NRL REPORT NO. R-3157

SPECTRAL EMISSIVITY AND ELECTRON EMISSION CONSTANTS OF THORIA CATHODES FORMED BY CATAPHORESIS

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SPECTRAL EMISSIVITY AND ELECTRON EMISSION CONSTANTS OF THORIA CATHODES FORMED BY CATAPHORESIS

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ABSTRACT

A method is described for forming thoria cathodes by electrochemical means, namely cataphoresis. In this method a thin layer of thoria is deposited over an underlying metal.

A temperature scale is set up and the spectral emissivity is determined for this type of coating. Also, the electron emission constants were measured over a range of temperatures and it was found that these constants are different for d-c and pulsed emission.

In addition, data are presented which set an upper limit to the resistivity of thoria as a function of temperature.

AUTHORIZATION

This report discusses some results pertaining to the problem on cathodes which was initiated within the Naval Research Laboratory. The problem has been assigned number 34R27-01.

PROBLEM STATUS

This is essentially an interim report on the problem of Cathodes for High Frequency Tubes, a problem which is being continued.

SPECTRAL EMISSIVITY AND ELECTRON EMISSION CONSTANTS OF THORIA CATHODES FORMED BY CATAPHORESIS

INTRODUCTION

In extending the range of operation of vacuum tubes to higher and higher frequencies, the demands upon the cathode become more and more severe. Substantial progress is now limited by the properties of present-day cathodes. Realization of this situation has led to the initiation of a considerable amount of research and development in the cathode field. Of the various avenues under exploration, cathodes fabricated in one manner or another of thorium oxide (thoria, ThO_2) appear to offer the greatest hope for early dividends.

The early work in the field of thoria cathodes indicated that the electron-emissive properties of this type of cathode were superior to those of other types of cathodes such as the barium-strontium oxide, but the work was limited in at least two respects. First, there was very little fundamental knowledge of the emissive properties of thoria available. For instance, the lack of a temperature scale made it impossible to evaluate the electron-emission constants of thoria with any degree of accuracy. Second, those cathodes which were made using thoria would not stand up under mechanical or thermal shock.

As a consequence of the above, it was felt that another approach to the method of cathode fabrication would be very desirable, particularly if it led to cathodes more suitable from a mechanical standpoint. A method which suggested itself was that of cataphoresis. This is a process whereby finely divided particles of an insulator can be deposited onto a metal in a manner resembling ordinary plating. This technique has been applied successfully in the formation of the ordinary barium-strontium oxide cathodes and for applying insulating coatings of alumina to vacuum-tube heaters.* In the case of thoria, it appeared that cataphoresis offered the possibility of forming cathodes of shapes and design not possible by the then existing techniques.

When the details of how to coat thoria cataphoretically were completed, it naturally followed that a study should be made of cathodes formed in this way. Work was directed towards obtaining data regarding the spectral-emissivity and electron-emission constants of thoria cathodes formed by cataphoresis.

FABRICATION OF THORIA CATHODES BY CATAPHORESIS

The thoria used in the cataphoretic process was procured from the National Bureau of Standards. It was a 200-mesh powder obtained by means of the decomposition of thorium nitrate.

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* Bidgood, E. S. and Kent, G. H., "Cataphoresis and Alundum Coatings," The Electro Chemical Society, April 16, 1945, Vol. 87, pp. 321-329

To make the coating bath, the thoria was suspended in ethyl alcohol to which had been added a small amount of thorium nitrate in order to increase the conductivity. A bath which yields good coatings is obtained by adding 5 grams of 200-mesh thoria and 0.075 grams of thorium nitrate to 100 millimeters of 95-percent ethyl alcohol.

To secure satisfactory coatings, it was found that the required current density depended very markedly upon the diameter of the wire or the sleeve being coated. In all cases, the criteria of a satisfactory coating were that it be well adherent and that it appear uniform under visual, microscopic, and pyrometric (when heated) observation. It was observed that coatings which were satisfactory on the basis of the above-mentioned criteria had similar microscopic appearances independent of the diameter of the wire or sleeve being coated. This fact will be used later in the discussion of spectral emissivity. The marked dependence of the current density upon the geometry of the object to be coated (for securing a satisfactory coating) is clearly brought out by the fact that a wire 0.005 inches in diameter requires a current density of 75 milliamperes per square centimeter, whereas a cylinder 0.155 inches in diameter requires a current density of 600 microamperes. Of course the coating time is markedly different. To secure a coating 0.001 inches thick in each case requires 2 seconds for the 0.005-inch wire and 15 minutes for the 0.155-inch sleeve.

In general, coatings between 0.0010 inches and 0.0015 inches in thickness appear to be most satisfactory from all standpoints.

