THE PHOTOELECTRIC PROPERTIES OF SILVER

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Abstract

Silver is carefully outgassed and its photoelectric properties studied during outgassing and after stable conditions are reached. An outgassing curve is plotted for the 1200 hours of heat treatment given the silver before final readings were taken. For thoroughly outgassed silver curves are plotted showing photoemission as a function of temperature for fixed wave-lengths of incident light. These curves show that for wave-lengths near the long wave limit there is a marked increase in emission with temperature, for wave-lengths farther away there is no change with temperature, and for wave-lengths still farther away there is a slight decrease in emission with increased temperature. Curves for emission per unit of incident light intensity as a function of wave-length show that the long wave limit at 600°C is 2700±20A while at room temperature it is 2610±30A.

The study of the photoelectric properties of silver was undertaken as a part of the general program of this laboratory which includes extensive study of the properties of thoroughly outgassed metals. In this laboratory the photoelectric properties of iron, cobalt, and tantalum have been studied by Cardwell,[1] molybdenum by Martin,[2] rhodium by Dixon,[3] and gold by Morris.[4] Previous work of DuBridge,[5] Warner,[6] Kazda,[7] and Goetz[8] dealt with platinum, tungsten, mercury, and tin respectively.

The purpose of this work is to study the variation of the photoelectric sensitivity and of the long wave limit of silver during prolonged outgassing, to determine the ultimate long wave limit when outgassing ceases and stable conditions are reached, and finally to study the effect of temperature on the photoelectric characteristics. The reflecting power for various wave-lengths of incident light is also studied as a function of temperature to determine its possible effect on the observed photo-emission.

The apparatus was similar to that used by Cardwell[1] and consisted essentially of a strip of silver approximately 0.025 mm thick and 3 mm wide suspended from tungsten seals in the form of a loop inside a molybdenum receiving cylinder, the whole being enclosed in a Pyrex tube having a quartz window

[1] Cardwell, Proc. Nat. Acad. Sci. **14,** 439–445 (1928); **15,** 544–551 (1929); work on tantalum not yet published.
[2] Martin, Phys. Rev. **33,** 991–997 (1929).
[3] Dixon, Phys. Rev. **37,** 60 (1931).
[4] Morris, Phys. Rev. **37,** 1263 (1931). Present Issue of Phys. Rev.
[5] DuBridge, Phys. Rev. **29,** 451 (1927).
[6] Warner, Proc. Nat. Acad. Sci. **13,** 56 (1927).
[7] Kazda, Phys. Rev. **26,** 643 (1925).
[8] Goetz, Phys. Rev. **33,** 373 (1929).

sealed on with a graded quartz to Pyrex seal. The tube was connected through two liquid air traps, and a mercury "cut-off" to a water-cooled mercury diffusion pump backed by a Cenco Hyvac fore-pump. The vacuum system included a McLeod gauge and an ionization gauge of the Dushman and Found[9] type for measuring pressures. Wax or grease vapor was guarded against by having the stopcocks and the one wax joint on the opposite side of the liquid air traps from the research tube.

The silver for this study was obtained from the Adam Hilger Co. of London and was 99.99 percent pure containing minute traces of copper, lead, manganese, and calcium.

The photoelectric currents were produced by radiation from a quartz mercury arc and were measured by a Compton quadrant electrometer. Resistances ranging from 10^7 to 5×10^{11} ohms (depending on size of currents to be measured) were shunted across the electrometer quadrants so that the "steady deflection" method could be used.

During the outgassing the undispersed radiation from the arc was used, but for the $f(\lambda)$ curves, and for the temperature curves on a fixed wavelength, a Bausch and Lomb single monochromator was placed between the arc and the specimen. A vacuum thermopile, whose currents were measured by a Kipp ZC low resistance galvanometer (sensitivity 6×10^{-10} amps. per mm at a meter) with a two meter scale distance, gave the relative intensities of the various incident wave-lengths. The thermopile (when carefully evacuated) and its galvanometer system showed very good steadiness which made the intensity readings reproduce readily. However, even with these conditions the fainter lines gave deflections so small that the natural errors of reading made the relative errors large in these cases. A study is being made at present of means of increasing these deflections so that greater precision can be attained. Only points which are quite dependable have been plotted in the accompanying curves.

