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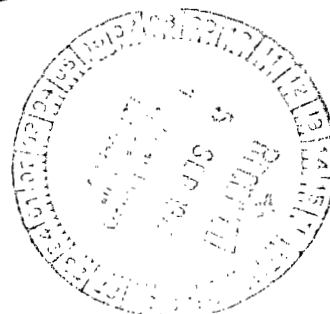
DETERMINATION OF WORK FUNCTIONS NEAR MELTING POINTS OF REFRACTORY METALS BY USING A DIRECT-CURRENT ARC

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16. Abstract

Effective work functions of refractory metals at temperatures near their melting points were determined by using a direct-current arc. A metal wire connected as the cathode was melted by striking an arc discharge in an argon atmosphere. A melted sphere was formed with a definite emitting area which was calculated from the sphere diameter measured after terminating the arc. Effective work functions were calculated from the Richardson-Dushman equation by using this emission area. The procedure is experimentally advantageous because surface cleanliness of the specimen is not critical, high vacuum is not required, and the anode-cathode spacing is not critical.

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SUMMARY

A direct-current arc in argon at atmospheric pressure was used to determine effective work functions of refractory metals, including tantalum, tungsten, molybdenum, and niobium. The procedure is experimentally advantageous because surface cleanliness of the specimen is not critical, high vacuum is not required, and the anode-cathode spacing is not critical. The experimental procedure involves striking an arc to a metal wire cathode to form a melted ball having an emitting area defined by its diameter. The literature melting point of the metal is taken as the emitting temperature. By using these parameters and the known arc current, effective work functions were calculated from the Richardson-Dushman equation. The calculated work functions agree with recommended handbook values to within about 0.1 volt and have typical repeatabilities of 0.02 volt. By varying the arc current, Richardson plots can be made over a temperature range from a few hundred degrees below the melting point to about 50° over the melting point of the test metal. A Richardson plot over this temperature range is presented for tantalum.

INTRODUCTION

The free-running direct-current arc at near atmospheric pressure is generally considered to be characterized by thermionic emission of electrons from the cathode (ref. 1). However, the arc has not been used as a method for quantitatively determining thermionic work functions. One literature reference was found which alluded to this possibility (ref. 1), but quantitative calculations were not reported. Current reviews of various methods of determining work functions do not refer to the direct-current arc (refs. 2 and 3).

Recently, the first author developed an argon arc configuration for use in spectrochemical analysis (ref. 4). Conditions were reported for achieving spatial stability of

the arc by means of a cathode with a spherical tantalum tip. In the development of this cathode, studies were made of various refractory-metal cathodes with respect to cathode temperature, arc current, and cathode emitting area. Under certain conditions, the relations among these parameters were reproducible and consistent with the Richardson-Dushman equation

$$j = A_o T^2 \exp\left(\frac{-e\varphi}{kT}\right) \tag{1}$$

where

j emitting current density, A/cm^2

A_o Richardson emission constant $(120.4 \ A/(cm^2)(K^2))$

T cathode temperature, K

e elementary charge $(1.602\times10^{-19} \ C)$

φ work function, V

k Boltzmann constant $(1.380\times10^{-23} \ J/K)$

Further investigation has demonstrated that the arc discharge can be advantageous for determining thermionic work functions of refractory metals at, or near, their melting points. This method is simple and a measurement can be made in about 5 minutes. Some other advantages of the arc method are negligible contamination of the emitting surfaces, high vacuum is not required, and electrode spacing of about 1 centimeter is not critical. The determinations are highly repeatable, and the work functions determined agree with the recommended literature values.

The results of this work are explained by using a simple model of the arc which assumes that the electron emission from the cathode is purely thermionic and that all the arc current is electronic. Possible errors due to positive ion currents and electric fields are also discussed.

APPARATUS AND MATERIALS

The apparatus used in this work consisted of an airtight chamber, a direct-current arc supply, refractory-metal wires, and an optical pyrometer. The relevant characteristics of these items are described in this section.