For large-diameter objects, where the coating rate was slow, difficulty was experienced due to the settling out of too much thoria during the process. This was overcome by means of a stirrer which kept the bath in agitation. In this type of bath, the anode was made of 40-mesh screen in the form of a cylinder. Thus the object to be coated was surrounded by a quite uniform field provided by an anode through which the particles could pass. This particular setup is illustrated in Figure 1.

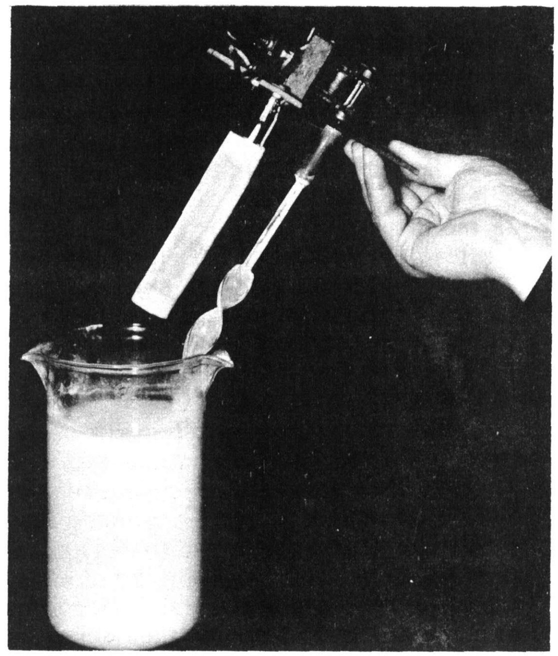


Fig. 1 - Coating Bath

PARTICLE SIZE

Some remarks regarding the size of the particles involved in the coating process may be in order at this point. In view of the fact that the thoria was so-called "200 mesh," it might appear that a large fraction of the particles in the coating may approach 50 microns. To check this, some of the coated material (prior to heating) was scraped off and checked for particle size by the following three methods:

1. oil immersion microscope (see Figure 2 for an actual photograph),
2. X-ray diffraction pattern (see Figure 3),
3. electron microscope (see Figure 4).

The data obtained from the oil immersion microscope indicate that an occasional particle may be as large as 4 microns but most are less than 2 microns in diameter.

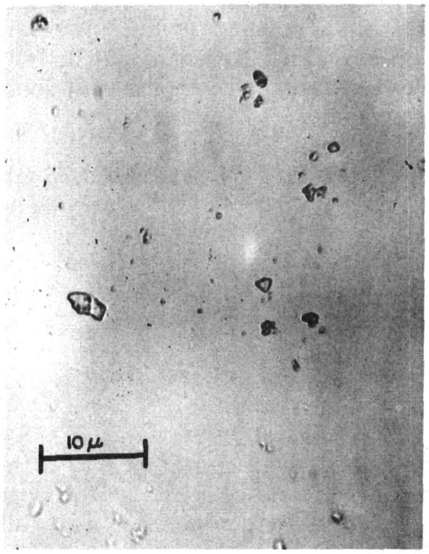


Fig. 2 - Particle Size by Oil Immersion Microscope

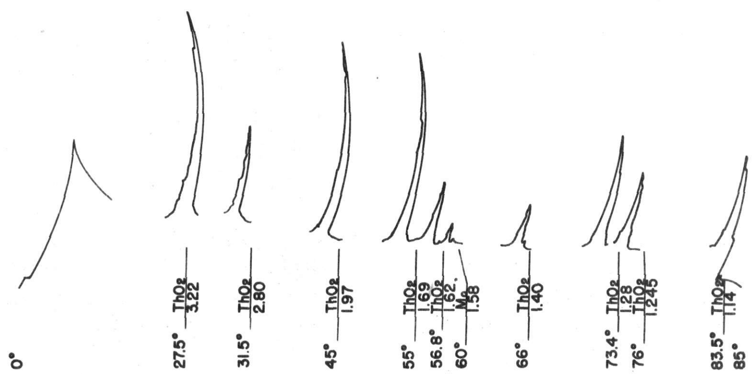
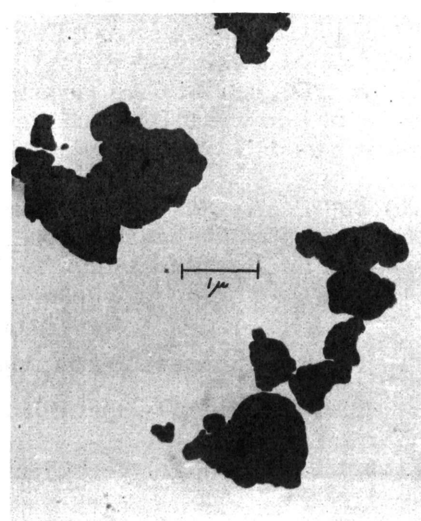


Fig. 3 - Geiger Counter Recording of X-Ray Diffraction Pattern from THO_2 on Mo Background

Fig. 4 - Particle Size Study by Electron Microscope (3200X)



The X-ray method sets a lower limit of 0.05 microns upon the crystal size but does not yield information regarding the distribution of sizes greater than that. It does, however, yield the interesting result that the coating is essentially pure thoria and does not exhibit the presence of thorium nitrate or other impurities.

