken after 4 hours total heating;
Curve II, taken after 40 hours total heating;
Curve III, taken after 112 hours total heating;
Curve IV, taken after 184 hours total heating;
Curve V, taken after 300 hours total heating.

of the long wave-length limit were made. The long wave-length limit of thoroughly out-gassed molybdenum was found to lie between 3650 A.U. and 4047 A.U. Upon interposing a screen which transmitted the 3650 line of mercury strongly, a small but decided photoeffect was always observed. When a screen was used that transmitted the 3650 line very weakly leaving the lines above 3650 with approximately the full intensity, the effect was very small, so small that it was at times doubtful whether an effect was present. When a screen was used that cut out the 3650 line completely no effect was observed. It is probable then that the 3650 line is the last active line in the mercury spectrum and it is undoubtedly a very close approximation to the long wave-length limit of "gas-free" molybdenum. It is at any rate certain that the next mercury line that could be isolated with the screens used, 4047, is not active. The work function corresponding to a wave-length limit of 3650 A.U. is 3.38 volts while a wave-length limit of

[5] Dahm, Jour. Opt. Soc. **15**, 266 (1927).

4047 A.U. yields a value for the work function of 3.05 volts. The average value of the photoelectric work function so determined may therefore be given as $3.22\pm.16$ volts. These results were repeated daily for more than a week with no conflicting results. Independent observations were made by two observers.

(3) *The determination of the thermionic work function from the slope of the logarithmic graph of Richardson's equation.* In a few cases other observers have compared the value of the photoelectric work function with the value of the thermionic work function obtained from the same specimen. DuBridge[6] has compared the photoelectric and thermionic work functions of platinum and finds them to agree within the limits of experimental error. Warner[7] reports a close agreement between the two work functions of tungsten. In the case of molybdenum, thermionic currents between the temperatures of 1300°K and 1600°K were measured with a Leeds and Northrup galvanometer having a sensitivity of 2.2×10^{-10} amperes per millimeter at a scale distance of approximately two meters. Figure 4 is a logarithmic graph of Richardson's equation from data taken after the specimen had been heated a total of 330 hours. The slope of this curve yields a value for the constant b in Richardson's equation of 39,600. The corresponding value of the thermionic work function is 3.48 volts. The maximum error introduced into the result due to inaccuracy of temperature determination was estimated at 2 percent. The value of the thermionic work function determined from these experiments may then be given as $3.48\times.07$ volts. The photoelectric and thermionic work functions of molybdenum are thus found to agree within 0.26 volts which is within the limits of error of this experiment, inasmuch as the apparatus was not expressly designed for thermionic measurements.

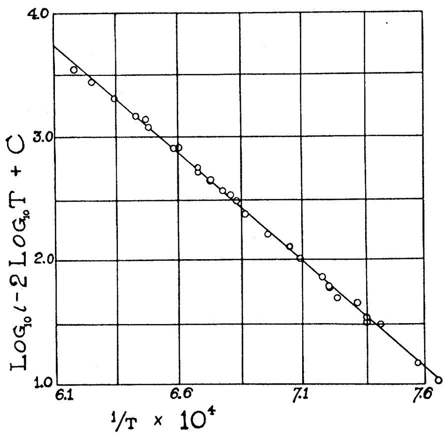


Fig. 4. Logarithmic graph of Richardson's equation from data taken after specimen had been heated 330 hours.

(4) *The variation of the photoelectric sensitivity with temperature.* Very few experimenters have investigated a temperature variation of the photoelectric effect over a wide range of temperature. DuBridge[1] reports for platinum an increase in the photocurrent with temperature up to 1100°C. Cardwell[2] finds that iron shows a decrease up to the temperature at which the iron undergoes a change in crystal structure and then begins to increase. The present work with molybdenum indicates a steady decrease in photocurrent with temperature which amounts to approximately 30 percent in going from room temperature to 1000°C. Figure 5 is a curve in which the

[6] DuBridge, Phys. Rev. **31**, 236 (1928).
[7] Warner, Proc. Nat. Acad. Sci. **13**, 56 (1927).

total photocurrent is plotted as a function of the heating current. The circles with dots in the centers indicate observations taken with increasing temperature and the circles with crosses in the centers represent points taken with decreasing temperature. The temperatures in this interval were below the range of the optical pyrometer. It was not possible to take observations of the photocurrent at temperatures above 1000°C owing to the fact that the enormous thermionic currents completely masked the photoeffect. No

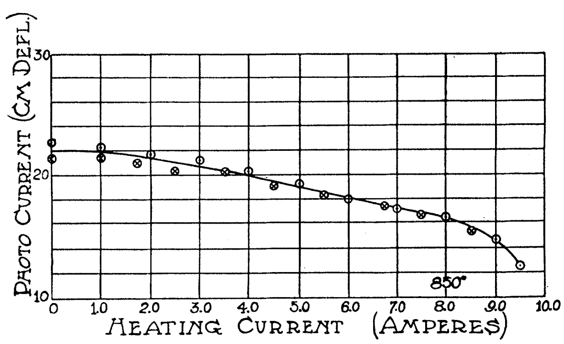


Fig. 5. Total photo-current as a function of heating current.

evidence was obtained in these experiments to determine whether or not the variation in photoelectric sensitivity with temperature is actually due to a change in the work function. The thermionic work function, which is an average value between 1300°K and 1600°K, was higher than the value obtained from the wave-length limit at room temperature. All that can be inferred from these data is that the temperature variation is in the proper sense to be caused by such a change in the work function.

Summary

Specimens of molybdenum subjected to long periods of heat treatment in a high vacuum showed an increase in photoelectric sensitivity as the heat treatment progressed, accompanied by a shift in the long wave-length limit from approximately 2600 A.U. to approximately 3800 A.U. The value of the photoelectric work function was found to be $3.22 \pm .16$ volts. The value of the thermionic work function between the temperatures of 1300°K and 1600°K was found to be $3.48 \pm .07$ volts. The photoelectric sensitivity of molybdenum showed a decrease with rise in temperature in the range from 0°C to 1000°C.

In conclusion the author desires to express his sincere appreciation to Professor C. E. Mendenhall under whose direction the work was done, to Professor R. C. Williamson and Professor H. B. Wahlin for many helpful suggestions, and to Mr. Howard E. Nelsen for his valuable assistance in the final part of the work.

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