# Average Thermionic Constants of Polycrystalline Tungsten Wires

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(Received January 6, 1950)

Because of its property of producing large crystals, the "doped" variety of tungsten wire is used in the study of the thermionic properties of single crystal surfaces of tungsten. In order to determine the effect of the impurities added to produce this property, the average high field thermionic constants of polycrystalline doped tungsten wire and undoped tungsten wire were measured. The thermionic constants from the doped wire are somewhat lower than those from the undoped wire which agree well with previously published values. Chemical and spectroscopic analyses before and after heat treatment are included. It is concluded that the differences in thermionic properties between the two types of wire are probably due to different distributions of the types of crystal surfaces exposed.

## I. INTRODUCTION

IN order to study experimentally the thermionic properties of the different crystal surfaces of tungsten, it has been found convenient to make use of the crystal growth properties of "non-sag" or "doped" tungsten wire.[1,2] With the proper heat treatment, it is possible to grow large crystals in this type of wire which occupy the entire cross section of the wire and are several cm long.[3,4,‡] As a result of the working given the wire during the drawing process, the crystals are generally oriented with a face diagonal parallel to the wire axis. The crystal growth properties of this type of wire result from about 1 percent of "dope" consisting of $Na_2O$, $K_2O$, $CaCl_2$, $Al_2O_3$ and $SiO_2$ added before the sintering process.[3] Because of the addition of these impurities, there is some question as to whether the thermionic properties of such wire are characteristic of clean tungsten. Because of the importance of past and future experimental results using single crystals grown in doped tungsten wire, it was decided to measure the average high field thermionic constants of doped and undoped polycrystalline tungsten wire in order to permit a direct comparison. The definition and physical meaning of the average high field thermionic constants, $\varphi^{**}$ and $A^{**}$ of polycrystalline surfaces are discussed by Herring and Nichols.[5]

The doped tungsten wire used for the measurements presented in this paper was Callite Corporation #200H (this wire is similar in properties to General Electric Company Type 218). The undoped tungsten wire was from General Electric lot exp. 8983 dated 1/13/38. This lot was supposed to be very pure.

## II. EXPERIMENTALLY DETERMINED AVERAGE EMISSION CONSTANTS OF DOPED POLYCRYSTALLINE TUNGSTEN WIRE

Two specimens were measured; one was polished smooth to remove the die marks[6] and the other was unpolished. These were mounted one at a time in a tube using suitable guard rings and arranged to measure the total thermionic emission current from the wire over a 2-cm length. The tube was pumped, outgased, gettered, and sealed off by methods already described.[7] The temperatures were determined by the Forsythe and Watson[8] temperature scale using the function $A/d^{\frac{1}{2}}$ according to the Jones-Langmuir notation.[9] The wire diameters were determined before and after the experiment (in order to correct for evaporation effects during heat treatment) by weighing a measured length.[9] In the case of polished wire, the diameter was checked to the nearest fringe of mercury green light by a wedge interferometer method. All heating of the wires was accomplished by use of alternating current in order to eliminate direct current etch effects.[10,11]

The average high field thermionic constants $\varphi^{**}$ and $A^{**}$ were determined as follows. A Schottky plot was made at a temperature of 1700°K over a voltage range 600 to 3000. The points plotted a straight line to within experimental error over this range. The slope of the straight line drawn through the points agreed with the corresponding theoretical value based on the mirror image theory to better than 5 percent for the polished specimens. The experimentally determined slope was about 10 percent larger than the theoretical slope, based on a smooth surface, in the case of the die marked specimens. Richardson plots of the emission current over a temperature range 1350 to 2200°K were made at

* Research done in 1939–40 while the author was a National Research Fellow.
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[3] C. J. Smithells, *Tungsten* (D. Van Nostrand Company, Inc., New York, 1936), second edition.
[4] C. S. Robinson, J. App. Phys. **13**, 647 (1942).
‡ The author has been informed by Mr. George Moore, of the Bell Telephone Laboratories, that there is a difference in the properties of prewar "non-sag" type of tungsten wire and the corresponding postwar production in that it is very difficult to produce large crystals in the latter. This may be due to different impurities occurring in the ores or manufacturing processes.
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TABLE I. Average emission constants of doped wire.

| Type of wire | $\varphi^{**}$ | $A^{**}$ | Heat treatment |
|---|---|---|---|
| Doped (Callite #200H) polished smooth | 4.464 | 42 | Temperature raised steadily from 1000°K to 2600°K over a period of twenty hours. Then 2.5 min. at 2700°K. |
| | 4.455 | 36 | Above plus 125 min. at 2850°K and 105 min. at 2900°K. (Wire diameter reduced about 3 percent by evaporation.) |
| Doped (Callite #200H) unpolished | 4.449 | 40 | 10 min. at 2700°K, 8 min. at 2850°K, 3 min. at 2900°K, 40 hr. at 2300°K. |

