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Temperature Dependence of the Work Function of Single-Crystal Faces of Copper*

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Measurements of the temperature dependence of the work functions of the (100), (110), (111), (211), and (221) crystal faces of copper have been made in the temperature range 20 to 700°C. The measurements were obtained by a diode retarding-field method *in vacuo* below 10^{-9} torr. Constant current operating conditions permitted a direct continuous monitoring of changes in the anode work function. While absolute work function measurements could not be obtained by this method, a precision measurement of the temperature dependence was possible. The single-crystal anodes were given rigorous heat treatment in high vacuum resulting in drift-free measurements which were reproducible. The results from the (100) and (111) faces, when combined with previously reported values of the absolute work function, demonstrate a relationship in which the work function smoothly approaches a value independent of crystallographic orientation at the melting point. A simple thermodynamic argument is presented to explain the results. Published measurements of the temperature dependence of the work function of single-crystal faces of tungsten are shown to be consistent with this interpretation.

I. INTRODUCTION

SEVERAL measurements of the temperature dependence of the work function have been reported in the literature.[1–4] These measurements are subject to criticism for one or more of the following reasons: Polycrystalline samples were used; the measurements were the result of a limited number of point determinations; the temperature range was limited; only one crystal orientation was studied; and measurements were performed in inadequate vacuums. In order to overcome some of these difficulties, an experiment was set up to measure, in a continuous fashion, changes in the work functions of single-crystal surfaces over an extended temperature range. While the diode retarding-field method selected for the measurements did not lend itself to accurate determination of the absolute work function, it offered the advantage of a sensitive indication of small changes in the work function.

Measurements were made on (100), (110), (111), (211), and (221) faces of single crystals of high-purity copper. All the samples used were examined both before and after measurements using x-ray back reflection techniques, and one of the samples was examined in an electron diffraction apparatus for surface condition. Rapid evaporation from the samples at high temperature limited the useful temperature range to below 700°C. In all the sealed-off tubes used for the measurements vacuums were better than 10^{-9} Torr.

II. DESCRIPTION OF THE EXPERIMENT

The retarding-field method is most easily understood in terms of a simple diode. If the operating conditions of the diode are adjusted in such a way that the electrons leaving the cathode must pass through a retarding field, the current I reaching the anode is given by Richardson's equation

$$I=CT_c^2\exp[-q(\Phi_A-V_A)/kT_c], \tag{1}$$

where Φ_A is the anode work function, V_A is the anode-cathode potential difference, T_c is the cathode temperature and C is a constant involving the universal constant A, the cathode area, and the electron reflection coefficient of the anode. If the cathode temperature and anode current are held constant while the anode work function changes,

$$d\Phi_A=dV_A\,. \tag{2}$$

Changes in the anode work function will be compensated by changes in the potential across the diode.

In practice the tube used in conjunction with the retarding-field method need not be a simple diode. If an image of the cathode is produced in front of the anode, the current versus voltage characteristic will still be of the form of Eq. (1). Electron optic effects may, however, alter the effective cathode temperature. For any structure, if the cathode temperature, the voltage applied to all auxiliary electrodes, and the anode current are maintained constant while the anode work function changes, the condition $d\Phi_A=dV_A$ is still satisfied. Even under space-charge-limited conditions the compensation provided by a constant current circuit ensures that the electron beam does not see any change in electric field as a result of the changes in anode work function.

The tubes used to obtain the measurements consisted of a polycrystalline tungsten ribbon emitter, an accelerating electrode with a pinhole aperture, the sample anode, an anode heater, and a Pt-Pt 10% Rh thermocouple to measure the temperature of the anode. This

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arrangement has several advantages over a simple diode. The accelerating electrode allows electrons from only a small portion of the ribbon emitter to reach the anode, thus defining an essentially unipotential effective cathode. When the anode is operated at a retarding potential with the accelerating electrode at a fairly large positive potential, a virtual image of the cathode is produced very close to the anode, thus simulating a closely spaced diode. The diode can then conduct large currents under retarding potential conditions. This lowers the dynamic impedance of the diode and the impedance level at which the retarding potential is measured. The accelerating electrode also serves as a heat shield between the anode and emitter making their temperatures independent. Accurate absolute measurements of the anode work function cannot be made with the arrangement since the cathode is not truly unipotential, nor single crystal, the electron beam is slightly defocused at the accelerating electrode, and the cathode temperature must be known to extreme accuracy. As was previously explained, these effects do not, however, affect the accuracy of the measurement of changes in anode work function.

