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THERMIONIC PROPERTIES OF URANIUM WIRE

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Three independent measurements of the work function of uranium have been reported. The values obtained were 4.32,¹ 3.63,² and 3.27³ ev. Since some of these measurements were made with uranium wire and since, as shown by the authors,⁴ uranium is very readily oxidized at pressures of 10^{-7} mm Hg to give a relatively non-volatile oxide, one surmises that some of these determinations were subject to error because of vacuum conditions. Attempting to investigate the validity of this criticism, the authors have measured the thermionic properties of a uranium wire in such a manner that some information regarding the cleanliness of the surface can be deduced. The two types of measurements accomplished were (a) the change in the thermionic constants of the Richardson equation with time of heating in hydrogen, and (b) the dependence of current on the retarding potential.

The electrode assembly consisted of an 11-cm length of 28-mil uranium wire mounted coaxially with a cylindrical tantalum anode (1.7 cm long and 1.0 cm in diameter) and with two guard rings (3.0 cm long and 1.0 cm in diameter). A small hole in the anode permitted a measurement of the temperature of the wire with an optical pyrometer. Since uranium exhibits a pronounced tendency to creep it was necessary to mount the wire so that the only force aligning it was a small tantalum weight. The wire, with maximum impurities (total) of the order of 100 ppm, was cleaned electrolytically in a sulfuric acid-glycerine solution just prior to mounting in the assembly. The vacuum vessel was then sealed at once. During this operation helium (purified by passing it over hot uranium chips) was passed through the cell, so that no oxidation of the wire occurred during this operation contrary to the condition which existed in Hole and Wright's experiment.³ The cell was evacuated by a divergent nozzle mercury vapor pump in series with a two-stage mercury diffusion pump. It was attached to the vacuum assembly in a manner so that it could be baked out and then immersed in liquid nitrogen.

¹O. Klein and E. Lange, Z. Elektrochem. 44, 542 (1938).

²H. C. Rentschler, D. E. Henry, and K. O. Smith, Rev. Sci. Instr. 3, 794 (1932).

³W. L. Hole and R. W. Wright, Phys. Rev. 56, 785 (1939).

⁴E. G. Rauh and R. J. Thorn, J. Chem. Phys. 22, 1414 (1954).

Aside from an initial one-hour heating of the wire at 975°C in a vacuum of 10^{-7} mm Hg, the wire was heated for approximately 78 hr in hydrogen (10^{-4} mm Hg) obtained by decomposing uranium hydride. The electron emission was measured at 10 volts as a function of temperature at intervals during this time. Although the partial pressure of water in equilibrium with 10^{-4} mm Hg pressure of hydrogen and solid UO_2 is of the order of 10^{-18} mm Hg, the aging was carried out in this manner to attempt to duplicate some of the procedure of Hole and Wright. The results of these measurements are listed in Table I. At the end of 938 min the aging in hydrogen was discontinued and a series of measurements of the current as a function of applied voltage was carried out at 1285°K. A typical curve is shown in Figure 1.

Table I

EFFECT OF AGING ON THERMIONIC CONSTANTS

Time of Aging in H_2 with Wire at 930°C (min)	A^b (amp/cm ²)	ϕ^c (ev)	Current at 1190°K (amp)
60 ^a	1.69×10^9	5.89	1.22×10^{-10}
130	1.29×10^6	5.05	3.20×10^{-10}
220	1.86×10^4	4.54	5.92×10^{-10}
290	4.33×10^3	4.35	9.34×10^{-10}
290+	5.41×10^2	4.11	1.31×10^{-9}
580	2.49×10^2	4.01	1.59×10^{-9}
650	5.79×10^2	4.07	2.04×10^{-9}
938	8.75×10^2	4.07	3.00×10^{-9}

^aIn vacuum of $\sim 10^{-7}$ mm Hg.

^bError in A is about a factor of 1.9.

^cError in ϕ is ± 0.07 ev.

The data in Table I show that up to about 580 min of aging both A and ϕ in the Richardson equation decrease in such a manner that the current at the mean temperature of the measurements increases. Although we cannot explain quantitatively this trend at present, we do at least observe that the initial A values are certainly not characteristic of a clean metal

FIGURE I.
A PLOT OF ELECTRON CURRENT vs.
RETARDING POTENTIALS

surface, but that the values after aging approach that for a clean metal surface. Since "positive ion" currents of the order of 10^{-10} amp were observed, one wonders whether the observed trend could have been caused by diffusion of alkali atoms to the surface. Composite surfaces of dissimilar metals or metal oxides, however, generally yield $\bar{A}$ values⁵ less than the clean metal value (60-120). Since those observed are all larger, it appears doubtful that any appreciable fraction of the surface was covered with a composite surface of a dissimilar metal. Initially the surface was certainly coated with a layer of uranium dioxide. The observed change then must have been associated with some change in this layer.

A more interesting property of the wire is given by the current-voltage data in the retarding potential region. For clean metals⁶ the current from a wire to a cylindrical anode is given by the Schottky equation,

$$i = i_0 \left\{ \frac{2}{\sqrt{\pi}} S^{1/2} e^{-S} + 1 - \frac{2}{\sqrt{\pi}} \int_0^{S^{1/2}} e^{-x^2} dx \right\},$$

in which i_0 is the saturation current and $S = (Ve/kT)$ is proportional to the retarding potential V . For composite surfaces the current-voltage data deviate from this relation.⁵ The deviation of the experimental values of the current from those calculated (see Figure 1) for the uranium wire is approximately the same as that observed for the alkaline earth oxides on tungsten. It is interesting to observe that no adequate theoretical explanation has been given for this deviation. The empirical reflection coefficient,

$$R(p_x) = e^{-(p_x^2/2m\omega)},$$

introduced by Nottingham⁷ into the Schottky equation is quite inadequate, as shown by the corresponding curve in Figure 1. The suggestion of Hadley that the deviation is caused by a resistive voltage drop in the coating is interesting, but requires a resistance which is dependent upon the applied voltage.

The foregoing data and discussion demonstrate that it is impossible to measure the work function of uranium metal under the conditions which were employed by Hole and Wright. The fact that they obtained a value as low as 3.27 ev must be attributed to either an experimental error or else to an impurity on the surface such as an alkali metal so that the work function of their oxide-coated surface was reduced. This latter possibility would

⁵See for instance, G. E. Moore and H. W. Allison, Phys. Rev. 77, 246 (1950); C. P. Hadley, J. Appl. Phys. 24, 49 (1953).

⁶L. H. Germer, Phys. Rev. 25, 795 (1925).

⁷W. B. Nottingham, Phys. Rev. 49, 78 (1936).

appear to be reasonable since they obtained a value of A typical of such composite surfaces. The measurements reported herein show that the work function is probably less than 4.0 ev. Hence the value of 4.32 ev obtained by Klein and Lange is most probably too high. There remains, then, the value of 3.63 ev obtained by Rentschler, Henry and Smith. This value appears to be the most reliable because the uranium surface was prepared by sputtering in an inert gas. This method, together with the procedure of measuring the threshold frequency to obtain the work function, should have eliminated at least in principle the difficulties. The sputtering should have freed the metal from the oxide and the measurements at low temperature should have prevented the diffusion of impurities to the surface.