A careful study of the monochromator was made in the spectral region near the long wave limit with results similar to those shown by Goetz,[8] but with perhaps a little less purity than he shows. The combination of 0.2 mm slit-widths for both entrance and exit slits was found to be as narrow as was consistent with the accuracy desired from the thermopile readings. The photocurrent and intensity measurements were taken together in rapid succession so that the effect of all arc fluctuations was eliminated. There is much left to be desired in obtaining really monochromatic illumination of sufficient intensity for photoelectric work. A double monochromator is to be substituted for the single monochromator used here as a partial answer to this problem. The impurity of the incident light was not sufficient to cause appreciable error in the points plotted on the $f(\lambda)$ curves since they are for lines sufficiently intense so that the error is small. However this lack of purity did eliminate from use certain faint lines near stronger ones so that the number of points available for a given $f(\lambda)$ curve was limited.

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

The temperature of the filament was determined from its resistance. The resistance of the filament was measured by measuring the *IR* drop across it, and then the *IR* drop across a tenth-ohm oil-cooled standard resistance, using a Wolff potentiometer for potential measurements. The data for resistance as a function of temperature were taken from a paper by Northrup.[10]

During the initial stages of outgassing the pressures varied from 10^{-7} to 10^{-6} mm of Hg but in the latter part, when stable conditions had been reached and liquid air was placed on the second trap, the pressures varied only from 1 to 3×10^{-8} mm of Hg. At this stage no increase in pressure could be detected when the filament was heated.

Outgassing Procedure

The receiving cylinder of the photoelectric tube was carefully outgassed before placing it in the tube. It was heated at white heat for six days in an auxiliary vacuum system and then transfered to the research tube. The silver filament was immediately sealed in place and the whole tube sealed to the vacuum system. The cylinder was exposed to the air less than four hours. Immediately on obtaining good vacuum conditions the long wave limit of the silver was obtained and heating started by a conduction current through the filament. The heating was started at a low temperature and increased very gradually since metals evaporate much more rapidly when gas-filled.[11] Since silver has a rather low melting point it had to be heated at a low temperature at all times and treated rather carefully to preserve it during the long outgassing required.

Results

Figure 1 shows the outgassing curve. Photoelectric emission due to total arc radiation is plotted as ordinate against time of heating as abscissa. The temperatures written in along the curve show where the heating current was increased thus putting the filament at the temperature indicated. Between the temperatures written in it was maintained at the lower temperature of the interval. The general shape of this curve is similar to that for gold, cobalt, rhodium, and tantalum showing an increase in emission during the initial stages of outgassing and a subsequent decrease finally reaching a fixed value which is not changed with continued heating. It is interesting to note that the high maximum was passed over at 325°C and that increase in temperature did not cause the emission again to rise but to decrease to its final stable value.

After 760 hours of heating of the filament only, the whole tube was baked at about 500°C for 6 days at the end of which time the pressure was less than 10^{-7} mm of Hg with the furnaces at 500°C. The filament was maintained, during baking, at 100°C or more above the rest of the tube to prevent metallic vapors from condensing on it. After removing the furnaces the photo-emission was a little below its value before baking, but at the end of about seventy-five

[10] Northrup, Jour. Frank. Inst. **178,** 85 (1914).

[11] Cardwell, Proc. Nat. Acad. Sci. **15,** 544–555 (1929); Berlinger, Wied. Ann. **33,** 289 (1888).

hours of heating at 600°C it had recovered. Two hundred additional hours of heating at this temperature did not change the emission showing that stable conditions had been reached. This made a total heating time of about 1200 hours before final readings were taken. The filament was flashed many times at over 850°C for short intervals to determine whether higher temperature would change its ultimate characteristics, and no change was observed. The silver evaporated rapidly at these higher temperatures.