The samples were grown by a Bridgman method from high-purity copper supplied in the form of turnings.[5] An x-ray back reflection method was used to check for crystallinity and to orient the samples which were then cut to shape on a lathe. After cutting, the samples were mechanically polished with French emery paper in grades from 0 to 0000 successively. To remove any disturbed matter introduced on the surface during the machining and mechanical polishing, immediately before use the samples were electrolytically polished using an electrolyte of 470 parts distilled water to 530 parts orthophosphoric acid. Electron diffraction patterns taken from one of the samples showed clear spots and Kikucki lines indicating undisturbed single-crystal faces.

When the samples were mounted directly on a tungsten lead by force fitting it was found that recrystallization occurred on heating. From visual observations it was apparent that recrystallization was due to strain introduced in the crystal at the tungsten lead. The samples were finally mounted in an oxygen-free high conductivity (OFHC) copper block and held in place by a loosely coupled retaining pin. As well as matching the thermal expansion of the crystal, the block housed the tungsten heater spiral used to control the crystal temperature, afforded a mounting location for the thermocouple, and protected the crystal from direct contact with the heater.

To ensure sample surfaces that were as clean as possible, a number of special precautions were taken during the assembly of the tubes and the tubes were subjected to a rigorous heat and vacuum processing. While the tubes were being mounted on the vacuum station the samples were maintained in a protective atmosphere of argon. The tubes were pumped and outgassed until a pressure of below 1×10^{-9} Torr could be maintained with the samples at 600°C. They were then sealed off with a Bayard Alpert gauge. The gauge was run during the life of a tube to provide continuous pumping. Immediately before measurements were taken the tubes were run with their anodes at 600°C for at least 12 h. If any rise in pressure occurred, the tube was reprocessed.

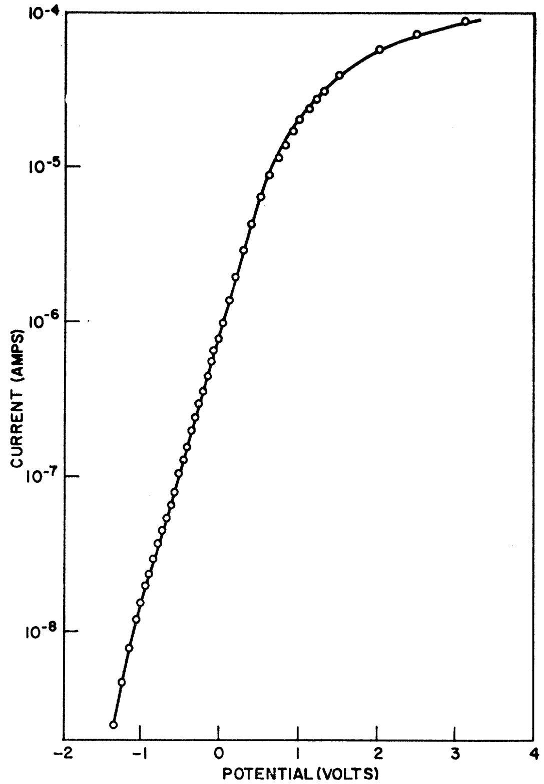

FIG. 1. Retarding field I–V characteristic.

Detailed current-voltage characteristics with the anode at room temperature were taken on two of the retarding potential tubes. The voltages were measured with a precision potentiometer, the currents with a

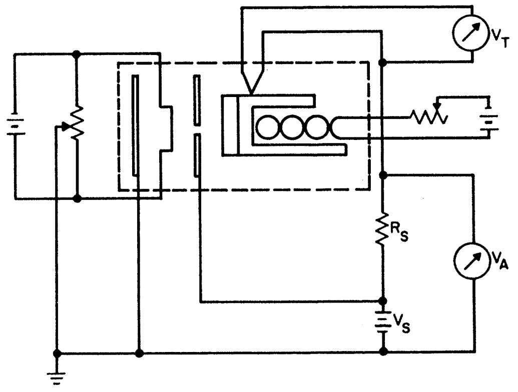

FIG. 2. Schematic diagram of experimental tube and associated circuitry.

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[5] Supplied by Canadian Copper Refiners Ltd., Montreal, P. Q.