Airtight Chamber

The airtight chamber is shown schematically in figure 1. It consisted of a quartz cylinder sandwiched between steel plates with provisions for introducing gases and for evacuation. An airtight seal was made between the quartz ring and the steel plates by means of rubber gaskets recessed in grooves machined in the steel plates. The plates were connected to the electrical supply with the test wire as the cathode, as shown. A bellows seal in the cathode retractor allowed the spacing between the electrodes to be varied from contact to about 15 millimeters.
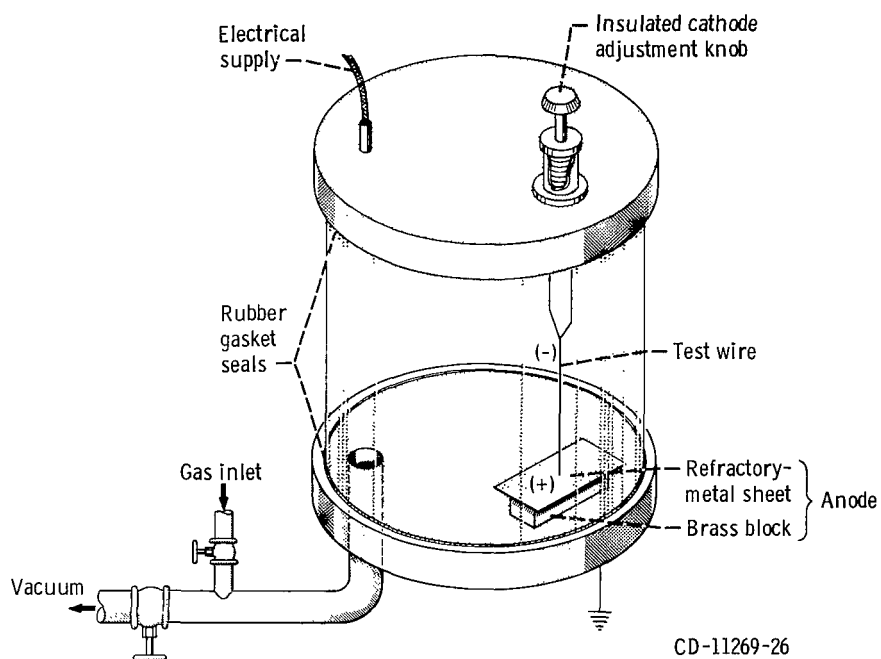

Figure 1. - Schematic of arc chamber for work function determinations.

Direct-Current Arc Supply

The arc supply was full-wave rectified, thyratron controlled, and inductor-capacitor filtered. The root-mean-square ripple was about 3 percent at 30 amperes. The primary voltage was 220 volts at 60 hertz. The secondary voltage applied to the electrodes was about 180 volts. Currents from a few amperes to about 60 amperes could be supplied. The current to the arc supply was controlled by a feedback loop to ensure constant current output irrespective of electrode spacing or vapor composition in the arc column.

Refractory-Metal Wires

The polycrystalline metal wires used in this work and their diameters in millimeters were as follows: tungsten (W), 0.3; rhenium (Re), 1.75; tantalum (Ta), 0.75; molybdenum (Mo), 1.0; and niobium (Nb), 1.0. These materials were of ordinary metallurgical grade and were nominally between 99.5 and 99.9 percent pure.

Optical Pyrometer

Temperature measurements for the data used to make Richardson plots were made with a micro-optical pyrometer located about 1.52 meters (5 ft) from the arc. The method of calibrating the pyrometer and correcting for the optical effects of the quartz cylinder and the emissivity of the cathode metal are cited in the section PROCEDURE.

PROCEDURE

Three variations of the procedure for determining work functions are described in this section. These procedures were used to determine work functions from (1) current density measurements at the cathode melting point; (2) a plot of the linear form of equation (1), commonly called a Richardson plot; and (3) the slopes of Richardson line segments as a function of temperature by a more detailed analysis of the data from procedure 2. Method 1 was applied to Nb, Mo, Ta, W, and Re wires. Methods 2 and 3 were applied to Ta wires only to illustrate the procedure by which the effective thermionic emission constant, as well as the work function, can be determined.

Determination of Work Functions at Cathode Melting Point

The refractory-metal wire to be tested was mounted as the cathode, in contact with an anode configuration, as shown in figure 1. The anode was a piece of sheet stock, of the same metal as the cathode, resting on a brass block. This anode configuration provided conductive cooling, reducing the evaporation of the anode material.

The chamber was evacuated to about 10^{-3} torr and backfilled with argon to about 700 torr. The arc current source was adjusted to deliver about 30 amperes, the precise current being read from the current meter during operations. The arc voltage was applied; and, after a few seconds with the electrodes in contact, the wire cathode was withdrawn to form the arc gap. The final arc gap was adjusted to about 1 centimeter. The cathode

spot formed on the wire tip and fused the wire to form an approximately spherical emitting area. The arcing was continued until the sphere ceased to increase in size. Normally, about 30 seconds of arcing was sufficient to achieve the maximum sphere size. When no increase in sphere size was observed over a period of 15 to 20 seconds, the sphere size was assumed to be at thermal steady state. Once this had occurred, the emitting sphere would not further increase in size. The arc was then terminated, the wire cathode was removed from the arc chamber, and the diameter of the spherical tip was measured.

The work function calculations were made by using the Richardson-Dushman equation (1). The current density j was determined by the ratio i/a, where i is the arc current and a the emitting area as determined from the measured sphere diameter by the relation $a = \pi d^2$. The emitting temperature T is the metling point of the cathode metal, taken from reference 5.

Richardson Plots

Equation (1) can be written

$$\ln\left(\frac{j}{T^2}\right) = -\varphi\left(\frac{e}{kT}\right) + \ln A \tag{2}$$

where A is the effective emission constant as distinct from A_o, the fundamental emission constant. Therefore, by plotting $\ln(j/T^2)$ as a function of e/kT, a linear graph was obtained with a slope of negative φ and an intercept of $\ln A$.

