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THERMIONIC ELECTRON SOURCES

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ABSTRACT

A survey of the emission characteristics of modern thermionic electron sources is presented. In addition to a discussion of recent advances among the more commonly used emitters such as oxide cathodes, thoriated cathodes, and metal cathodes, a tabulation of the thermionic properties of over one hundred various new matrix and refractory-coated cathodes is given.

PROBLEM STATUS

This is a final report on one phase of the problem; work is continuing on other phases.

AUTHORIZATION

NRL Problem R08-05
Project RR 008-03-46-5652

Manuscript submitted June 8, 1961.

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FOREWORD

This review article was initially prepared for Vol. IV of "Methods of Experimental Physics," Academic Press, New York. The information given in this report is substantially the same as that contained in the above article, with the exception of a number of entries which were added to Tables 1 and 2.

The author, while endeavoring to report only reliable results in this review, realizes that verification of all the data is virtually impossible, especially, for example, in results translated from foreign journals where only sparse details of experimental methods are given. The validity of these results is often a subjective matter, and the author urges the reader also to follow this approach.

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THERMIONIC ELECTRON SOURCES*

INTRODUCTION

The basic equation for the rate of thermal emission of electrons from a heated solid is given by the Richardson-Dushman equation†

$$J = AT^2 e^{-\phi/kT} \tag{1}$$

where J is the thermionic emission in amps/cm^2, A is a fundamental constant equal to 120 amps/cm^2 deg^2, k is the Boltzman constant, T is the temperature (°K), and ϕ is the potential barrier that the electrons must overcome to go from the Fermi level inside to the vacuum level outside of the solid. Since this barrier is generally temperature dependent, at least as a first-power contribution, it can be written as

$$\phi = \phi_o + \alpha T. \tag{2}$$

Substituting this into Eq. (1) gives

$$J = A e^{-\alpha/k} T^2 e^{-\phi_o/kT} \tag{3}$$

where α is the temperature coefficient of the work function and ϕ_o is the work function at absolute zero. If the thermionic characteristics of a solid are plotted in terms of a Richardson plot ($\log(J/T^2)$ vs T^{-1}) it is seen that the intercept (extrapolated value to $1/T = 0$) should give the value "A" = $120\, e^{-\alpha/k}$ and the slope yields ϕ_o.

The value of α for metals is governed largely by such physical properties as the principal thermal expansion effect and the internal electrostatic effect of atomic vibrations (1). This is computed to be of the order of 10^{-4} to 10^{-5} ev/degree which is in the range of values indicated from the intercepts of experimental Richardson plots ("A" $\simeq$ 10 to 100). However, inaccuracies involved in extrapolating from a limited temperature range cause an error in α which is of a magnitude comparable to α itself; this limits its detailed analysis with respect to physical properties. Hence, for metallic-type emitters and the majority of the various composite cathodes, the emission is generally described in terms of the empirically determined constants ϕ_o and "A" as obtained from Richardson plots.

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*This survey will attempt to give an up-to-date summary of the emission characteristics and physical properties of various different types of emitters rather than to stress the methods of measuring these characteristics. A more detailed description of this phase of thermionics is given in Chap. 7.7, Vol. 6B, of "Methods of Experimental Physics," New York:Academic Press.

†The effects of a reflection coefficient are neglected in this discussion.

For semiconductors, the variation in the occupation probability of electronic states in the conduction band is the predominant factor controlling α, which for these cases can be as much as an order of magnitude higher than was the case for metals. This can be measured experimentally with a reasonable amount of accuracy, thereby warranting the inclusion of the theoretical value of α in the emission equation for the interpretation of the thermionic properties of semiconductors. For a nondegenerate, one-donor-level semiconductor having a wide band gap, this reduces to the fairly simple form

$$\alpha \simeq \frac{k}{2} \ln (4.82 \cdot 10^{15}\, T^{3/2}\, N_D^{-1}) \tag{4}$$

which when substituted into Eq. (3) gives

$$J = BT^{5/4}\, N_D^{1/2}\, e^{-(\chi + E_D/2)/kT} \tag{5}$$

where $B = 1.76 \cdot 10^{-6}$ amp/cm$^{1/2}$deg$^{5/4}$, N_D is the donor density in cm^{-3}, E_D is the donor-level energy below the bottom of the conduction band and χ is the electron affinity (difference between the bottom of the conduction band and the vacuum level). The quantity $\chi + E_D/2$ is the theoretical value of ϕ_o for this model as was calculated from the position of the Fermi level at 0°K.