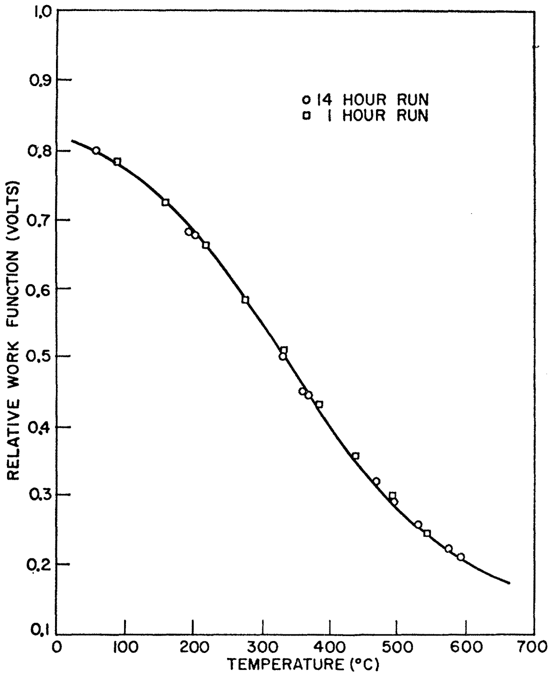

FIG. 3. Temperature dependence of the work function of the (100) face of a copper crystal.

Keithley Model 610 electrometer. Both tubes showed a linear section in their ln$I$ versus V curves (Fig. 1) extending from 1×10^{-8} A to 5×10^{-6} A when a 45-V battery was used as a supply for the accelerating electrode. This indicated that the tubes behaved as simple diodes in this region.

A schematic diagram of the tube and the circuit used to measure changes in the work function of the anode with temperature is shown in Fig. 2. The value of R_s was maintained large enough that the series combination of V_s (45 V) and R_s simulated a constant current generator.[1] This permitted direct monitoring of changes in the anode work function. Shielded wire was used throughout and the potential across the tube was measured with a Keithley Model 610 electrometer coupled to a recording galvanometer.

III. DISCUSSION OF RESULTS

Two types of measurement involving the (100) face were taken to determine the effects of the tube design and instrumentation. The first consisted of a set of point-by-point values obtained by adjusting the anode heater current and allowing a constant temperature to be reached before reading the retarding potential. The temperature was changed in both directions during this measurement. A complete set of points was obtained over a fourteen-hour period. The second type of measurement was taken in a continuous fashion by recording the retarding potential as a function of time after turning off the anode heater. Temperature markers were placed on the recorder chart by mechanically deflecting the recorder pen when the thermocouple voltage passed fixed points. A complete set of points was obtained in one hour.

The results of one set of each type of measurement are shown in Fig. 3. Since in using this method of measurement only changes in the work function can be accurately measured, the first set of points has been arbi-