TABLE II. Average emission constants of undoped wire.

| Type of wire | $\varphi^{**}$ | $A^{**}$ | Heat treatment |
|---|---|---|---|
| Undoped (G.E. lot exp. #8983) polished smooth | 4.557 | 55 | Temperature raised steadily from 1000°K to 2600°K over a period of 6½ hours. Then 1.5 min. at 2700°K, 0.7 min. at 2900°K, 63 hours at 2200°K. |
| | 4.519 | 49 | Above plus 22 min. at 2900°K, and 36 hr. at 2200°K. |
| Undoped (G.E. lot exp. #8983) unpolished | 4.529 | 53 | 17 min. at 2875°K, 1 min. at 2950°K, 78 hr. at 2200°K. |

a collecting voltage of 1100. The average thermionic constants $\varphi_v^{**}$ and $A^{**}$ were determined from these Richardson plots by fitting a least squares straight line to the data assigning the error to the $1/T$ coordinate. In all cases in this section and in Section III, the probable error in $\varphi_v^{**}$ was less than 0.013 volt and in $A^{**}$ less than 5 amp/cm² deg² as determined from the deviations from the least squares straight line. The "zero field" value $\varphi^{**}$ is given by $\varphi_v^{**}+kSV^{\frac{1}{2}}/e$ where $S$ is the slope of the experimental Schottky plot ($\ln i_v$ *versus* $V^{\frac{1}{2}}/T$) and $V$ is the collecting voltage at which the thermionic currents for the Richardson plots were measured.[5] The results are summarized in Table I.

These results are not in good agreement with previously accepted values of about 4.52 volts and 60 amp/cm² deg² for clean polycrystalline tungsten.[12–18]

## III. EXPERIMENTALLY DETERMINED AVERAGE EMISSION CONSTANTS OF UNDOPED POLYCRYSTALLINE TUNGSTEN WIRE

In order to compare the above results with those from undoped tungsten wire, two specimens were cut from G.E. lot exp. #8983 dated 1/13/38; one specimen was polished and the other was used unpolished. The results are summarized in Table II. The heat treatment consisted of short flashes at the high temperatures separated by long periods of heating at 2200°K.[19] These results are in better agreement with the previously accepted values.[12–18]

## IV. PURITY OF SPECIMENS

The following data on purity of tungsten wire as it comes from the mill—i.e., after sintering, swaging, and drawing—were supplied by Mr. P. Dorticos.[20]

TABLE III. Data on purity of the specimens.

| Type of wire | NVR | MO | Fe |
|---|---|---|---|
| "Doped" (GE 218 non-sag) | 0.004 percent | 0.002 | 0.011 |
| Undoped | 0.001 | 0.16 | 0.007 |

TABLE IV. Results of spectroscopic analysis of specimens.

| Element | Doped | Undoped |
|---|---|---|
| Mo | 5 | 100 |
| Ni | 10 | 1 |
| Fe | 5 | 5 |
| Ca | 40 | 30 |
| Al | 20 | 5 |
| Si | 3 | 3 |
| Cu | 1 | 1 |
| Mg | 5 | 2 |

Table III gives the results in percent from "wet analysis" on G.E. Type 218 doped wire and undoped tungsten. NVR is non-volatile residue determined by passage of $CCl_4$ and air over a boat containing tungsten wire in an electrically heated furnace. The tungsten passes over as tungsten oxychloride. The NVR is made up of $SiO_2$, $Na_2O$, $K_2O$, $CaCl_2$, and $Al_2O_3$. It is to be noted that the impurities in the undoped wire are very small with the exception of the Mo. Dorticos comments that the undoped sample shows unusually high Mo content. It is not clear whether the undoped sample is the same as G.E. lot # exp 8983 used for Table II. According to the results of Freitag and Krüger,[17] this concentration of molybdenum would have a negligible effect on the work function. It should be noticed that with the exception of the Mo, the impurity content is about the same in both samples. Since about 1 percent NVR was originally added to the doped variety to control crystal growth, most of the NVR has been eliminated during the sintering and swaging processes.

A spectroscopic analysis[20] is given in Table IV. This table should be read horizontally—i.e., the numbers given are relative and apply only to the same elements. This table agrees with Table III and, with the exception of Mo, shows about the same order of magnitude of impurities in each case.

For his work on tungsten in 1923–1924, Dushman used a variety of wire known as General Electric K

[12] C. Davisson and L. H. Germer, Phys. Rev. **20**, 300 (1922).
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[20] Letter from Mr. P. Dorticos, Lamp Department, General Electric Company, Cleveland Wire Works (May 19, 1941).