Equation (5) is called the Fowler-Richardson equation and should be used in the analysis of this type of semiconductor rather than the Richardson-Dushman equation. Fortunately, however, if the data are presented in the form of a Richardson plot rather than a Fowler-Richardson plot $[\log(J/T^{5/4})$ vs $T^{-1}]$, the slope will still give a value very close to $\chi + E_D/2$ owing to the predominant temperature dependence of the exponent. The intercept, on the other hand, will no longer give a direct determination of the density of donors N_D.

Semiquantitative interpretations will be made for a few examples using the slope and intercept of these plots as applied to semiconductors; however, because of the inaccuracies involved in the extrapolation from limited temperature regions, the thermionic properties of the various cathodes will be presented, as much as possible, in graphs of current as a function of temperature. From these plots, the values of the "effective work function" (total electron barrier: $\phi_o + \alpha T$) can be determined by comparison with theoretical curves obtained from Eq. (1). For the cases where space does not permit a graphical presentation, the effective work function and the temperature range over which the measurements were made will be tabulated. These values may be figures taken directly from the literature or, if not available as such, computed from the published Richardson or Fowler-Richardson data.

The thermionic characteristics of many cathodes other than those described here have been investigated and are available in the literature; however, many of them have properties that are of only academic interest and offer little as yet in the way of a practical thermionic electron source. Consequently, in limiting the number of entries, only those cathodes which look promising and/or are currently being used for various experimental applications, are discussed here.

THE OXIDE-COATED CATHODE

The oxides of the alkaline earths (Ba, Sr, Ca) have been employed in the manufacture of cathodes for over fifty years and still serve as the most widely used emissive surfaces because of their high electron emission at relatively low temperatures. These cathodes

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are normally fabricated by applying a mixture of the alkaline-earth carbonates and some suitable organic binder onto a base metal (generally Ni). The carbonates are then thermally decomposed in vacuum to obtain the thermionically active oxide surface.

Fabrication and Processing

There are various methods of applying the carbonate-binder mixture to the base metal, such as dipping, dragging, or spraying, the last being most widely used (2). For smooth surfaces, plating or cataphoretic coating techniques can be successfully employed (2), as well as a new technique called Centrifugation (3). Another method which is receiving considerable attention recently is the technique of mixing the carbonate and binder into a plastic sheet which is then wrapped around the Ni base, hence the name "Sarong" coating (4). A design similar to this, employing a self-supporting film of polynormal butyl methacrolate containing the alkaline earth carbonates, has been described as the "Printed Cathode" (5). Both of these cathodes are reported to have the advantages of more uniform coating thickness and density than the sprayed cathodes.

The coating thickness depends somewhat on the cathode's application but generally ranges between 40 and 100 microns with a density between 3 and 8 mg/cm^2. The consistency of the coating can be varied by using different binder solutions as well as by using different solutions for precipitating the carbonates. For example, the precipitation from ammonium carbonate results mainly in spherulites, whereas precipitation from sodium carbonate yields prismatic needles (6).

After the cathode has been coated, it is mounted and sealed onto a vacuum system where it is exhausted. It is desirable to bake the tube at 400° to 450°C to clean the metal and glass parts. Also during this time, the binder products are decomposed and thereby removed from the cathode coating. Following the bakeout, the cathode is slowly heated by its own filament to a temperature of approximately 1050°C. The carbonates decompose to the oxides, liberating CO_2 between 500° and 900°C. Hence, the speed at which the temperature is raised is governed largely by the CO_2 pressure within the tube, which should not exceed about 10^{-4} mm Hg pressure.

When the cathode has reached this maximum temperature it is normally capable of giving a reasonable current, but as this is generally different from cathode to cathode, further activation is normally necessary. This is accomplished either before or after the tube is sealed off by reducing the temperature to 850°C and drawing a small dc current. The vacuum necessary for good operation should be in the 10^{-7} mm region or better.

Emission Characteristics

The oxide cathode is thought to be an n-type semiconducting solid with a band gap of the order of 4.4 ev, having at least two donor levels at 1.4 and 2.0 ev below the bottom of the conducting band and having an electron affinity of about 0.6 ev (7). Since the Fermi level is governed almost entirely by the higher lying donor level, the interpretation of this surface based on the one-donor-level semiconductor model seems justified.