The electron microscope reveals that the particles are largely between 0.25 and one micron in size.

It may be concluded from these results that the cataphoresis process is selective in that it favors the smaller particles. The larger particles settle out of the bath before they can take part in the coating process. This is actually observed to occur.

TEMPERATURE SCALE

In order to determine the temperature of a heated body, it is customary to make observations of the so-called "Brightness Temperature" by means of a calibrated optical pyrometer. Before the true temperature can be determined, it is necessary to establish a relation between the true and brightness temperatures.

The relation was determined in this case by sighting alternately onto the surface of a coated sleeve 0.155 inches in diameter and into its interior through a number of 0.045-inch holes which had previously been drilled in the sleeve.

In order to make possible a rapid study of a number of different sources, the sleeves were mounted in an inverted bell jar, through which a slow flow of hydrogen was maintained.

To insure that the interior of the sleeve behaved like a "black body," it was made 4 inches long so that the end cooling effects were negligible. Thus the observations through the holes determine the true temperature whereas the surface observations determine the brightness temperature at the effective wave length of the pyrometer (0.65 microns in this case).

It was observed that the temperature scale obtained, i.e., the relation between true and brightness temperature, depended to some extent upon the coating procedure. However, it appeared that coatings similarly prepared and which were microscopically similar, yielded results which agreed within the limits of experimental error. It was felt safe to "extrapolate" these observations to include wires of all diameters which had coatings microscopically similar. As a consequence, as will be seen below, the temperature scale as determined for the 0.155-inch sleeve was used in determining the electron-emission constants from data obtained from very much smaller coated wires.

The actual data relating true and brightness temperature obtained from a number of sleeves are plotted in Figure 5, together with an averaged curve. These data can also be expressed in the form of an empirical relation:

$$T_t = 1.172\, T_o + 177.5$$

where: T_t = true temperature in degrees K

T_o = brightness temperature in degrees C.

From the well-known relationship between true and brightness temperatures,

$$\frac{1}{T_t} - \frac{1}{T_b} = \frac{\mathrm{Log}_{10}\, E\lambda}{9588}, \qquad (1)$$

where T_t = true temperature in degrees K

T_b = brightness temperature in degrees K

E_λ = spectral emissivity at λ = 0.65 microns,

one can determine the spectral emissivity of the thoria cathodes. The data are plotted in Figure 6 together with an averaged curve. It will be seen that the spectral emissivity centers about 0.35. Previously determined values vary between 0.08 and 0.57. †,‡ However, it should be emphasized that emissivity depends markedly upon the manner of preparation, and it is felt that the results given here should be confined to the case of thoria cathodes prepared by cataphoresis in the manner described above.

ELECTRON EMISSION

Description of Emission Study Tubes

Having set up a temperature scale for the cataphoretic type of thoria coating, it was possible to determine the electron-emission constants. In order to obtain these data, a number of tubes were constructed of the form illustrated in Figures 7 and 8. It will be seen that this tube contains three closely spaced anodes. The outer two serve as guard