Richardson plots require data of emitting temperature T as a function of emitting current density j. Such data were obtained by first forming a molten spherical emitting surface at the tip of the refractory-metal test wire while running the arc at a moderately high current, for example, 50 amperes for tantalum. Then, the arc current was reduced at intervals of about 2 amperes while the cathode emitting temperature was read at each current interval with a micro-optical pyrometer. After reaching a lower current of about 10 amperes, the arc current was then increased and the emitting temperature again recorded at about 2-ampere intervals up to about the starting current.

The temperature readings were obtained with a micro-optical pyrometer which was calibrated by using a National Bureau of Standards tungsten ribbon lamp placed inside the quartz cylinder to correct for optical effects. The pyrometric temperature readings were then corrected for the emissivity of the tantalum (0.36) from reference 6, using a method of correction from reference 7.

This procedure produced the emitting temperature and current data, at constant cath-

ode emitting area, over a temperature range from about 3000 to 3300 K. These data were treated first by computing a least-squares linear fit having a slope of $-\varphi$ and an intercept equal to ln A. A quadratic fit was also determined to detect significant deviation from the predicted linearity. Next, a FITLOS (ref. 8) curve-fitting procedure was applied to examine in more detail what appeared to be nonlinear distribution of data at the high-temperature end of the plot. The force-fitting provision of this program was used, allowing a 1-percent deviation of the data from the fit for each segment of the curve. The necessary number of segments and locations of spline joints were determined by the computer's utilization of the data. This procedure allowed detection of significant deviations from the least-squares linear and single quadratic fits in various segments of the total range of data.

Such a fit, being a smooth coupling of up to 10 quadratics, can follow the data more closely through its nonlinear excursions. It thereby is a fairly good detector of regions of nonlinearity. Deviations of this fit from linearity were indicated by significant variations in its first derivative.

This experiment was conducted three times, and the data obtained were processed in the manner described in this section.

RESULTS

Effective Work Functions

Effective work functions were determined for metals including W, Ta, Mo, Re, and Nb. Table I is a summary of effective work functions obtained from measurement of

TABLE I. - SUMMARY OF WORK FUNCTION

DETERMINATIONS BY DIRECT-CURRENT

ARC METHOD

Metal	Melting point,[a] K	Work functions, V	
		By arc method	Recommended value[b]
Mo	2883	4.3	4.3
Nb	2741	4.0	3.99
Re	3453	5.1	5.0
Ta	3269	[c]4.13	4.12
W	3683	4.5	4.5

[a]Ref. 5.
[b]Ref. 2.
[c]Standard deviation for five consecutive determinations, 0.013 V.

sphere diameters formed at 30 amperes and by application of equation (1). Also listed in table I are the recommended values from reference 2 for these metals. Metal cathodes formed in typical experiments are shown in figure 2. The repeatability of the work functions for Ta was 0.013 electron volt, standard deviation, for five consecutive determinations. This repeatability was typical of the other refractory metals. The work functions were also in good agreement with the recommended values for refractory metals from reference 2.
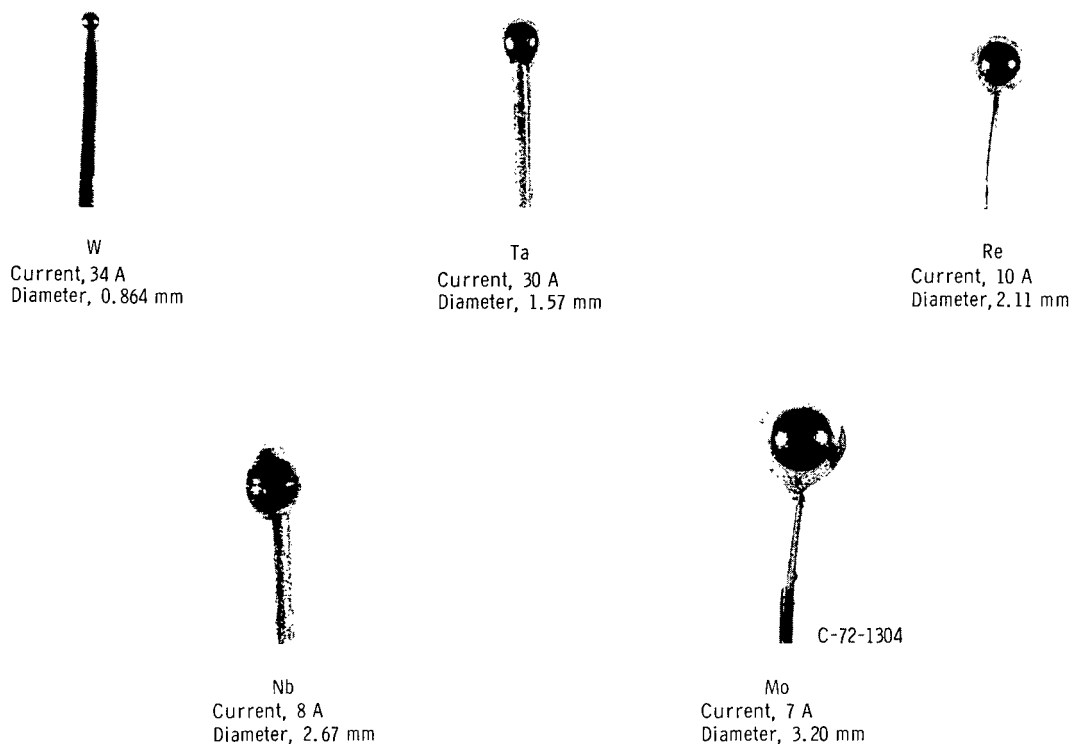

