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Work Function of Iron Surfaces Produced by Cleavage in Vacuum*

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Kelvin measurements of the contact potential difference between iron surfaces prepared by cleavage in high vacuum and freshly flashed tungsten surfaces are reported. From these measurements, the work function of iron could be found since the work function of the tungsten was known. The work function of the cleavage plane of iron was 4.17±0.03 electron volts at liquid nitrogen temperature. Evidence indicating that these measurements were made on clean surfaces is presented. The work function which has been determined is believed to be that of the (100) plane of iron.

I. INTRODUCTION

NUMEROUS measurements of the work function of iron have been reported.[1–10] Most of these were probably on surfaces which were contaminated by at least a monolayer of adsorbed gas because either the pressure in the experimental tube was too high to maintain a clean surface or the method of preparation did not produce a clean surface. Iron can probably not be cleaned simply by heating in vacuum.[11] The measurements by Riviere[10] on films evaporated in very high vacuum do not seem to suffer from these objections.

This report describes contact potential difference measurements between iron surfaces produced by cleavage at liquid nitrogen temperature in high vacuum and freshly flashed tungsten ribbons. Particular attention was given to the preparation of the surfaces to insure that they were clean. Since the work function of tungsten was known, the work function of clean iron could be found.

2. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. The Method of Measurement

The measurements were made by the Kelvin method using a dynamic capacitor, the elements of which were a cleaved iron crystal surface and a vibrating tungsten ribbon. The use of electronic feedback allowed rapid and continuous measurements to be made. A known voltage from a $K-1$ potentiometer was placed across the dynamic capacitor to check the calibration of the measuring system. The time constant of the circuit was approximately 1 second. A block diagram of the measuring system is shown in Fig. 1.

The feedback voltage, E_f, which was recorded continuously during the measurement was related to the contact potential difference (cpd) by the following equation:

$$E_f=\text{cpd}(1+1/G), \tag{2.1}$$

G is the gain of the system including the conversion efficiency of the dynamic capacitor. The conversion efficiency is defined as the ratio of the rms ac voltage across the dynamic capacitor divided by the dc voltage across it. The maximum capacity of the dynamic capacitor used in this experiment was only $\sim 10^{-13}$ farad and the conversion efficiency was approximately 5×10^{-3}. The use of a high gain amplifier, however, brought G up to 1000 making the feedback voltage the same as the cpd to 0.1%.

Because of the small size of the dynamic capacitor, the effect of stray capacity between the dynamic capacitor elements and the surrounding elements will be considered in detail. The effect of stray capacity was to make the measured or apparent cpd differ from the actual cpd as follows:

$$\text{cpd}=[\text{cpd (apparent)} - (\sum_{i\neq h,l} \Delta C_{hi}(V_i-V_h)/\Delta C_{hl})], \tag{2.2}$$

where the subscripts h and l refer to the high-impedence (tungsten) and low-impedence (iron) elements of the dynamic capacitor and i refers to other elements in the experimental tube. ΔC_{hi} is the maximum difference in

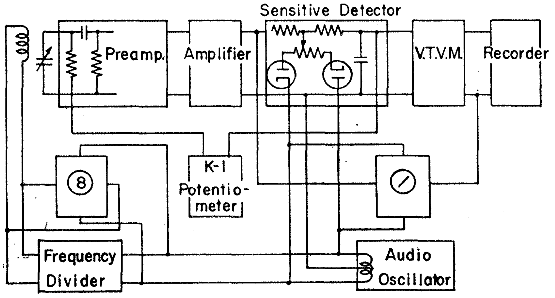

FIG. 1. Block diagram of the measuring circuit.

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[1] A. B. Cardwell, Proc. Natl. Acad. Sci. U. S. **14**, 439 (1928).

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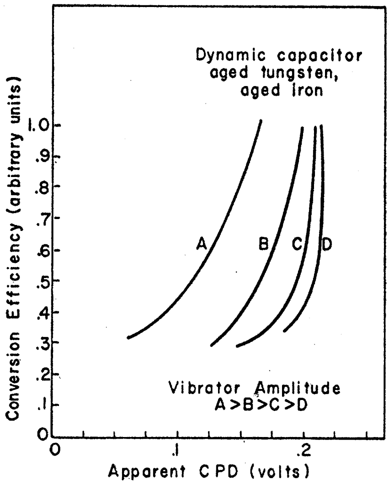

FIG. 2. Measured or apparent cpd plotted as a function of conversion efficiency. The conversion efficiency was increased by decreasing the spacing of the dynamic capacitor elements.

capacity between elements *h* and *i* during a cycle of vibration of the dynamic capacitor.