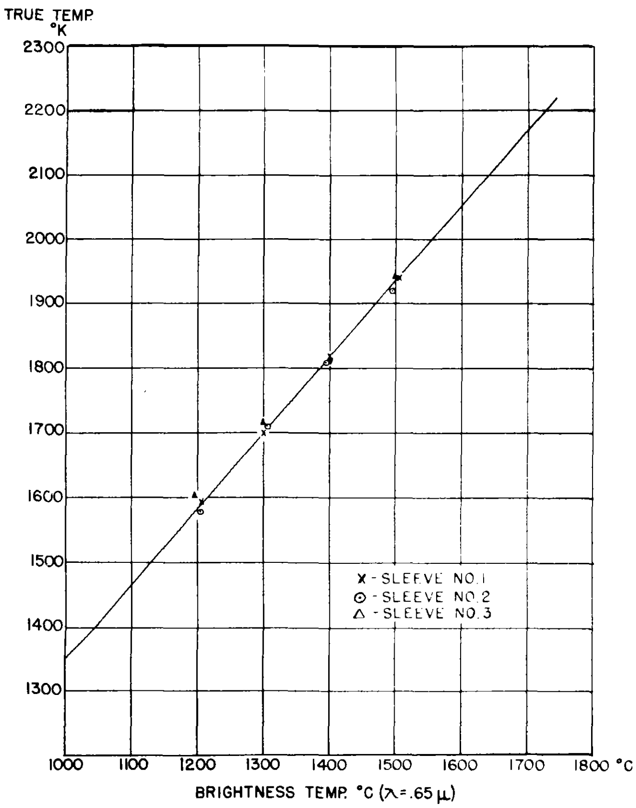


Fig. 5 - True Temperature vs Brightness for ThO_2 Coating on Mo Sleeve

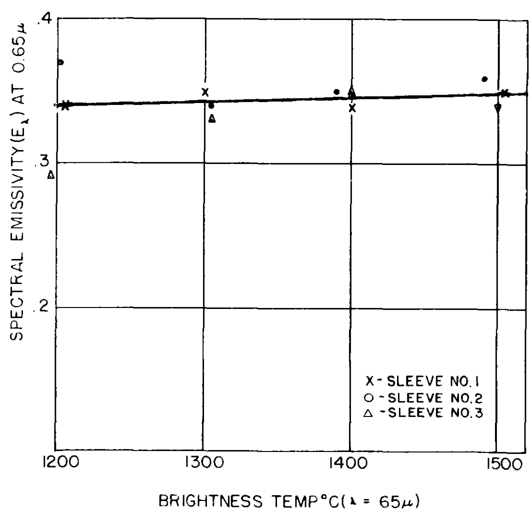


Fig. 6 - Spectral Emissivities for Thoria Applied Cataphoretically on Mo Sleeves

† Keighton, W. B., "Thoria: Its Properties and Analysis," Report of the Bartol Research Foundation, June 1, 1947, pp. 11-12

‡ Weinreich, M. O., Revue Generale de L'Electricite, August 1945

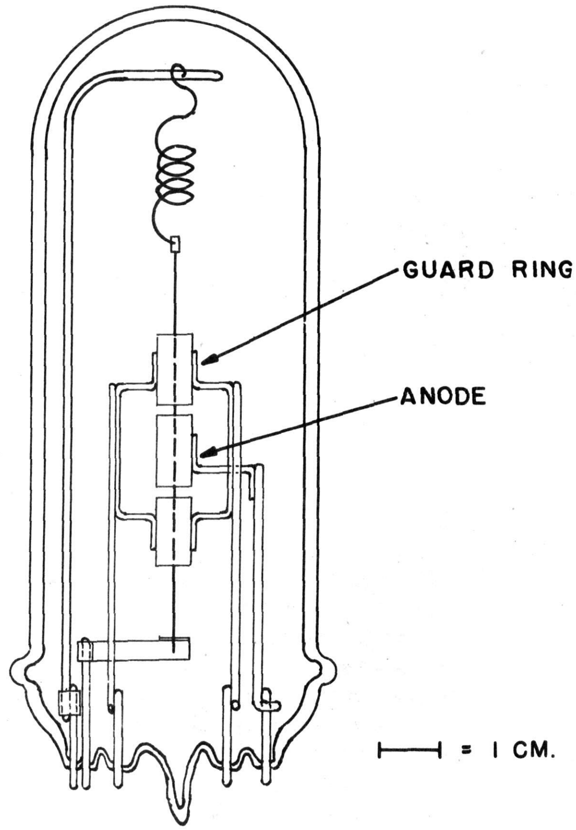


Fig. 7 - Guard Ring Diode

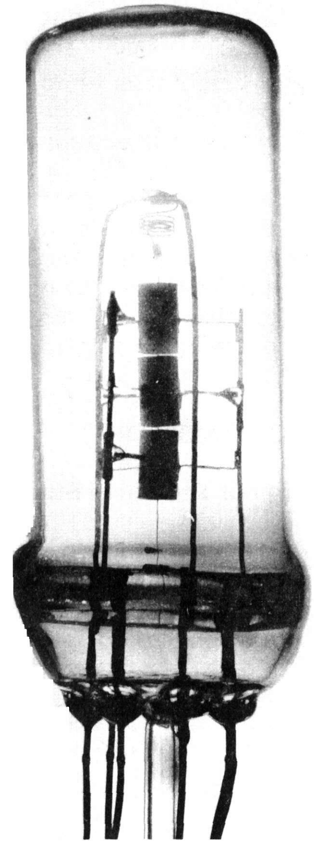


Fig. 8 - Guard Ring Diode

rings to insure a uniform field over the central region. The current to the middle section is used for the determination of the electron-emission constants. Actually these anodes were 0.5 inches long with an inside diameter of 0.25 inches and a separation of 0.060 inches.

The cathodes consisted of tungsten wire 0.005 inches in diameter coated to a diameter of 0.0075 inches to 0.0080 inches with thoria. The anodes were made of tantalum in order to permit good outgassing during exhaust. This outgassing was accomplished by means of electron bombardment. The tube was first baked at 425° C for 3 hours and then the cathode was brought up to 1550° C Br, (brightness). During this heating up of the cathode, an activation appears to take place which results in stable and reproducible emission being achieved when the 1550° C Br. temperature is reached.

The anodes were then outgassed. The current measured on the center section was 150 ma with a total anode current of roughly three times this value and all three sections at a potential of 400 volts. The anodes were kept at this temperature for about 30 minutes. The cathode and anode powers involved in this outgassing exceed any which occurred during later tests.