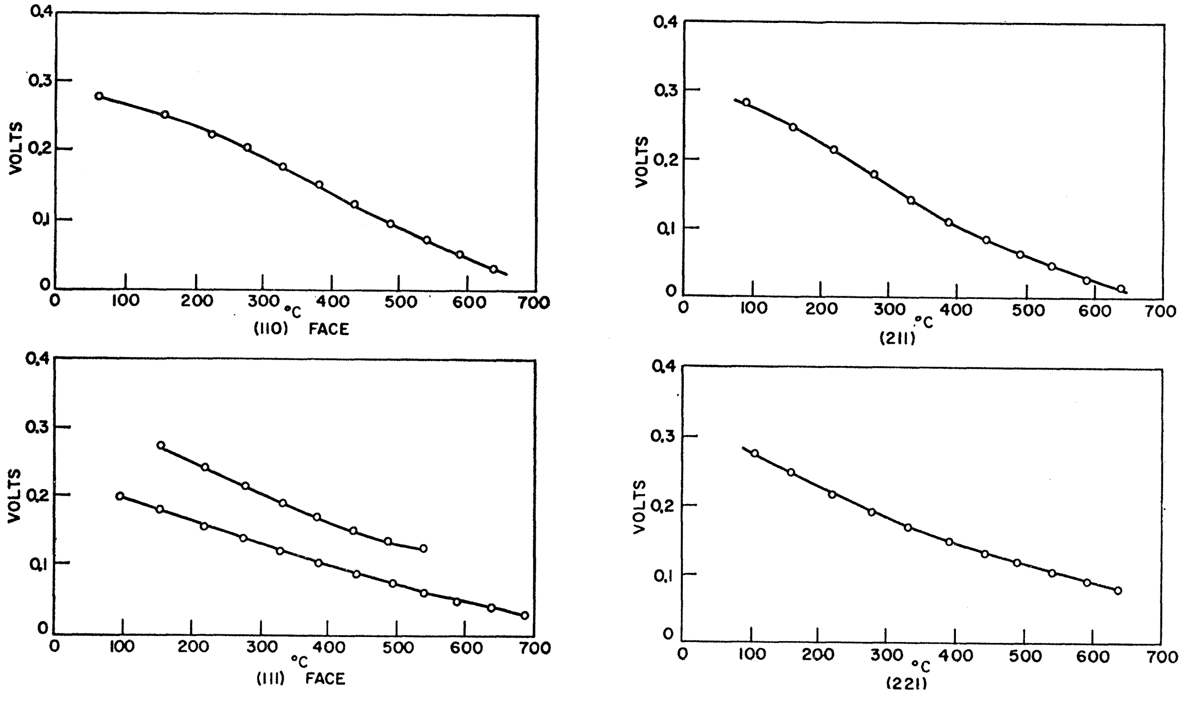

FIG. 4. Temperature dependence of the (110), (111), (211), and (221) faces of copper.

TABLE I. The temperature coefficient of the work function of single-crystal faces of copper.

Orientation	$d\Phi/dT$ at 600°K
(100)	-13.8×10^{-4} V/°K
(211)	-6.5
(110)	-5.2
(221)	-4.0
(111)	-3.4

trarily adjusted to make the two sets of measurements coincide at 592°C. The points from both types of measurement lie on a single smooth curve. These measurements show that there was no temperature-dependent contamination of the anode and no appreciable difference between the temperature measured by the thermocouple and the temperature of the anode surface during the 1-h run. The measurements over the 14-h period have been corrected for a small linear reproducible drift of 2.5 mV/h in anode potential which was independent of anode temperature. This was attributed to the slope of the plateau in the discharge characteristic of the storage battery used to supply the emitter heater current. This is a negligible correction for the data taken over a period of one hour and is still small in comparison with the temperature-induced change in the 14-h run. Assuming the argument of the exponential in Eq. (1) was of the order of 25 under the above conditions, the drift could be associated with a decrease in cathode temperature of the order of 1°K/h caused by a decrease in battery emf of the order of one part in a thousand per hour (assuming solely radiative cooling of the emitter and constant emitter resistance). Measurements made on consecutive days showed differences of 5 to 50 mV in the retarding potential measured at 600°C and ostensibly the same filament current, but no appreciable change was found in the change in retarding potential with temperature. Since the emitter battery was disconnected, recharged each night, and then reconnected, small changes in contact resistance and state of charge, and hence small changes in the cathode temperature were to be expected. Such changes could adequately account for the differences in the retarding potential observed. This in no way affected the changes in retarding potential with anode temperature. While the above measurements were made using an anode current of approximately 5×10^{-6} A, consistent test results were also obtained using currents one and two decades lower. The last of these results required correction for leakage resistance in the anode circuit.

Results of measurements made with copper samples of (211), (221), (110), and (111) orientations are shown in Fig. 4. The vertical position of the curves is not significant. The results of all the measurements are summarized in Table I where $d\Phi/dT$ at 600°K is listed.

Accurate values of the absolute work function in the temperature range used have not been measured for single crystal copper. Results of measurements by Rose,[6] however, indicated that the (100) face is positive with respect to the (111) face and that a difference of the order of 0.5 V exists. By photoelectric measurements Underwood[7] obtained values of 5.64, and 4.89 V for the (100) and (111) faces of well outgassed copper crystals at room temperature. In Fig. 5 the results of the present measurements have been fitted to Underwood's values of the work function at room temperature. Also shown is Bolshov's[8] thermionic measurement of the work function of copper at the melting point assuming that the Richardson constant A is 120 A/cm^2/°K^2.