The long wave limit of the silver specimen was initially in the neighborhood of 2000A and shifted to the longer waves during the first part of the outgassing reaching a value above 3300A at 405 hours where the emission was a maximum. It then shifted to the shorter waves as the emission decreased reaching a final value in the vicinity of 2700A when stable conditions

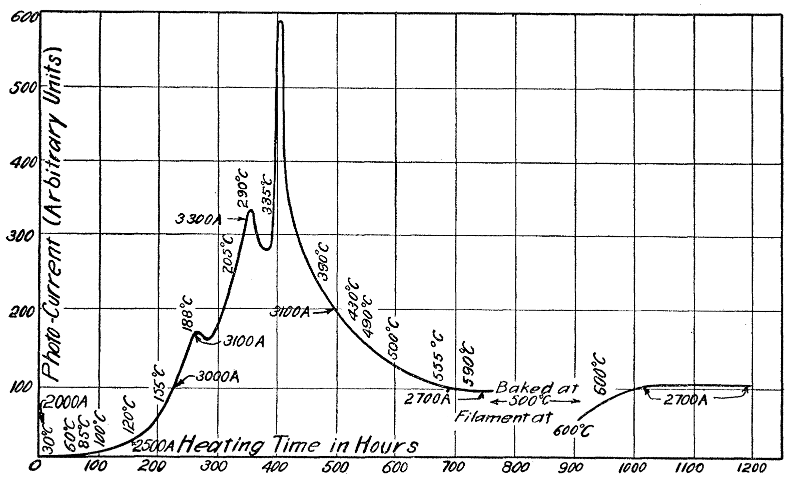

Fig. 1. Outgassing curve using full-arc radiation.

were reached. The long wave limits for various times have been indicated on the curve. This trend of long wave limits is in general agreement with what one would expect from the shape of the curve in Fig. 1.

At various times during the heat treatment, "fatigue" curves were taken by shutting off the heating current and reading the photo-emission as a function of the time of standing. During the initial stages this "fatiguing" caused a decrease (never large) of photo-emission but when stable conditions were reached no fatigue could be observed during more than an hour of standing. It is interesting to note that the fatigue, when it appeared, was always a decrease in photo-current even though the continued outgassing meant a shift to smaller photo-currents so that one would expect returning gas to increase the sensitivity. This phenomenon has not been explained satisfactorily, but has been observed on other metals.

Readings from this point on were taken using the Bausch and Lomb monochromator previously discussed.

TEMPERATURE CURVES

Figure 2A shows temperature curves for various wave-lengths of incident light while Fig. 3 shows the $f(\lambda)$ curve for 600°C and the one for room temperature. It is obvious that either set of curves could be plotted from the other but both sets were taken independently and repeated many times.

In Fig. 2A the photo-emission is plotted as a function of the heating current through the filament (hence of temperature) for various wave-lengths of incident radiation. The absolute values of the emission represented by these curves cannot be compared. The 2537A curve was plotted and then the curves for other wave-lengths (except 2652A) translated so that they agree with 2537A at room temperature. Observed points have been plotted for 2537A

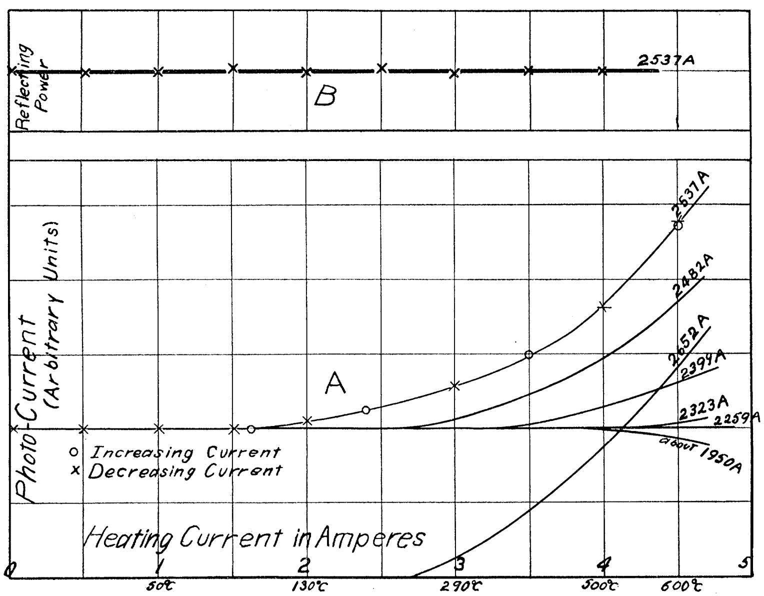

Fig. 2. A. Temperature curves for fixed wave-lengths of incident light. B. Reflecting power as a function of temperature for 2537A incident light.

but to save confusion the points on the other curves have not been plotted. Observations were taken for both increasing and decreasing currents and were reproduced very nicely as indicated by the points plotted. 2652A is not effective below about 2.7 amperes heating current hence it has been plotted to a different scale. The corresponding temperatures have been written in on the heating current scale.