W
Current, 34 A
Diameter, 0.864 mm

Ta
Current, 30 A
Diameter, 1.57 mm

Re
Current, 10 A
Diameter, 2.11 mm

Nb
Current, 8 A
Diameter, 2.67 mm

Mo
Current, 7 A
Diameter, 3.20 mm

C-72-1304

Figure 2. – Examples of spherical emitting surfaces formed on refractory-metal cathodes.

Determination of φ and A by Richardson Plots

Richardson plots, from which φ and A values for equation (1) can be determined, can also be made by the arc method. Data for tantalum are shown in figure 3 with a linear least-squares fit (solid line) and a quadratic fit (dashed line) superimposed. The standard deviation of the quadratic fit (0.085) is not significantly better than that of the linear fit (0.093), thus indicating the linear fit to be as precise as the higher degree fit. This linear least-squares fit was used to determine φ and A in the Richardson-Dushman equation (1), which predicts a linear relationship between $\ln j/T^2$ and e/kT, having a slope of $-\varphi$ and an intercept of $\ln A$, in equation (2). From such a fit of the data in figure 3, over the full temperature range shown, $\varphi = 4.50$ volts, and $A = 343.9$ A/(cm^2)(K^2). Another similar experiment was conducted; and when the data obtained were treated in the manner described, yielded $\varphi = 4.46$ volts and $A = 311.04$ A/(cm^2)(K^2).

Applying a FITLOS curve-fitting procedure to the data resulted in the curve having a standard deviation of 0.082 shown in figure 4(a). This sectioned fit revealed a region of
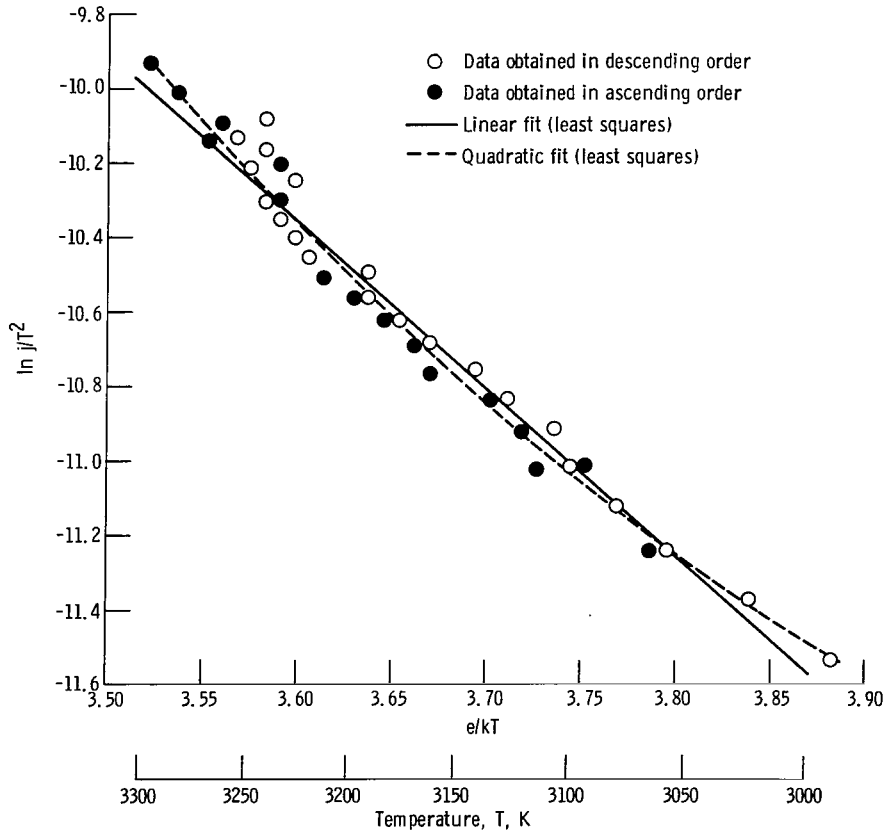

Figure 3. - Richardson plot for tantalum near melting point. Work function φ, 4.50 volts (slope = $-\varphi$); effective emission constant A, 343.9 A/(cm^2)(K^2).

