THE PHOTOELECTRIC AND THERMIONIC PROPERTIES OF PLATINUM COATED GLASS FILAMENTS

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Abstract

The photoelectric and thermionic properties of platinum sputtered glass filaments are discussed, special attention being given to the effect of temperature, and to electrolysis of potassium through the glass to or from the sputtered coating. When electrolysis is away from the surface, the photoelectric threshold is independent of the temperature up to 450° and is close to 2720A. With electrolysis toward the surface the threshold remains at 2720A up to 260°C above which it shifts toward the red with rising temperature, reaching a maximum value of about 4300A at 410°C. Electrolysis produces identical effects on the photoelectric and thermionic emissivity for electrons; the effect on positive ion emission is similar, also, except that a peculiar maximum in the emissivity occurs for a specific electrolysis potential. Ultraviolet radiation has no effect on the thermionic emission of electrons or positive ions from this type of filament.

IN A recent article from this Laboratory by F. G. Cottrell, C. H. Kunsman and R. A. Nelson[1] a new method was presented for the production and control of positive ions. The present paper is a continuation of this study, and deals with the photoelectric and low temperature thermionic phases of the problem.

Apparatus

The type of emitter chosen for this research consisted of a platinum filament over which a thin layer of potassium glass* was fused, the diameter being about 1.5 mm. A reserve supply of potassium was provided by immersing the filament in molten potassium nitrate and electrolyzing potassium through the glass onto the filament; the potassium formed a golden brown layer over the filament surface. The emitting surface was a thin layer of platinum deposited on the glass by cathode sputtering; short distances at the ends were kept free to insulate the platinum coating from the filament. Electrical contact to the platinum coating was made by twisting a fine platinum wire tightly around the filament. With this type of filament, potassium could be electrolyzed to or from the platinum coating as desired by placing a suitable potential (V_E) between the coating and the filament.

A schematic drawing of the apparatus is shown in Fig. 1. The temperature of the filament was given by a thermocouple twisted about the coating. The emission currents were read with a Compton electrometer shunted with a

* A donation of the Corning Glass Works.

[1] Cottrell, Kunsman and Nelson, J. O. S. A. **20,** 152 (1930), and in press.

high resistance leak and potentiometer, which enabled currents to be read from 10^{-15} to 10^{-10} amps. The collecting electrode was made of copper, while the filament supports were made of nickel or tungsten. Ultraviolet light was admitted through a 1 inch quartz window with a graded glass seal.

A Hilger monochromatic illuminator was used to resolve the light of a hot mercury arc of the Uviarc type operating at 75 volts and 1.85 amps. The intensities of the various lines were measured with a Hilger thermopile, using the same slit width as that used in the photoelectric measurements, namely 0.5 mm.

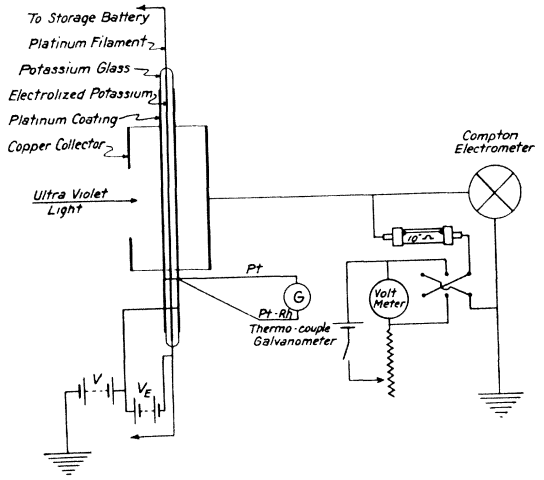

Fig. 1. Diagram of apparatus.

The nature of the filament did not permit of a systematic outgassing process. The pressure in all cases, however, was below the sticking point of mercury in the McLeod gauge (10^{-6} mm of Hg).

Results

Photoelectric emissivity. In determining the photoelectric threshold the current per unit of light intensity method was used. Corning glass filters and direct radiation from the arc were used also where greater intensity was needed.