These curves show an effect which was noted first in gold by Morris[4] and later in tantalum by Cardwell,[1] namely, that for wave-lengths in the neighborhood of the long wave limit there is an increase in photo-emission with temperature, for shorter waves there is no effect produced by temperature, and for still shorter waves there is a decrease in photo-emission with increasing temperature. This effect is shown best by tantalum, whereas for silver the decrease in emission with increased temperature comes at wave-lengths so short that air and quartz absorb some of the incident light and thus make the incident intensity very small. The decrease is definite but the slits of the monochromator had to be widened until there is considerable doubt as to the wave-length at which the decrease began to appear.

In Fig. 2B is plotted a curve showing that the reflecting power of silver for 2537A is independent of temperature up to 600°C. Identical results were obtained for 2482A, 2323A, 2259A, and 2200A. These curves were taken by reversing the field between the silver filament and the molybdenum receiving cylinder so that the filament was charged positively with respect to the cylinder. The incident radiation had been carefully focused on the silver filament. Thus the light which was reflected from the filament and became in this

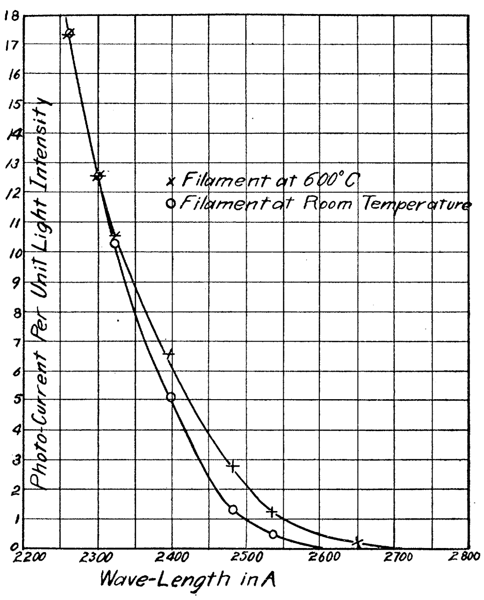

Fig. 3. $f(\lambda)$ curves.

way incident on the cylinder caused photoelectrons to be emitted. These electrons were collected on the filament and measured. The reverse photo-current would thus be proportional to the reflecting power of the filament, and the behavior of this current with respect to temperature would measure any change in reflecting power which might occur with change of temperature. Since these curves indicate no change in reflecting power, the change in photoemission with temperature cannot be explained on the basis of changing reflecting power.

The curves in Fig. 3 show the long wave limit at about 600°C to be at 2700 ± 20A while at room temperature the long wave limit is 2610 ± 30A. The curves for intermediate temperatures lie in between these two but for temperatures of 200°C or less the curves fall on top of the room temperature curve as nearly as can be determined. This is to be expected from the shape of the curves in Fig. 2. From the Einstein photoelectric equation these values of the long wave limit make the work function at 600°C equal to 4.56 ± 0.06 volts and for room temperature 4.73 ± 0.07 volts.

Whereas 2652A is the last point on the 600°C curve, it was determined, with an electrometer sensitivity of 8000 mm per volt on rate of charge, that 2699A was effective but that no line above showed an effect.

Conclusions

There is a definite shift in long wave limit of thoroughly outgassed silver with temperature. The shift amounts to about 90A between room temperature and 600°C. The temperature curves in Fig. 2 indicate that for wavelengths near the long wave limit there is a marked increase in sensitivity with increase in temperature, that wave-lengths farther away show no change with temperature, and that wave-lengths still farther away show a decrease in emission with increase in temperature.

The work function of thoroughly outgassed silver is shown to be 4.56 ± 0.06 volts at 600°C and 4.73 ± 0.07 volts at room temperature. Work is being carried forward to make more accurate determinations of the $f(\lambda)$ curves with more nearly monochromatic illumination.

In conclusion, the writer wishes to acknowledge his indebtedness to Mr. W. L. Hole, whose help was invaluable during this work, and to Professor C. E. Mendenhall, under whose direction this work was carried out.