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maximum inflection in an otherwise smooth, near-linear fit. Another presentation, show-ing the first derivative of the fit to these same data, appears in figure 4(b). Here the sig-nificance of the inflection point, relative to the average derivative, and its precise loca-tion on the abscissa are clearly demonstrated. The negative slope φ and the anti-log of the intercept A obtained from a linear least-squares fit of the data on the lower temper-ature side of the discontinuity were 4.04 volts and 60.64 $A/(cm^2)(K^2)$, respectively; and a similar fit on the higher temperature side yielded $\varphi = 4.80$ volts and $A = 1072$ $A/(cm^2)$ (K^2). The fits of both segments have standard deviations of 0.04. Data obtained from two other similar experiments yielded results comparable to the data of figure 4.
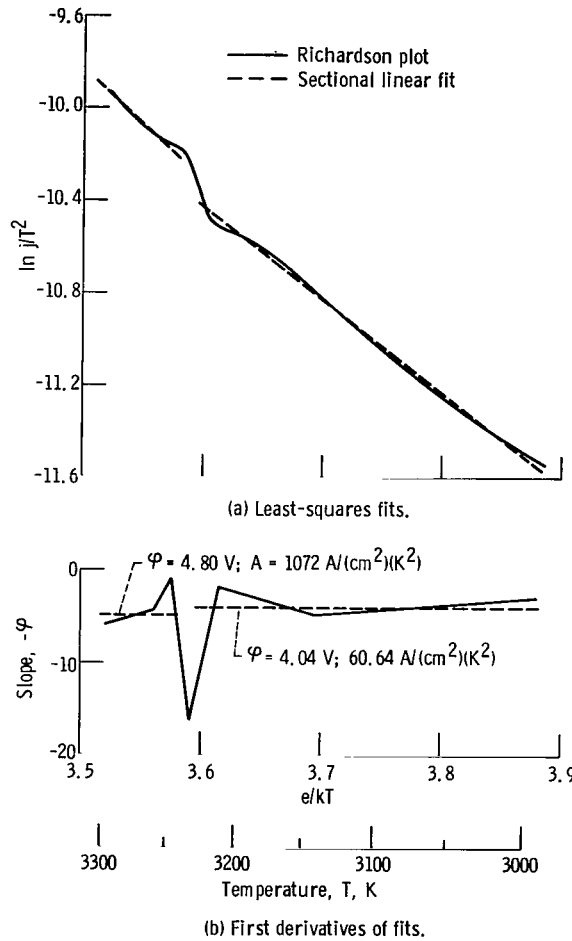

(a) Least-squares fits.

(b) First derivatives of fits.

Figure 4. – FITLOS smoothing of Richardson plot and
sectioned linear fit.

DISCUSSION OF RESULTS

The work function determinations made at the melting point of the cathode materials exhibit good repeatability and apparent accuracy. An important factor in achieving good repeatability by this method is the use of a precisely fixed emitting temperature, which allows use of the well-known melting point. An examination of equation (1) shows that the emitting temperature is the most critical variable because it appears in the exponential term. Another factor in the experiment which is conducive to good repeatability is the formation of a melted emitting sphere, which provides a well-defined emitting area.

The experimental procedure for determining work functions by the arc method is relatively simple. Only nominal evacuation of the airtight chamber is required, and no special preparation of the specimen surface is necessary. Other experimental parameters, including the anode-cathode spacing and the argon pressure in the chamber, are also not critical.

The interpretation of these work functions measured from liquid metal surfaces must be considered in light of theories for the solid state. It is well known that work functions are dependent on the crystalline structure of the metal surface. For melted cathode surfaces obtained in this work, the work functions can be considered to be representative of an equivalent solid crystalline form, for example, a hexagonal close-packed structure (ref. 9). Following this reasoning, the work functions calculated for liquid surfaces of a refractory metal such as tantalum can be considered to be equivalent to the (110) plane of a body-centered cubic metal. However, no calculations were made along these lines; and further discussion of the theoretical interpretation of these data is outside the scope of this report. These remarks, however, are intended to emphasize a problem in interpreting the results reported herein and suggest a possible approach to explain these results for liquid surfaces in terms of the solid state.

In spite of the problems of theoretical interpretation of these data, the consistency and apparent accuracy of the effective work functions suggests that this technique can be useful for investigating thermionic parameters of metals and alloys at very high temperatures.

Work Functions and Effective Emission Constants from Richardson Plots

A comparison of the linear and quadratic graphs shown in figure 3, and of their fit precisions, showed only minor differences, indicating that the data essentially conformed to equation (2). The data used to plot the Richardson line are subject to systematic pyrometric errors. Although the pyrometer calibration error was less than 20 K, including the correction for the quartz cylinder, the true emissivity of the curved Ta surface at

3000 K is now known. The value of emissivity from the literature (0.36) used to correct the pyrometer temperature readings only approximates the emissivity under the experimental conditions. However, from comparison of the experimental temperature of the melted sphere (3230 K) with the literature value for the melting point of Ta (3269 K), we estimated a probable total temperature error of about 50 K.

Examination of the FITLOS plot in figure 4 revealed that the most distinct deviation from linearity occurred within a relatively small region of e/kT. The sharp variation of the first derivative in that region and the nearly constant derivatives on either side of this maximum inflection point are indicative of an abrupt change in the thermionic emission from an otherwise well-behaved thermionically emitting surface. The truest fit, in terms of the fit precision, was obtained when the data were fit in two linear segments - one above this inflection point and one below.