The effect of stray capacity was investigated by varying the spacing between the dynamic capacitor elements and by varying the amplitude of the vibrator. A small decrease in spacing between the dynamic capacitor elements causes a large increase in ΔC_{hl}, since the separation between them is small. Such a change in spacing has little effect on ΔC_{hi} since elements *h* and *i* are widely spaced. Therefore, as the spacing between elements *h* and *l* is decreased, the apparent cpd should approach the cpd. When the amplitude of vibration is decreased, both ΔC_{hl} and ΔC_{hi} are decreased. The effect on ΔC_{hl} can be compensated for by decreasing the spacing between elements *h* and *l*. Therefore, as the amplitude is decreased but ΔC_{hl} kept constant, the effect of stray capacity should decrease.

Since it was not possible to measure the spacing between the dynamic capacitor elements directly, the apparent cpd was measured as a function of the conversion efficiency of the dynamic capacitor. The conversion efficiency is inversely proportional to the spacing between the elements in the limit of small spacing. The gain of the amplifier was varied to keep the total gain of the system, *G*, near 1000. Figure 2 shows the results of these measurements. As expected, the apparent cpd approaches a limiting value, which is taken to be the real cpd, as the spacing is decreased. Also, the effect of stray capacity is smaller for smaller amplitudes of vibration. Since all the measurements reported here were made with the smallest amplitude of vibration and with the smallest spacings shown in Fig. 2, the effect of stray capacity introduced a probable error of less than ±0.002 volt in the cpd measurements.

B. Reference Surface

Tungsten was used for the reference surface because it can be cleaned in vacuum simply by heating to high temperature and because it has a reproducible work function. Tungsten ribbons, kindly supplied by E. Taft of the General Electric Research Laboratory, were prepared by heating to 2700°K for 1 hour in vacuum. Since the ribbons came from the same stock, were given the same heat treatment and, as a result, were observed to have the same small grain size as the ribbons studied by Apker, Taft, and Dickey,[12] it has been assumed that their work function is the same, namely, 4.49±0.02 electron volts.

Large-grained polycrystalline ribbons prepared by high-temperature heat treatment, or by pulling tungsten ribbons through a temperature gradient were also used as reference surfaces. Since it proved impossible to determine their work functions directly, the cpd measurements in which they were used did not give information on the work function of iron. However, they were useful in evaluating the technique.

C. Iron Crystals

The iron crystals used in this experiment were cut from a single crystal rod of Armco iron purchased from the Virginia Institute for Scientific Research. The nominal impurities in this material were 0.02% carbon, 0.03% manganese, 0.009% phosphorous, 0.016% sulfur in addition to unknown amounts of nitrogen and oxygen. Pieces 0.050 in.×0.250 in.×0.500 in. were cut from this rod with each face within 4 degrees of a (100) plane.

Cleavage of the crystals was achieved, after cooling them to liquid nitrogen temperature, by placing a chisel which had been ground to an angle of 45 degrees into a narrow notch cut in the edge of the crystal and applying a slowly increasing force until fracture occurred. The cleavage was not a cutting operation since in no case did the chisel reach the bottom of the notch. The resolved cleavage force was measured to be about 30 tons per square inch in agreement with that observed when direct tensile stresses were applied to iron crystals.[13]

FIG. 3. Photomicrograph of a cleaved iron surface showing an area 0.0037 ×0.005 square inch.

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[12] Apker, Taft, and Dickey, Phys. Rev. **73**, 46 (1948).

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Examination of the cleaved surfaces showed that while they were quite rough, more than 95% of the surface was made up of valleys and plateaus parallel to the (100) plane. These were separated from each other by boundaries which were on twin planes of the crystal. This is consistent with the assertions of Biggs and Pratt[14] that twins are produced by deformation which occurs before and during cleavage. Figure 3 is a photomicrograph of a cleaved surface.