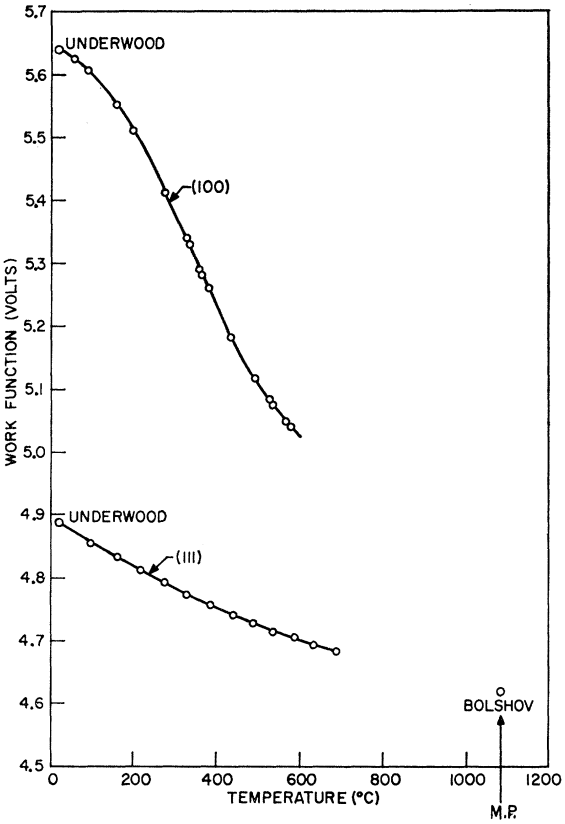

FIG. 5. The results from Figs. 3 and 4 are used to demonstrate the relationship between Underwood's photoelectric measurements on copper at room temperature and Bolshov's thermionic measurement at the melting point.

Bolshov observed that the thermionic emission from pure copper varies continuously as the temperature is raised through the melting point. It is thus reasonable to expect that the work functions of all faces of a crystal should approach a common value near the melting point. The present results show that this approach is apparent over a surprisingly large temperature range and might well be an important factor in determining the temperature dependence of the work function of thermionic emitters.

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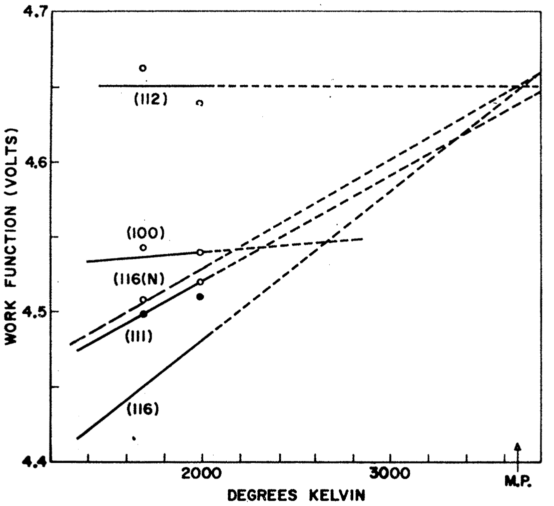

FIG. 6. The work functions of single-crystal faces of tungsten as a function of temperature. Solid line, Smith; dashed line, Nichols (116(*N*)); ○ Hutson; ● Hutson (116).

The following thermodynamic reasoning shows that the approach of the work function to a value independent of orientation may be observed generally. The work function of a single crystal with only one type of crystal face exposed can be expressed as

$$q\Phi = (\partial G/\partial n)_{P,T}, \tag{3}$$

where G is the Gibb's free energy and n the number of electrons in the crystal. Since melting is a first-order phase transition, the Gibb's free energy is unchanged during the transition, i.e.,

$$G_s(n,P,T_m) = G_l(n,P,T_m), \tag{4}$$

where the subscripts s and l refer to the solid and liquid, respectively. If the crystal is given a small net charge the nature of the transition will be unchanged, and if the melting point T_m is unaltered,

$$G_s(n+\Delta n, P, T_m) = G_l(n+\Delta n, P, T_m). \tag{5}$$

Thus

$$(\partial G_s/\partial n)_{P,T_m} = (\partial G_s/\partial n)_{P,T_m} \tag{6}$$

and

$$\Phi_s = \Phi_l.$$

However, $\partial G_s/\partial T \neq \partial G_l/\partial T$ for first-order transitions and a discontinuity in $d\Phi/dT$ should be expected.

A pattern similar to that for copper is found for tungsten. Smith's[9] thermionic measurements are plotted in Fig. 6 assuming that the Richardson constant A is 120 A/cm^2/°K.[2] The extrapolated values for the (112), (116), and (111) faces tend to converge near the melting point. The (100) face does not fit this pattern.

Hutson's[3] contact potential measurements are also included in Fig. 6. These are matched to Smith's work function determination for the (100) face at 2000°K. Hutson's result for the (116) face is bracketed by Smith's measurement and an earlier result due to Nichols.[10] If a reflection coefficient of the type found by Hutson is used in the interpretation of Smith's thermionic measurements or if Hutson's results at 1700°K are adjusted downwards 5 mV in accordance with Smith's[11] suggestion that the reflection coefficient may be spurious, the qualitative features of the results are unchanged.

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