The interpretation of the inflection point in the Richardson plot is believed to be related to a solid-liquid transition of the emitting surface as a function of arc current. When the cathode tip was first formed by melting, the interface between the solid wire and the melted sphere was approximately at the melting point of the cathode material. However, the average sphere temperature was slightly higher because of the small temperature gradient existing between the sphere surface, wherein the arc energy is input, and the wire-sphere interface. Therefore, when the arc current was reduced a few amperes below the initial current used to form the sphere, the emitting surface froze, resulting in an abrupt change in emissivity and in apparent emitting temperature. The difference between the melting point and the average sphere temperature was about 55 K, as indicated by the temperature range of the upper curve segment in figure 4(a).

The small temperature gradient associated with the emitting surface was the basis for interpreting the inflection point of the Richardson plots. The change in emissivity accompanying the freezing or melting of the emitting sphere caused a shift in the apparent temperature as measured with an optical pyrometer. This systematic change in emissivity qualitatively accounts for the displacement of the two sections on the graph. The work function determined from the slope of the lower temperature section (higher e/kT) of figure 4(a) is not necessarily the same as those determined by calculation from equation (1). As pointed out in reference 2, the slope of the Richardson line is a measure of φ_0, the work function at absolute zero, and does not reveal a temperature dependency $d\varphi/dT$ of the work function. Such a dependency is usually constant and is, therefore, indistinguishable from a change in the A value. The slope and intercept of the higher temperature section of the Richardson plot of figure 4(a) are significantly greater than the slope and intercept of the lower temperature section, apparently indicating a change in $d\varphi/dT$ of Ta at the melting point. This explanation is in agreement with reference 10, in which both experimental results and a theoretical derivation are given for copper to substantiate the existence of a discontinuity of $d\varphi/dT$ at the melting point. In our experiment, visual

observations also tended to support this interpretation. The appearance of the emitting surface became visually duller as the current density was lowered through the level corresponding to the observed maximum inflection point on the Richardson plot. Nevertheless, it was not possible in the experiment to directly detect the solid-liquid transition instrumentally. Therefore, direct experimental evidence establishing unambiguously that the inflection point of the Richardson plot was indeed a result of a phase transition could not be obtained.

Thermionic Model of Direct-Current Arc

The calculation of work functions by the arc method will be accurate only if the cathode emission in the direct-current arc is quantitatively described by the parameters of equation (1). Insofar as the cathode emission might deviate from this simple model, the work functions can be inaccurate. Although proof of the accuracy of the work function measurements is not within the scope of this report, it is instructive to qualitatively examine possible sources of errors and, where possible, to estimate their magnitude on work function determinations. Because of the simplifying assumptions made in the method of calculating work functions described herein, it might appear surprising that the arc technique has even an apparent validity. The straightforward calculations of work functions from the Richardson-Dushman equation do not take into account energy paths such as positive ion currents and electric fields. However, on closer examination, it is possible to postulate a model of the arc in which the accumulative error in work functions is less than about 0.1 electron volt. In discussing the effects of various error sources, it is necessary to describe the arc in more detail.

Arc Characteristics

The arc used in this work was a free-running and self-sustained discharge in a static argon atmosphere with nominal purity of 99.99 percent. The pressure was about 700 torr but was not critical. The cathode-to-anode distance was about 12 millimeters and the gap voltage was about 14 volts. The classification of this arc on the basis of voltage-current characteristics compared with other arc types is shown in figure 5. Figure 5(a) is a typified diagram showing the relative location of the arc used in this work with respect to other gas discharges. The main curve, in figure 5(b), is the static voltage-current relation of this arc. Arcs of this type, in which the voltage is relatively independent of current, are typically collision-dominated discharges having ion and electron densities of the order of 10^{14} to 10^{15} per cubic centimeter (ref. 11). However, the arc column composition is inhomogeneous, especially in the region of the cathode. In this region there

(a) Typical glow-to-arc transition.
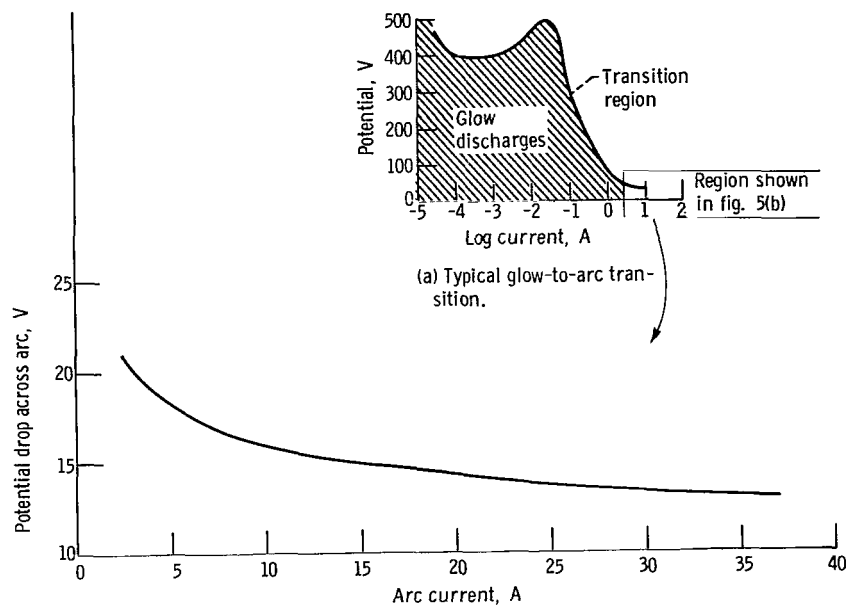
(b) Experimental characteristics of argon arc used.