Emission Studies

The cathode is set initially at about 1500° C Br. and the current (to the middle anode) is measured as a function of the anode voltage. This process is then repeated at a series of lower cathode temperatures.

These current and voltage data are now plotted on two-thirds power paper giving the familiar saturation curves illustrated in Figure 9. In turn, by plotting the log I against the $\sqrt{V_p}$, where I is the saturation current obtained from the curves in Figure 9 and V_p is the corresponding anode voltage, the so-called Schottky Plot§ is obtained. An example of a Schottky Plot is given in Figure 10. It can be shown that the value of the anode current to be used in determining the electron-emission constants is the current which corresponds to zero anode voltage. This current is obtained from the Schottky Plot by extrapolating the linear portion of the characteristic curve down to zero voltage (broken lines in Figure 10).

From the values of the plate (anode) current at zero field and the measured cathode area, it is possible to determine the value of the current per unit cathode area at zero field. This current density is denoted by I_0. From I_0 and the true temperatures of the cathode as obtained from the observed brightness temperatures and the temperature scale of Figure 5, it is possible to plot log I_0/T_t^2 vs $1/T_t$ where T_t is the true cathode temperature in degrees K (Figure 11). This is a so-called Richardson Plot whose slope determines the work function and whose intercept with the zero axis for $1/T_t$ (corresponding to $T_t = \infty$) determines the constant A of Richardson's Equation:

$$I_0 = A T_t^2 e^{-e\phi_0/kT_t} \quad (2)$$

where e = electron charge, k = Boltzman's constant, and ϕ_0 = work function.

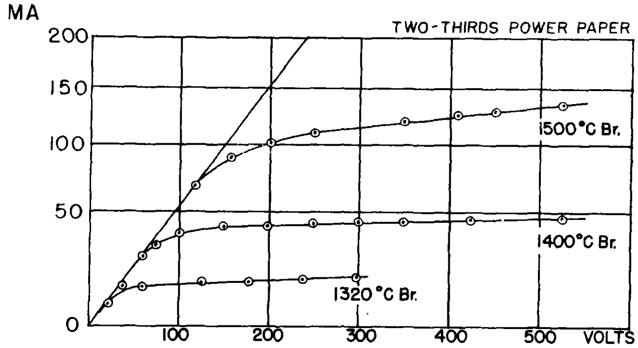


Fig. 9 - D. C. Emission from ThO_2 on ".005 W Wire (O.D. = ".0071)

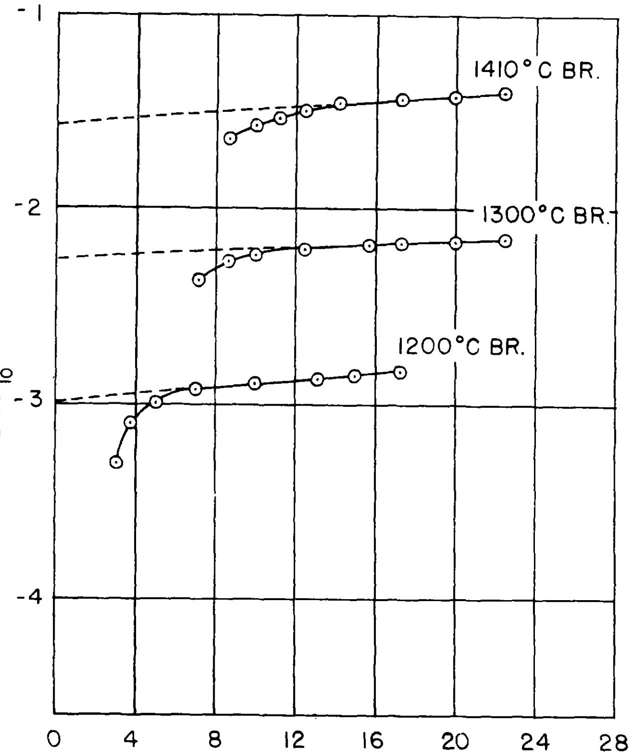


Fig. 10 - Schottky Plot - D. C. Condition Tube No. 7

An averaged curve through these data yields the following values for the emission constants for d-c emission from the thoria cathodes.