The exact nature of the donors responsible for the emission of this semiconductor is somewhat nebulous. Excess Ba, acting either interstitially (2) or in colloidal form (8), has been one of the more popular hypotheses. It is definitely established that Ba deposited on an oxide cathode by means of a mass spectrometer increases the cathode's emission (9); however, it has also been noted that little correlation exists between the natural excess barium content and the activity of oxide cathodes (10). Other possible lattice defects that can act as donors are F centers (2) (oxygen vacancies) or hydroxide ions (11).

Whatever the donors are, the majority are created when the cathode is first heated. This so-called thermal activation is the creation of donors by partial reduction of the oxide at the metal-oxide interface and is quite efficient, especially when used with the more active (high concentration of reducing agents) Ni-base metals. For the less active base metals, applying a slight dc field causes an additional electrolytic dissociation of the lattice, whereupon the alkaline-earth metal ions are driven towards the base and oxygen is liberated at the surface. At the base, the metal ions are neutralized and then migrate back into the oxide crystal.* This latter generation of donors is called electrolytic activation.

The thermionic emission characteristics of oxide cathodes, especially at higher temperatures, are usually taken by pulse techniques in order to avoid complications arising when a steady dc field is applied. Among some of these is the poisoning of the cathode by anode contaminants released under steady electron bombardment. For example, oxygen or chlorine can be desorbed from the anode by electrons in an energy range as low as 5 to 15 volts (9,12-14). These can then "poison" the cathode by a donor destruction process, such as filling an oxygen vacancy or becoming bound to an excess Ba atom.

Another effect of a dc field applied to oxide cathodes is the field-induced migration of donors towards the base, which depletes the number of donors near the surface and, hence, decreases the density of electrons available for emission (9,15).

Since the equilibrium condition for emission is based on a balance between donor generation and donor loss mechanisms, and since for the dc case these latter ones can vary to a large extent depending on individual tube construction, processing, etc., it is not uncommon to find that the steady-state dc emission in some tubes can be one or, sometimes, two orders of magnitude lower than that obtained during the first few microseconds after the voltage is applied. Consequently, the pulsed emission value is more indicative of the basic emission processes of the alkaline-earth oxide surface, whereas the dc emission level is a very subjective value, more strongly affected by environmental factors. Figure 1 shows the range of emission† in which modern, well-activated oxide cathodes may be expected to operate (see, for example, Refs. 16 to 18).

It is seen that the actual electron barrier for this surface varies somewhere between 1.4 and 1.6 ev in the normal operating range, with a tendency for the electron barrier to increase with temperature. If the emission properties are analyzed in terms of Eq. (5), it is observed that the value of $\chi + E_D/2$ is approximately 1.1 to 1.4 ev, and N_D is in the region of 10^{14} to $10^{17}/cm^3$. These values are in fair agreement with the semiconductor model mentioned earlier and therefore lend support to the Fowler-Richardson equation for the interpretation of the emission characteristics for this type of emitter.

Life Characteristics, Limitations, and Other Properties

There are many factors that are thought to contribute to the decrease in emission with life of oxide cathodes. Among the most common of these are processes whereby the overall donor concentration decreases. These processes can be either in the form of a decrease in the donor production rate, such as a depletion of reducing agents in the base metal (19-21) or the thermal evaporation of donors (19), or they can be an increase in the donor loss

*The same argument can also be used for F centers.

†Extrapolated to zero field. Actual saturated emission levels of nearly an order of magnitude higher can be obtained at strong fields.