In addition to the large structure, a fine structure is observed. This was probably due to small steps, or slipped and torn regions on the surface. A back-reflection Laue picture of the cleaved surface gave no indication of distortion deep in the crystal.

D. Experimental Tube

The experimental tube is shown schematically in Fig. 4. The iron crystal was mounted on a flange on the bottom of a monel bellows. The bellows could be extended by a screw to press the crystal onto a chisel for cleaving, and could be distorted to provide lateral motion of the crystal. The crystal could be moved one inch in the lateral direction. This motion was used to bring the freshly cleaved iron face close to the reference surface for measurement. In addition, it allowed up to three cleavages to be made without opening the tube. To cool the crystal, the entire tube was immersed in liquid nitrogen.

The tungsten frame which supported the reference surface was mounted on a Kovar rod by means of glass insulators. The rod was vibrated by the magnetic interaction between the rod and the driving coil. Since the driving voltage had half the frequency of the vibrator, it could be separated from the amplifier by a filter. Flexible leads to the tungsten ribbon allowed it to be flashed by resistance heating. A shield, which moved between the iron and tungsten when the iron was moved away from the reference surface, protected the iron from the evaporation products from the tungsten.

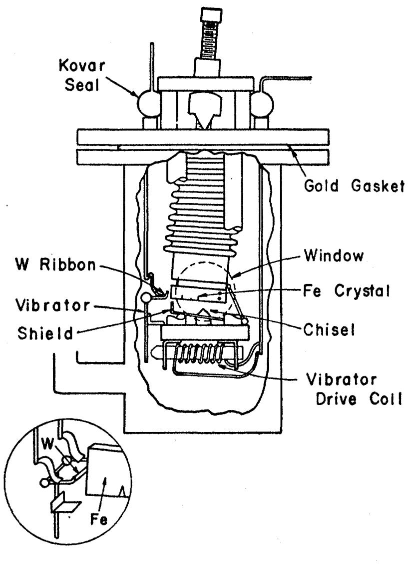

FIG. 4. Schematic of the experimental tube. Inset shows details of the vibrator assembly.

TABLE I. Summary of experimental data.

Run	Cpd (volts) extra-polated to $t=0$	Rise in pressure during cleavage (mm Hg)	Description of tungsten	Work function of tungsten (ev)	Work function of iron (ev)
1	0.385	$\approx 2\times 10^{-10}$	Large crystallites	...	...
3	0.395	$<10^{-10}$	Large crystallites	...	...
6	0.317	$<10^{-10}$	Large crystallites	...	...
7	0.310	$<10^{-10}$	Large crystallites	...	...
8	0.325	$<10^{-10}$	Large crystallites	...	...
9	0.270	$<10^{-10}$	Single crystal oriented within 8° of (114)	4.42 ± 0.05[a]	4.15
10	0.300	$<5\times 10^{-10}$	Small crystallites	4.49 ± 0.02[b]	4.190
13	0.325	$<5\times 10^{-11}$	Small crystallites	4.49 ± 0.02[b]	4.165
14	0.325	$\approx 2\times 10^{-10}$	Small crystallites	4.49 ± 0.02[b]	4.165

[a] Found by a linear extrapolation between the work function of the nearest principal planes of tungsten as measured by Smith (reference 15).
[b] From Apker, Taft, and Dickey (reference 12).

The tube was evacuated by a conventional mercury pump system with a bakable liquid nitrogen trap. An Alpert valve was used to seal the tube from the pumps. A Bayard-Alpert type ionization gauge and a molybdenum getter were connected to the tube. Baking at 325°C for 10 hours was usually sufficient to reduce the pressure to 5×10^{-9} mm Hg in the sealed-off tube. Upon immersion in liquid nitrogen, the pressure in the tube became less than 8×10^{-10} mm Hg.

3. RESULTS

Measurements on nine iron surfaces are summarized in Table I. Figures 5 and 6 show the change in cpd as a function of time. In runs 6, 7, and 8 and in runs 13 and 14, respectively, the same tungsten reference surfaces were used. Measurements were usually begun within 2 minutes after the iron was cleaved. The tungsten was flashed several times at 2400°K, the last time less than 15 seconds before the iron was cleaved. The slow change in cpd allowed the measurements to be extrapolated back to the time of cleavage to get the cpd between clean iron and clean tungsten.