§ Compton, K. T., and Langmuir, I., Reviews of Modern Physics, April 1930, Vol. 2, No. 2, pp. 147-149

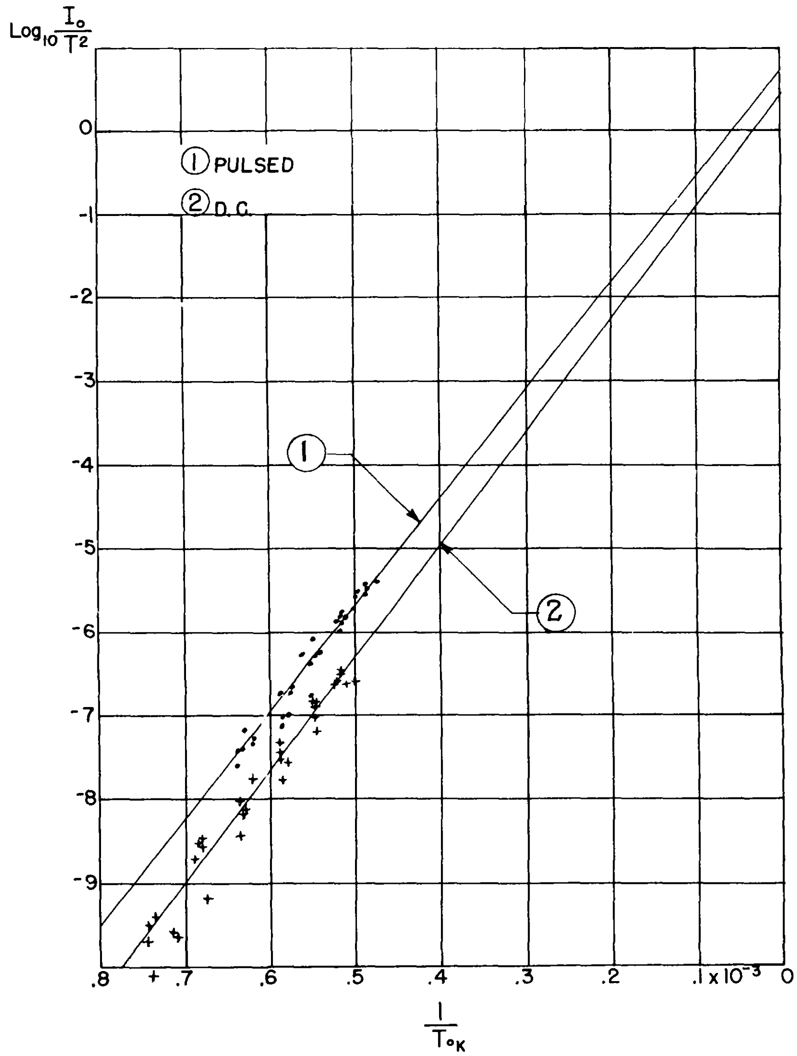


Fig. 11 - Richardson Plot
Work Function for Thoria Cataphoretically Applied

Φ = 2.67 volts

A = 2.63 amp/cm^2/degree^2

These results represent the average of measurements taken on six tubes. Examination of Figure 11 shows that the points have a spread of about 30 percent on either side of the Richardson line. This spread is, no doubt, in considerable part due to errors of measurement, particularly those involved in the determination of true temperature. There is undoubtedly some variation, however, which is genuine in the sense that different cathodes may have different values of the emission constants (both electronic and spectral) due to the unavoidable variations in their preparation. These spreads in the data are not considered serious for complex cathodes of this type.

Pulsed Emission Studies

Pulsed emission was measured by conventional techniques for the same six tubes used in the d-c studies. In most cases the pulse widths were 1.8 microseconds at a repetition rate of 540 cycles per second. This yields a duty cycle of 0.00097. Schottky Plots of the data were used to determine the zero field-current values required for the Richardson Plot.

An actual emission curve plotted on two-thirds power paper is shown in Figure 12. This is included in order to indicate the orders of magnitude of current and voltage involved in the pulsed emission studies.

Additional pulsed emission data are given in Figure 13 where the maximum space charge limited emission (M S C L E) in amperes per/cm² is plotted against the true temperature in degrees.

From the Richardson Plot given in Figure 11, the following values were obtained for the emission constants: $\Phi = 2.55$ volts; A = 5.62 amp/cm²/degree²

The remarks in the section "D-C Emission Studies," wherein the divergence of the points on the Richardson Plot are discussed, apply equally well to this case.