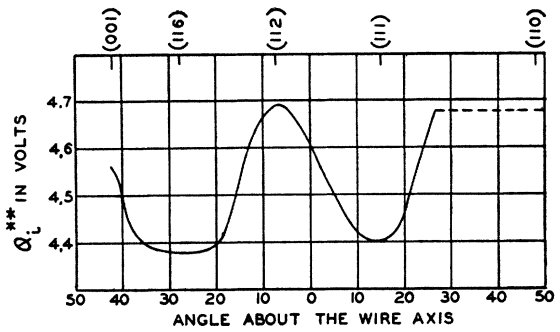


FIG. 1. Approximate values of $\varphi^{**}$ from a single crystal tungsten wire (see reference 2) plotted as a function of the angle about the wire axis. The Miller indices of the various crystal directions are indicated.

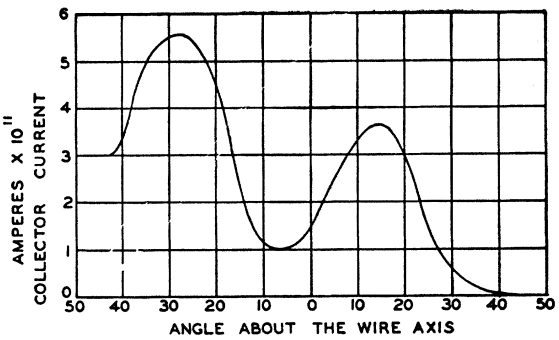


FIG. 2. Emission current from the single crystal wire of Fig. 1 at a temperature of 1465°K plotted as a function of the angle about the wire axis.

wire.[21] For further information, at the request of the writer, Dorticos[22] performed the following experiment on *K* wire and the G.E. 218 doped variety. A $\frac{1}{8}$-in. diameter rod of each material was heated in hydrogen, by passage of current, through six cycles of one hour at 2900°K followed by twelve hours at 2000°K. Then after this heat treatment a spectroscopic analysis yielded the results in Table V. The letter *p* means that the element indicated is present in average amounts; the sign + means a little more than average; ++ means in excess of that; and − means less than average, etc.; *A* means absent. These results show no substantial differences between K tungsten and 218 tungsten after such severe heat treatment. No analyses were made prior to heat treatment.

At the request of the writer, Smoluchowski[23] made a spectroscopic comparison between a raw Callite 200H wire (0.312 mm in diameter) and another section of the same wire which was recrystallized in very pure hydrogen and was severely heat treated in vaccum. The main observed difference was that the Cu and the Mo lines were very much weaker in the heat treated sample. Due to low dispersion and small samples, some other lines could not be well identified.

## V. DISCUSSION

The heat treatment given all specimens was sufficient to result in stable emission throughout all temperature cycles. Therefore the difference must be caused by some permanent effect brought about by the differences in the impurities originally present. Now the chemical analyses in Section IV show that the amount of impurities present after heat treatment is very small so that the effect cannot be attributed to a difference in the resistivity which would effect the temperature scale (about 5 percent difference in resistivity would be required) or to a volume effect on the work function. Since after sufficient heat treatment the thermionic emission was stable for all temperature cycles, impurities in the surface double layer seem doubtful. Although the doped tungsten wire after heat treatment shows about the same relative impurity content as does the undoped wire, the doping strongly effects the crystal growth properties.[3] *It therefore seems likely that the difference in work function between the doped and undoped specimens is caused by a different distribution of the types of crystal surfaces exposed.* In this connection crude calculations, using the patch theory, indicate that tungsten wire having perfectly random crystal orientation would display a somewhat larger work function than would the type of preferred orientation which the doped wire displays.[5] Unfortunately the literature on the final crystal orientation in the undoped type of wire does not seem conclusive.[5]

It might also be mentioned that about a 5 percent difference in the average emissivity of the surface would be required to explain the difference in the observed work function of the two types of wire on the basis of its effect on the temperature. Since it appears that the fractional amounts of the surface exposed in the two cases are not much different[5] (though apparently different enough to explain the effect on the basis of work function differences) it seems unlikely that the effect can be attributed to different emissivities of the various crystal surfaces exposed.

It is of some interest to compare the results of Table I with the data represented by Fig. 5 of reference 2# which were taken from a single crystal grown in doped (G.E. Type 218) tungsten wire. From these data it is possible to compute approximately the value of the apparent work function $\varphi^{**}$ of the tungsten single crystal wire as a function of the angle taken about the wire axis. These values are plotted in Fig. 1. It can be shown that the apparent high field work function, $\varphi^{**}$,

[21] Letter from Dr. S. Dushman, General Electric Research Laboratory (November 17, 1941).