The factors investigated in this research were (1) the effect of the electrolysis potential between the coating and the filament on the threshold, and on the emissivity; (2) the effect of temperature on the threshold, and on the rate of electrolysis; (3) the effect of electrolysis on the characteristics of the wave-length—current intensity curve, and (4) the effect of ultraviolet light on the thermionic emissivity of both electrons and positive ions.

The effect of an electrolysis potential (V_E) on the photoelectric activity is shown by line *A* of Figure 2.

It will be noted that the emissivity for λ 2653 is changed by an order of 30 fold, when V_E is changed from 1.5 v. negative to 3.0 v. positive. These

voltages, however, are not corrected for the fall of potential along the filament which for this temperature was about 3.0 v., the filament drop being negative to the coating. The zero, therefore, should be moved 1.5 v. to the right in Fig. 2, to give the correct electrolysis potential.

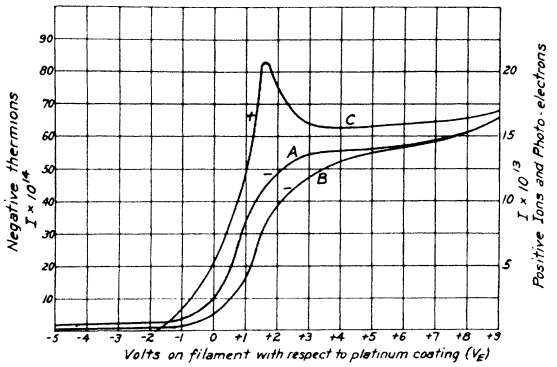

Fig. 2. A. Photoelectric emission, λ2653, temp. 337°C; B. Thermionic emission of electrons, temp. 632°C; C. Thermionic emission of positive ions, temp. 422°C.

In these experiments a constant difference of potential of 45 volts was maintained between the coating and the collector. Saturation was obtained at slightly less than 2 volts and showed no change up to 135 volts.

The effect of temperature on the rate of electrolysis is shown in Figure 3.

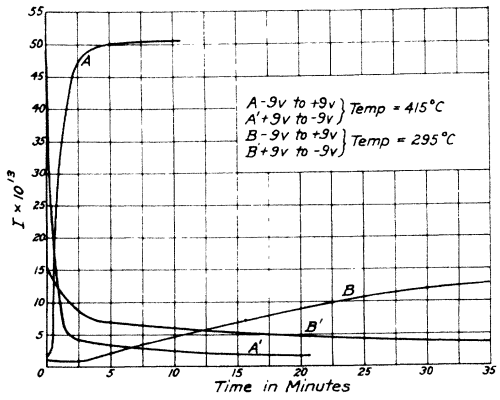

Fig. 3. Effect of temperature on the rate of electrolysis.

It will be noted that at 295°C one hour is required for a steady state to be reached when the electrolysis potential is changed from 9 v. positive to 9 v. negative, or vice versa. At 415°C steady conditions are reached in about 4 minutes, while at higher temperatures the change is too rapid to be measured. At 260° no effect could be observed from changing the electrolysis potential, as is illustrated by line *C* of Figure 4.

A lag exists between the time when V_E is made positive and when an increase in photoelectric activity is observable, the duration of the lag decreasing with rising temperature. On the other hand, the emissivity falls off rapidly the instant a negative electrolyzing potential is applied.

The effects of temperature and electrolysis potential on the threshold and on the specific activity for various wave-lengths are illustrated in Fig. 4.

Line C, as has just been stated, represents the current per unit intensity at 260°C for $V_E = +9$ v. and $V_E = -9$ v. This is the lowest temperature at which an electrolysis effect could be observed. These results were obtained with a fresh filament. After the filament had been worked in at temperatures up to 400°C the threshold shifted to a position represented by line D.