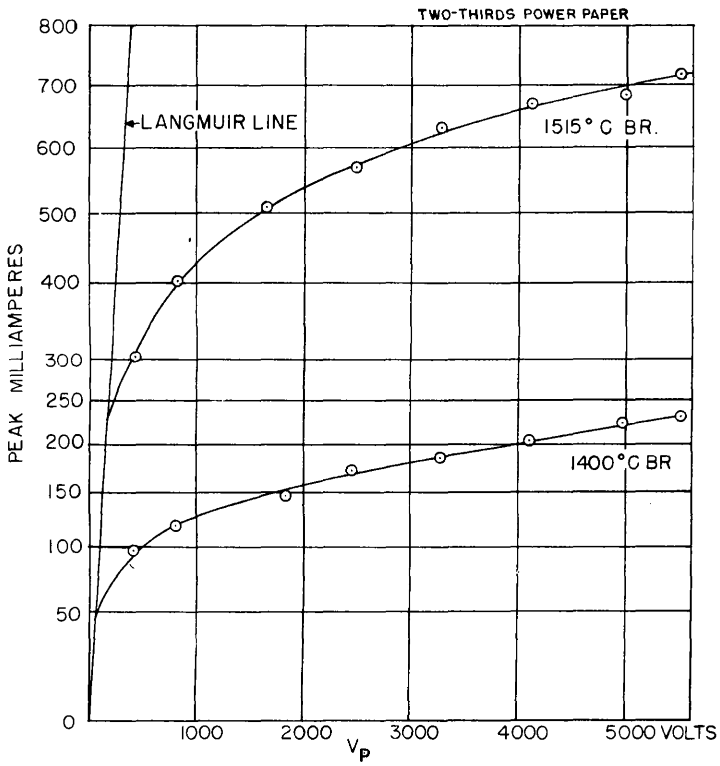


Fig. 12

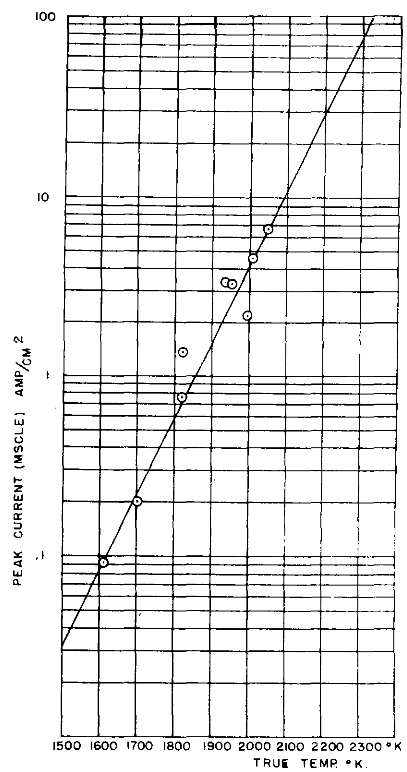


Fig. 13 - Peak Emission Data

Shape Factor

In the Schottky Theory (footnote § , page 7), it is shown that a quantity referred to as the Shape Factor S is given by the slope of the Schottky Line. According to this theory it can be shown that if the emitting surface is smooth, the Shape Factor should be given by:

$$S = \frac{4.39E^{\frac{1}{2}}}{T_t} \tag{3}$$

where E is the field at the surface of the cathode and is calculable from the geometry of the diode and from the anode voltage. A comparison of the Shape Factor determined from the Schottky Lines with that given by equation (3) is valuable in that it indicates the smoothness or roughness of the surface. Equation (3) yields S = 0.005 at 1400° C Br. An averaged value of the shape factor gives an S = 0.007 for the d-c data at 1400° C Br. and gives S = 0.004 for the pulsed data at 1400° C Br. The close agreement between the three values indicates that the surface is substantially smooth. The low spectral-emissivity values may also be considered as evidence in favor of this view.

The discrepancy between the measured value of S (0.004) as obtained from the pulse data and the calculated value (0.005) is greater than the experimental error of the system. A possible explanation for this discrepancy is that the Schottky theory is not completely adequate when applied to coated emitters.

Discussion of Emission Studies

An examination of the data for both the pulsed and d-c emission cases as plotted in Figure 11 shows that there is a very real difference between the two cases. The magnitude of the difference between the two cases is brought home if it is noted that over the temperature region where it is expected that thoria cathodes will be of greatest value, the pulsed emission (corrected for zero field conditions) is more than five times the corresponding d-c value. In this respect thoria cathodes of the type studied are similar in their behavior to the conventional barium-strontium oxide cathodes. However, a very real difference does exist. In the pulsed-emission studies the pulse length was increased to as much as 100 microseconds with the duty cycle going up at the same time to 0.1, without any observable decrease in emission. This indicates that the decreased emission for the d-c case as compared with the pulsed case must occur at pulse lengths greater than 100 microseconds or at duty cycles in excess of 0.1, or both. (The corresponding results for barium-strontium oxide cathodes are quite different.)** This checks with some unpublished observations at the Bartol Research Foundation. They report that, in d-c studies, the emission is observed to decrease over a period of several seconds after the application of the anode voltage.

HIGH-TEMPERATURE CONDUCTIVITY OF THORIA

When anode current is plotted against voltage on two-thirds power paper, the region of space charge limited emission should lie along the so-called Langmuir Line. This follows from the Langmuir equation which can be put in the form:

$$V = kI^{\frac{2}{3}} \tag{4}$$

** Sproull, Robert, "An Investigation of Short Time Thermionic Emission from Oxide-Coated Cathodes," Physical Review, 1943, Vol. 67, pp. 166-178