After following the change in cpd for 10 to 20 minutes, the tungsten ribbon was flashed, thus restoring it to its condition at $t=0$. This allowed the change in work function of the tungsten to be separated from that of the iron. The change in work function of the iron was observed to be comparable to that of tungsten. The decrease in cpd with time observed in runs 10 and 14 is believed to be due to a change in composition of the gas in the tube caused by either adsorption in the cooled tube or a small leak in the tube induced by the nitrogen bath.

Measurements of the pressure in the system indicated

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[14] W. D. Biggs and P. L. Pratt, Acta Met. 6, 694 (1958).

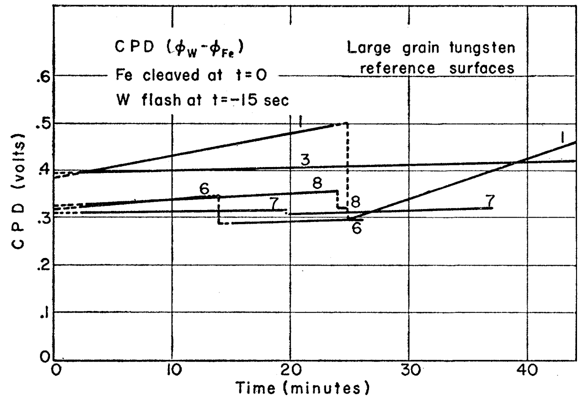

FIG. 5. Cpd as a function of time between freshly flashed tungsten and cleaved iron. Dashed lines indicate extrapolations.

that little or no gas was evolved during the cleavage. The apparent pressure rise observed in runs 1 and 14 (Table I) is believed to be due to electrical pickup in the measuring circuit caused by motion of the tube at the instant of cleavage. Even if the apparent pressure rise was real, it was less than 2% of the observed pressure rise when approximately one monolayer of gas was flashed off the tungsten reference ribbon, which was comparable in area to the cleaved surfaces.

4. DISCUSSION

On the basis of the three measurements in which the small grained polycrystalline ribbon was used as a reference surface, the work function of the cleavage face of iron has been found to be 4.17±0.03 electron volts. The limits of precision of the cpd measurement are ±0.01 volt; however, imperfect knowledge of the work function of the reference surfaces causes the limits of error on the work function to be extended. The measurement in which a single crystal of tungsten was used is in agreement with the above value, although there the limits of error are ±0.05 electron volt because of the way in which the work function of the tungsten was determined (see the note on Table I). Using the value of 4.17 electron volts for the work function of iron, the work function of the large-grained polycrystalline tungsten used in runs 1, 3, 6, 7, and 8 can be found. These were between 4.56 and 4.48 electron volts, well within the range of work functions observed for tungsten of different crystallographic orientations.[15]

The following arguments suggest that the iron surfaces produced by cleavage were clean. (1) The work function of the cleaved surfaces was reproducible. In the runs in which the same reference surfaces were used (runs 6, 7, and 8 and runs 13 and 14), the cpd was the same to ±0.01 volt. (2) The rate of change of the work function of iron was comparable to that of freshly flashed tungsten. (3) The quantity of gas given off during cleavage was too small to appreciably contaminate the surface. (4) Contamination of the surface by diffusion of impurities from the bulk to the surface is unlikely at liquid nitrogen temperature. τ, the mean time an atom stays in an interstitial position in iron is found to be greater than 10^{12} seconds for N_2, C, and H_2 at this temperature by putting experimental diffusion data[16–18] into the expression for τ derived by Zener.[19] (5) The surface is probably not contaminated by surface diffusion of impurities. Gomer *et al.* have shown that while oxygen[20] and hydrogen[21] are not mobile on a clean tungsten surface below 400°K and 180°K, respectively, they can diffuse over contaminated surfaces to the clean surface at lower temperatures. It is estimated that the rate of diffusion had to be less than 2×10^{-6} cm/sec for Gomer to see this effect on a small field-emission tip. For iron surfaces of the dimensions used in the experiment reported here to be covered by the same process would require at least 5×10^4 seconds, a time too long to affect this experiment.