The long wave-length limit for a worked-in filament with $V_E = -9$ volts was very close to 2720 A, as is shown by line D. After the filament was

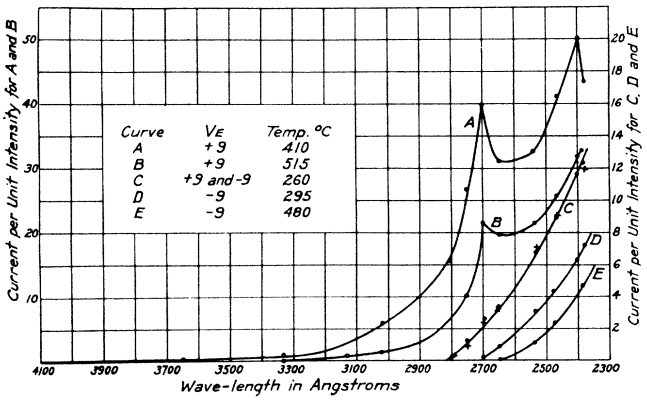

Fig. 4. Effects of temperature and electrolysis potential on the threshold and on the specific activity for various wave-lengths.

once worked in, the temperature coefficient became zero for all temperatures up to 425°C. At temperatures above 425°C the threshold shifted downward as is shown by line E, the shift increasing with the temperature.

The electrolysis of potassium to the surface (V_E positive) at temperatures above 260°C results in an enhanced photoelectric activity increasing with V_E as is shown by line A of Fig. 2, and with temperature, as is shown by comparing lines A and B of Fig. 3. The increase in emissivity is accompanied by a nearly corresponding shift in the threshold toward the red.

The conditions for maximum threshold are shown by line A of Fig. 4, in which case it was just possible to detect a photoelectric current with λ4350A. As the temperature was raised above 260°C, the threshold moved from about 3130A to 4350A, at 425°C. The exact value depended on the previous treatment of the filament, being higher when the filament had been cooled down with a strong positive electrolyzing potential applied. At temperatures above 425°C the threshold again shifted toward shorter wave-lengths, and the shape of the line became more regular as is shown by

line B of Fig. 4. At visibility the threshold shifted to about 3050A. The shift in the neighborhood of redness is due to the combined effect of temperature and fatigue, for the total emissivity cannot be restored by lowering the temperature.

The specific photoelectric activity is apparently abnormally high in the region around 2700A and 2400A as is shown by the breaks in curves A and B. These irregularities are more pronounced for fresh filaments and when electrolysis to the surface has just been increased by raising the temperature or by increasing the electrolysis potential.

The long wave-length limits, as determined above, were checked with Corning filters using the direct radiation from the arc. At 280° the photoelectric current was about 10^{-10} amp. when the light direct from the arc was passed through 12 mm of Pyrex, which should cut out λ3022A, and fell to 1.1×10^{-13} amps. for a 3.5 mm Noviol O filter, and to about 10^{-15} for 7 mm, which should exclude most of λ3650A; the threshold is, therefore, very close to 3600A. When the temperature was raised to 310°, the photoelectric current increased 4-fold.

The effect of fatigue is especially noticeable at high temperatures; the total activity can be reduced to a third of its initial value by holding the filament at redness for a period of minutes. The activities can usually be restored by reversing the sign of V_E and electrolyzing potassium ions away from the coating. Filaments have also been restored by washing in water and alcohol, and then lightly annealing with a small blue flame.

The thermionic emission of electrons. The thermionic emission of electrons from a fresh surface was detectable at temperatures above 425°C for positive electrolyzing potentials. The effect of V_E on the current is shown by line B of Fig. 2. The fall of potential along the filament is not corrected for in the graph; making this correction would shift the entire line 2 volts to the left.

The work function curves obeyed the Richardson equation fairly well, yielding a value for b of about 4×10^4. No significance can be applied to this value, however, since the character of the surface definitely changed with temperature.

Special tests were made to detect an enhancement of the thermionic emission in the presence of ultraviolet light. These tests were carried out by balancing out the photoelectric current with the leak potentiometer, while the thermionic current was observed, and then by balancing out the thermionic current and measuring the photo-electric emissivity. Both general and monochromatic radiation were used. No effect of the ultraviolet light could be observed either in the temperature at which thermionic emission became detectable or in the magnitude of the thermionic currents.

The thermionic emission of positive ions. The emission of positive ions became detectable at 270°C. This is very close to the temperature where the photoelectric measurements showed the electrolysis potential to become operative.

The effect of V_E on the positive ion emission at 422°C is shown by line C in Fig. 2. The fall of potential along the filament is such that the entire

line should be shifted 1.5 volts to the left, bringing the peak of the curve at approximately $V_E = 0$.