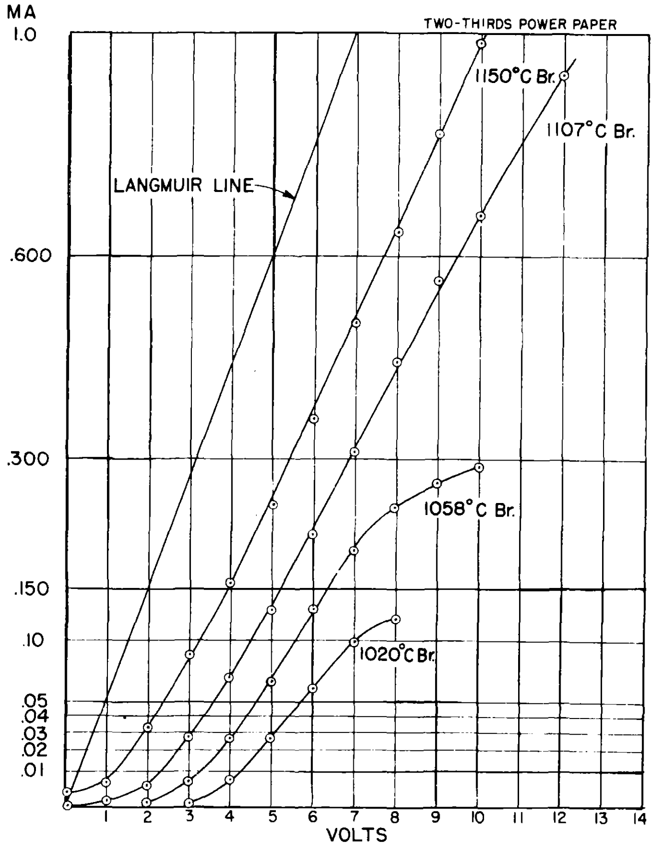


Fig. 14 - Curves Illustrating Effect of Coating Resistance

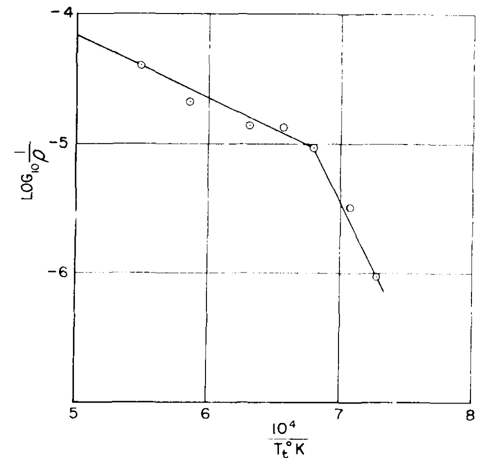


Fig. 15 - Log of Thoria Conductivity vs Reciprocal of True Temperature

where k is a constant which depends upon the geometry of the electrodes of the diode. This relationship holds in the region of space charge limited emission only.

In Figure 14, wherein are plotted the data for a number of different operating temperatures, it is seen that at low temperatures, the experimental curves do not fall along the Langmuir Line. This is ascribed to the finite resistivity of the thoria coatings. As the temperature is raised, the resistivity decreases, thus resulting in the observed data approaching the Langmuir Line. Similar results have been reported for the barium-strontium oxide cathodes.††

The difference between the experimental curve and the Langmuir Line is a measure of the voltage drop ΔV, through the thoria coating. From this voltage drop and the anode current, it is possible to determine the total resistance R between the underlying metal and outside surface of the thoria. If R is divided by the average cross-sectional area of the thoria coating, R' is obtained which is the resistance per unit area between the underlying metal and the outer surface of the thoria coating of the thickness involved (0.0012 inches). This resistance may be due in part to the properties of the interface between the tungsten and the thoria. A separation of the contributions to the measured resistance of the interface and of the thoria itself would require a more elaborate experiment. If it is assumed that the interface has negligible resistance, then the measured values can be used to set an approximate upper limit to the thoria resistivity. In that case:

$$\rho = R \frac{2\pi r_{av} l}{t} \qquad (5)$$

†† MIT Research Laboratory of Electronics, "Quarterly Progress Report," April 15, 1947, pp. 7-8 ·

where ρ is the thoria resistivity (if the interface resistance is neglected), r_{av} is the average radius of the thoria coating, l is the length of the coated section being measured, t is the coating thickness. ρ is plotted as a function of temperature in Figure 15. Here the R used for each temperature is an averaged value obtained from the slope of curve (not shown) that results when Δ V is plotted against the anode current.

The data involved in this resistivity determination included a small difference between two quantities, and are, as a consequence, subject to considerable error. The results as plotted in Figure 15 should be regarded as only approximate.

SUMMARY

A method is described for forming cathodes by means of a cataphoresis process wherein a thin layer of thoria is deposited over an underlying metal.

The spectral emissivity and electron emission of cathodes of the type described have been determined over a range of temperatures. The results in the case of electron emission are different for pulsed and d-c emission and thus lead to different values for the electron-emission constants.

In addition, data are presented which set an upper limit to the resistivity of thoria as a function of temperature.

* * *

PRNC-4166-1-9-48-100