[22] Letter from Mr. P. Dorticos, Lamp Department, General Electric Company, Cleveland Wire Works (April 13, 1942).

[23] Letter from Dr. R. Smoluchowski while at the General Electric Research Laboratory (May 25, 1942).

# Because of a numerical error, the values of $\varphi^{**}$ ($\varphi_0$ in the notation in this reference) in Table I of this reference are 0.03 volt too low. It should also be pointed out that in Fig. 5 of this reference the temperatures should be 1890°K and 1465°K.

averaged over the wire surface is given by [5,24]

$$\varphi^{**}=\sum_i w_i\varphi_i^{**}, \quad (1)$$

where $w_i$ is the fraction of the total emission which comes from the $i$th type of crystal surface whose apparent work function is $\varphi_i^{**}$. The corresponding value of the emission constant $A^{**}$ is given by

$$\log A^{**}=\log j_0/T^2+e\varphi^{**}/2.303kT, \quad (2)$$

where $j_0$ is the average current per unit area extrapolated to zero field. Figure 2 is a plot of the current measured as a function of the angle about the wire axis corresponding to a temperature of 1465°K. Using Eq. (1) in connection with Figs. 1 and 2, graphical integration yields a value of 4.45 volts for $\varphi^{**}$ and a corresponding value of 41 amp/cm$^2$ deg$^2$ for $A^{**}$. These approximate results are in agreement with those of Table I.

These results further emphasize[2,5] the fact that the average thermionic constants from polycrystalline emitters depend upon the types and relative amounts of the various crystal surfaces exposed and are generally not characteristic of a uniform surface.

[24] C. Herring, Phys. Rev. **59**, 889 (1941).

TABLE V. Results of spectroscopic analysis of specimens after heat treatment.

| Element | K Tungsten | 218 Tungsten |
|---|---|---|
| Ca | $p^{++}$ | $p^+$ |
| Fe | $p^+$ | $p^+$ |
| Mo | $p$ | $p^+$ |
| Ti | $p^+$ | $p^+$ |
| Cr | $p^{--}$ | $p^{--}$ |
| Ni | $p$ | $p$ |
| Al | $p^-$ | $p^-$ |
| Mg | $p^+$ | $p$ |
| Si | $A$? | $p^-$ |
| Na and K — no difference | | |

## VI. ACKNOWLEDGMENT

The author is indebted to Mr. P. Dorticos and to Dr. R. Smoluchowski of the General Electric Company for carrying out the chemical analyses reported in Section V. The author is also indebted to Professor W. B. Nottingham of the Massachusetts Institute of Technology for reading and critizing the manuscript.

PHYSICAL REVIEW VOLUME 78, NUMBER 2 APRIL 15, 1950

# The Radiative Collisions of Positrons and Electrons*

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(Received November 25, 1949)

The general matrix elements for the collision of two electrons ($e$-$e$ case) or a positron and an electron ($p$-$e$ case) accompanied by the emission of a quantum of radiation are formulated. It is expected that the two cross sections will differ considerably both because of the existence of a dipole for the $p$-$e$ case, and because of the essentially different nature of the exchange phenomenon in the $p$-$e$ case arising there from the possibility of virtual pair creation or annihilation rather than the indistinguishability of the particles. Two cases are calculated in detail; the non-relativistic limit and the extreme relativistic limit in which the quantum energy is restricted to $\leqq E$ in the laboratory system. In the former case the cross section for the $e$-$e$ case is found to vanish if the momentum of the quantum is neglected, while the $p$-$e$ cross section is comparable to that for the "bremsstrahlung" process. In the latter case the cross sections of the two cases are of the same order of magnitude the $e$-$e$ cross section being greater because of the exchange terms, the exchange terms of the $p$-$e$ case being negligible in all of the cases considered.

## I. INTRODUCTION

THE elastic scattering of electrons by electrons has been treated by Møller,[1] Breit,[2] and Bethe and Fermi,[3] using both correspondence principle methods and the quantum electrodynamics. The results of Møller have been adapted by Bhabha[4] to the case when one of the colliding particles is a positron.

The scattering of two charged particles by each other with the emission of a quantum of radiation has been treated by Møller[5] for particles of arbitrary masses. This author only carries out the complete calculation of the collision cross section for the limiting case that the mass of one of the particles becomes infinite, and thus obtains an expression identical to that obtained by Bethe and Heitler[6] for the "bremsstrahlung" process. The process is generalized in a paper by Havas[7] for the case that any number of quanta are emitted.

* Summary of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Harvard University.

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[7] P. Havas, Phys. Rev. **68**, 214 (1945).