Figure 5. - Voltage-current characteristics of gaseous discharges.

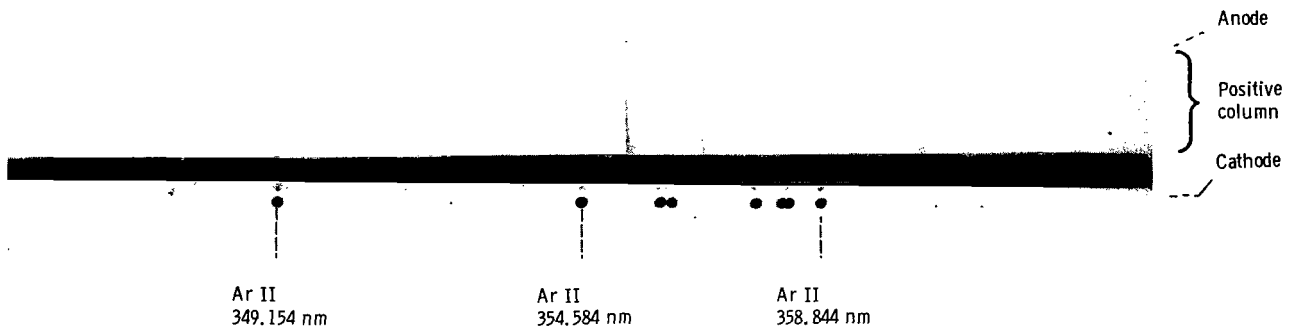Ar II 349.154 nm   Ar II 354.584 nm   Ar II 358.844 nm

Figure 6. - Spectra with arc column focused on spectrographic slit showing argon ion lines excited near cathode. Pressure, 700 torr (120 kN/m^2); magnification, approximately 1.

is an ion sheath, shown in the photographed spectrum of figure 6. The ion space charge can promote electron emission under saturation conditions and may also cause errors in work function measurements through formation of local electric fields. Furthermore, the presence of an ion sheath raises the possibility of errors due to positive ion current because in the use of equation (1) it was assumed that all the current is carried by thermionic electrons.

Because electrical neutrality of the plasma requires the presence of positive ions, the assumption that the current is totally electronic cannot be rigorously valid. In the following sections, the inaccuracies of work function determinations caused by deviations

from the simple arc model are discussed. From data available on similar arcs it can be tentatively shown that the error accruing from use of the simplified model is less than about 0.1 electron volt.

Electric Fields (Schottky Effect)

The presence of electric fields in the vicinity of the emitting surface can lower the measured work function by an amount equivalent to the work done on the electrons by the field. The Schottky effect describes the reduction of the work functions by the field and can be expressed by $\Delta\varphi = 3.79 \times 10^{-4} \, E^{1/2}$, where $\Delta\varphi$ is the change in apparent work function caused by the field E in volts per centimeter (ref. 3).

As can be seen by examination of this expression, to exert a significant influence on the total, the electric fields must be higher than could conceivably exist in an arc with a total voltage drop of only 20 volts per centimeter. In fact, a field of 10^4 volts per centimeter would reduce the effective work functions by only 0.038 electron volt. Therefore, the Schottky effect can be dismissed as a significant source of error in work function determinations by the arc method.

Positive Ion Currents

As mentioned previously, the contribution of positive ion currents at the cathode surface must be subtracted from the total arc current in order to obtain a proper value for thermal electron current for equation (1). Although it is widely accepted that electrons carry the major portion of the current in direct-current arcs, it is also certain that some portion of the current is carried by positive ions. This derives from the fact that the primary heat input to the cathode is by ions falling through the cathode field and impacting on the cathode surface. To ignore positive ion currents, as was done in this work, can result in an erroneously low work function. To estimate the magnitude of positive ion currents and the resulting error in work functions, it is necessary to quantify the energy balance at the cathode surface. This is a problem of such practical and theoretical difficulty that no method has been devised to obtain this information in arcs with thermally emitting cathodes. In this section we shall discuss two models of the cathode energy balance from which estimates of positive ion currents can be made.