Curve C is distinctly different from curves A and B in that it shows a critical value of V_E at which the maximum ion current is obtained.

The positive ion currents between 270°C and 450°C agree very well with those reported by Cottrell, Kunsman and Nelson, except that the value of ϕ computed from the Richardson equation is higher by about 0.5 volts. The high work function at the low temperature is to be expected from the fact that the rate of electrolysis also increases with temperature, thus increasing the available supply of possible ions at the surface.

A test for the photoelectric emission of positive ions was made, using direct radiation from the arc in which light of wave-lengths below the threshold of the copper collector was screened out by Corex A Blue Purple filters. No photoelectric emission of positive ions could be detected.

Discussion of Results

The fact that the emission of electrons thermally and by ultraviolet light are both affected by electrolysis to and from the surface becomes doubly interesting when the characteristics of curves A and B of Fig. 2 are considered. By making the necessary corrections for zero potential, it will be seen that the two curves are identical in form and position. This is a further proof for the contention that the same group of electrons in the metal contribute to photoelectric and thermionic emission,[2] and is in line with the results of DuBridge[3] and of Warner[4] who have shown that the work functions for the two types of emission are identical.

Line C for positive ion emission is also very similar to lines A and B for electron emission, except for the fact that it contains an optimum value of V_E. It will be noted that the photoelectric activity increases rapidly at the value of V_E where positive ion emission becomes detectable.

The similarity between the positive ion and electron curves as well as the presence of an optimum electrolysis voltage for positive ions is readily explained by applying to the Richardson equation the intrinsic force concept previously outlined by the writer.[5, 6, 7]

In the equation $i = ne(kT/2\pi M)^{1/2}e^{-b/T}$, n is the number of possible positive ions per unit volume at the surface of the emitter, while b is a measure of the work done in bringing such an ion through the surface region. From this it follows that any process which decreases n or raises b will decrease the positive ion current.

The electrolysis of positive ions away from the surface $(-V_E)$ decreases the value of n; line C of Fig. 2 shows that the positive ion emission is not de-

[2] Sommerfeld, Zeits. f. Physik **47,** 1 (1928).
[3] DuBridge, Phys. Rev. **31,** 236 (1928).
[4] Warner, Proc. Nat. Acad. Sci. **13,** 56 (1927).
[5] Brewer, Proc. Nat. Acad. Sci. **12,** 560 (1926).
[6] Brewer, Proc. Nat. Acad. Sci. **13,** 592 (1927).
[7] Brewer, J. Phys. Chem. **32,** 1006 (1928).

tectable for large negative values of V_E. The increase in the positive ion current as shown on the graph from $V_E = -1.75$ to $V_E = +1.5$, is without doubt due to an increase in the value of n.

The accumulation of an element of large atomic diameter such as potassium on the surface should, according to the intrinsic force concept, increase the value of b for positive ion emission just as it decreases b for negative emission. The decrease in emissivity beyond the critical value of V_E is due, therefore, to an increase in the thermionic work function for positive ions occasioned by the accumulation of potassium at the surface. Thus the electrolysis of potassium to the surface increases both n and b for positive ion emission, the observed emission curve being a resultant of these two effects.

The fact that an electrolysis potential larger than 3 volts positive has only a small effect on the emissivity, as may be seen from Fig. 2, raises the question as to the nature of the potassium on platinum surface. A condition such as this may result either from the surface being completely covered with potassium at this point, or from a state of polarization being reached in the surface layer which prevents a further accumulation of potassium.

Two facts may be mentioned which indicate that a state of polarization exists and that the surface does not become covered with free potassium. First, in Fig. 3 it will be seen that the emissivity drops markedly the instant a negative electrolyzing potential is applied. Had the surface been covered with a layer of potassium, lines A' and B' should have shown a time lag. The second fact is that it was never possible to obtain the threshold for pure potassium, the values found always lying between that for potassium and platinum. It would seem, therefore, that the surface can best be considered as a surface solution of potassium in platinum rather than a deposit of potassium on platinum.

The writer's best thanks are due Dr. C. H. Kunsman for his interest and advice, and Mr. R. A. Nelson for constructing the filament and rendering other valuable assistance.