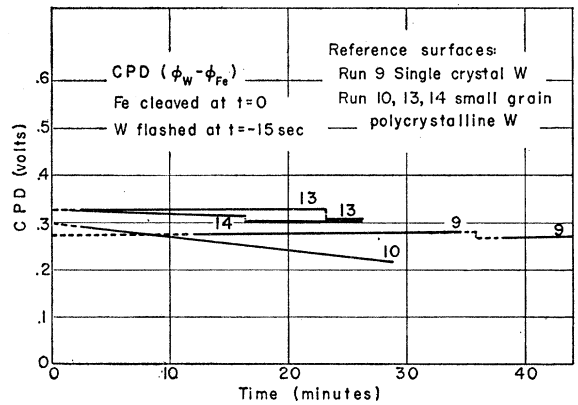

FIG. 6. Cpd as a function of time between freshly flashed tungsten and cleaved iron. Dashed lines indicate extrapolations. The work function of iron was obtained from these data.

The work function of the cleaved iron is believed to be that of the (100) plane of iron. Although the surface was rough, an estimated 95% of the surface was made up of regions parallel to the (100) plane. The large steps separating these regions probably had no effect since the surface was in an equipotential region during the measurement. Arguments of Morant and House[22] indicate that the small scale roughness would not affect the measurement. The approximately 5% of the surface which was not parallel to the (100) plane probably had

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negligible effect on the results.[23] In addition, the reproducibility of the work function of the iron suggests that a single-crystal plane is probably exposed by cleavage.

The exact agreement between the results reported here and those of Riviere[10] must be considered fortuitous. The exposed planes on a film evaporated on a cold glass substrate cannot be expected to be the same as those on a cleaved surface.

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[23] Even if the work function of 5% of the surface differed by 0.5 electron volt from the rest of the surface, it would change the measured work function by only 0.03 electron volt. For further discussion of the patch effect see C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949).

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Thermoelectric Power of Cold-Rolled Pure Copper*

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The difference between the thermoelectric power of severely cold-rolled and well annealed pure copper has been measured between about 8°K and 320°K. The absolute thermoelectric power of our annealed and cold-worked samples were determined over the same temperature range by measuring the thermoelectric power of a thermocouple formed from annealed pure copper and pure lead. The thermoelectric power of cold-rolled copper is positive relative to annealed pure copper over the entire temperature range, and the effect of cold work is largest at very low temperatures where the thermoelectric power of annealed copper displays a pronounced minimum. Our results are in fair agreement with recent work by Powell and by van Ooijen.

INTRODUCTION

We report here the result of measurements of the thermoelectric power (TEP) of severely cold-rolled pure copper between about 8°K and 320°K. The investigation of the TEP of cold-worked metals is a natural sequel to the studies of the resistivity due to cold work.[1] Indeed, the change in the TEP due to cold work has already been studied experimentally[2] and theoretically.[3] The experimental work of the past was carried out using relatively impure copper (99.98% and 99.97% pure). Studies of very dilute copper alloys have shown conclusively that minute amounts of certain impurities can change the TEP of copper by orders of magnitude at low temperatures.[4] Recently Powell has reexamined the TEP of cold-worked pure copper, using material of the highest purity available, and has obtained good agreement with previous work.[5]

EXPERIMENTAL PROCEDURE

Our samples were prepared from nominally 99.999% pure copper supplied by the American Smelting and Refining Company. The metal, in the form of cylindrical billets of about 5-mm diameter, was cold-rolled at room temperature into strips about 5 mils thick. Some of these strips were then annealed for three hours in vacuum (pressure less than 10^{-5} mm Hg) at 950°C. A thermocouple was formed using an annealed and an unannealed strip, and the thermal emf's were measured with a Leeds and Northrup microvolt amplifier. The temperature difference between the cold junction (in liquid He, liquid air, or ice bath) and the hot junction was measured by means of calibrated gold-2.1% cobalt *versus* copper and copper *versus* constantan thermocouples.[6]

We estimate that our errors are ±1.5% of the measured thermoelectric emf and ±0.1°K for the temperature measurements. We have also carried

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[6] We are grateful to R. L. Powell and M. D. Bunch of the National Bureau of Standards for providing us with some calibrated copper constantan and copper and gold-cobalt thermocouple wires.

FIG. 3. Photomicrograph of a cleaved iron surface showing an area 0.0037 ×0.005 square inch.