Voltage-dominated model. - Estimates of positive ion currents have been made by using a voltage-dominated model of the arc. Here we will consider how these estimates are made in order to place limits of error on the work functions determined by the arc method. A discussion of the approaches used in making these estimates is summarized in references 11 and 12. Estimates of positive ion currents in arcs by various workers

range from 1 to 36 percent of the total current. A typical treatment of energy relations writes the energy input to the cathode as $i_p(V_c + V_i)$, where i_p is the positive ion current, V_c is the voltage drop in the cathode fall, and V_i is the ionization potential of the gas atoms. The heat absorbed on recombinations of ions in the impact process can be written $i_p\varphi$, where φ is the electron work function of the cathode surface. Therefore, the net energy input is $i_p(V_c + V_i - \varphi)$, whereas this must be balanced by electron cooling expressed by $i_e\varphi$, that is, the product of the electron current and the electron work function. The energy balance is thus approximated by $i_e\varphi = i_p(V_c + V_i - \varphi)$. The positive ion current fraction can be written $i_p/(i_p + i_e) = \varphi/(V_c + V_i)$.

The value of V_c can be estimated as about one-half of the total arc voltage, or about 10 volts. The ionization potential of argon V_i is about 16 volts, and φ for refractory metals is about 4 volts. Using these values, the positive ion current can be estimated at about 20 percent of the total current. If 20 percent is taken as an estimate of positive ion current, the work functions derived by the arc method are low by about 0.06 electron volt.

As discussed in reference 11, this treatment neglects some potentially significant energy paths - notably loss of ion energy by collisions between atoms in the cathode fall region, and kinetic energy loss by recoil of neutralized ions at the cathode surface. If these processes are important, the work function errors are larger than estimated herein. On the other hand, additional heat input to the cathode can be derived by thermal conduction of the hot plasma to the cathode surface. Because of this effect the positive ion current has been estimated to be as low as 2 percent (ref. 13), a negligible amount for the purpose of this work. The energy exchange model in which the thermal energy predominates is discussed in the next subsection.

Collision-dominated model. - In the preceding analysis of positive ion currents, it was assumed that the voltage fields near the cathode surface provided the driving force for the energy distribution among electrons, atoms, and ions. However, at the high temperatures and high particle densities existing near the cathode, the thermal motions of the particles must be considered. It is rather well established for arcs of the type used in this work, that random thermal motions of the particles are predominate over voltage fields in determining arc mechanisms. This is to say that, as a first approximation, the electrons, atoms, and ions are in local thermodynamic equilibrium (LTE) (ref. 14). If LTE also exists within a few mean free paths of the cathode surface, the relative proportion of positive ion current to the total current $i_p/(i_p + i_e)$ can be estimated from the conservation of momentum and energy as $m_e^{1/2}/(m_p^{1/2} + m_e^{1/2})$. For argon ions this ratio is very small, indicating negligible positive ion currents and, therefore, negligible error in calculating work functions by the Richardson-Dushman equation.

Although this model can be supported experimentally for macrovolumes in the arc, it is not necessarily valid in microvolumes near the cathode. The existing data on ther-

mal populations were obtained spectroscopically, and it is not feasible to make such observations within a few mean free paths of the cathode surface. Without such direct experimental observation, the question of errors due to positive ion currents remains unresolved. However, from the foregoing discussion, when a voltage-dominated model is used, 0.06 electron volt would appear to be a reasonable estimate of the maximum error in the work functions calculated herein.

Observations in Helium Atmospheres

All the data presented in this report were obtained in argon atmospheres. However, some experiments were conducted in helium atmospheres at higher pressures to determine the criticality of experiment conditions on the experiment results. Substituting helium for argon and raising the gas pressure to about 4500 torr (600 kN/m^2) resulted in rather drastic variations of discharge conditions. The appearance of the arc in helium is quite different than in argon - the most notable effect being the shifting of the ion sheath away from the cathode region to near the anode. In addition, more energy is lost by thermal conduction in helium because the heat conductivity is about 10 times that of argon. It is also well known that the thermophysical properties of the arc are radically different in helium as compared with the arc in argon because of the higher excitation and ionization potentials of helium. Despite changes in discharge conditions caused by helium atmospheres, and by the higher pressures, the work functions for tantalum in helium were not significantly different than those obtained in argon.

CONCLUDING REMARKS

The use of a direct-current arc in an argon atmosphere provided a simple means for determining work functions of refractory metals in the temperature range near their melting points. The work functions are in agreement with recommended handbook values to within about 0.05 volt. The repeatability of the methods resulted from the operation of the cathode at precisely its melting point, which allowed use of melting point data for the emission temperature in the Richardson-Dushman relation, and from the formation of a well-defined emitting area. With this procedure it was also possible to determine work functions and effective emission constants by means of Richardson plots. These plots exhibit an inflection point at temperatures corresponding to the cathode melting points.

A need for further work on this procedure is indicated. The work functions determined on liquid surfaces need to be interpreted in terms of an equivalent crystalline

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orientation in the solid state. In addition, a more quantitative analysis of energy transfer mechanisms in the arc region near the cathode is necessary to independently establish the accuracy of the method.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 8, 1972,
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