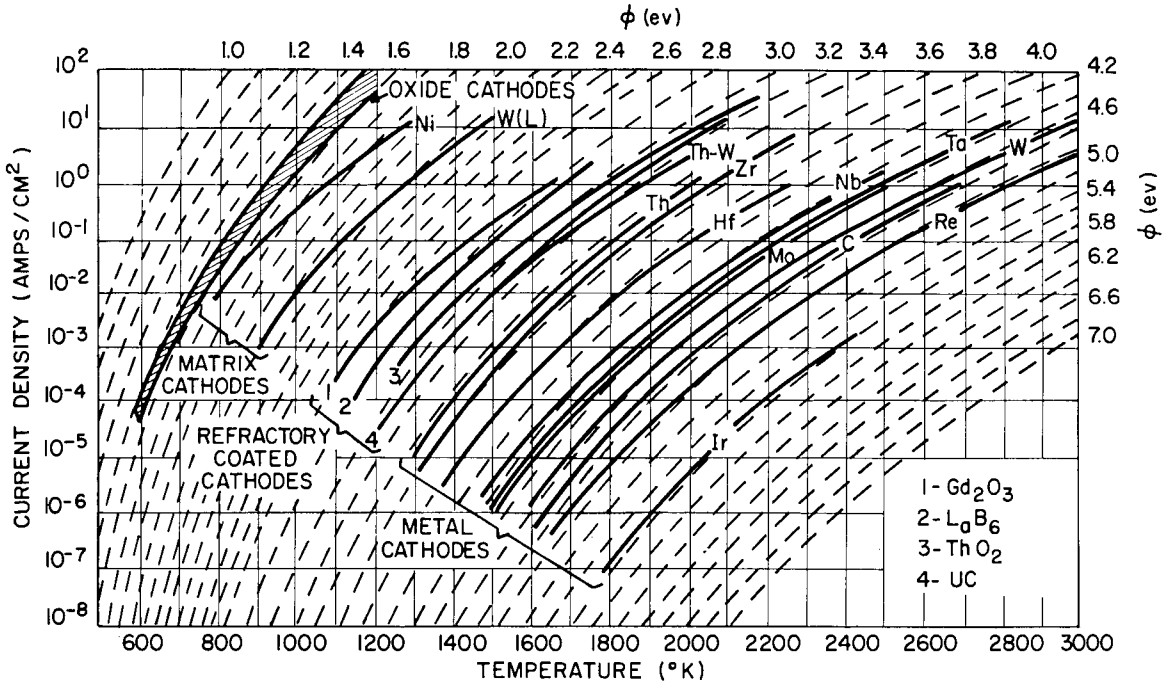

Fig. 1 - Emission characteristics of various modern thermionic cathodes. For the matrix cathodes and refractory-coated cathodes, each example represents the most emissive cathode in its particular class on which substantial data are reported to date. The position of the atomic symbol on the curves for the metallic emitters denotes the temperature at which the vapor pressure is 10^{-5} mm Hg. The original references for the various emitters are either given in this text, or can be found in the review articles noted in Refs. 16 and 33. The dashed curves give the emission level for the different effective work functions listed at the top and right edge of the graph.

rate as would be experienced from the buildup of residual gases (such as CO, O_2, Cl, etc.) in the tube.* It is generally a combination of these that determines the end of useful life. The exact quantitative figures that determine when the donor loss rate begins to exceed the donor production rate are strongly dependent on other properties of the individual tube (e.g., duty cycle, ambient temperature, and size).

Other factors which also determine the end of useful life in tubes containing oxide cathodes can be effects that actually cause the mechanical destruction of the coating. Among the more common are sparking (22), flaking (23), ion bombardment (24), or excessive heating which causes evaporation of the coating.

While some cathodes used for underwater telephone applications (low power level) have life times measured in terms of years (25), the ordinary oxide cathode lifetime is measured in terms of thousands of hours. Under these conditions, it is generally possible to draw dc emission currents of the order of 50 to 500 ma/cm^2; for pulsed conditions, emission densities of 10 to 100 amps/cm^2 have been reported (22).

In general, it can be said that oxide cathodes give good emission at a relatively low temperature, are moderately easy to process and activate, and have good life characteristics. They suffer from mechanical shocks and are subject to other mechanical problems,

*A good summary of recent results from many experimenters is given in "Vacuum," Vol. 10 (1960).

such as ion bombardment and sparking. They demand cleanliness in construction and are not too suitable for operation in a poor vacuum since they can become permanently poisoned by fairly low pressures of various deleterious gases that are commonly found in vacuum tubes.

MATRIX CATHODES

Because of the structural weaknesses and chemical instability just mentioned in oxide coatings, cathode development has been directed towards emitter construction capable of withstanding more mechanical, electrical, and chemical destructive forces which are prevalent in many modern cathode applications. This has led to the family of emitters known as "matrix cathodes."* Here the body of the cathode is in the form of a metal matrix throughout which is dispersed the active material (often a barium compound). This gives the advantages of a metallic-type structure for ruggedness while providing a much higher emission than that obtained from pure metals. A further advantage is obtained in certain types of matrix cathodes because of the diffusion nature of the active material from within the matrix which can provide a completely fresh surface after the previous surface has been destroyed (e.g., by ion bombardment). This eliminates the necessity of frequently replacing the cathode in many applications where poor vacuum conditions are encountered.

The history of matrix cathodes goes back to the nineteen twenties (26,27), and progress in their development continued throughout the thirties with Ni as well as refractory metals being used for the matrix element (28,29). At Siemens and Halske in Germany, Katz developed a "metal capillary" cathode (30) in 1942. A version of this cathode, using W and $BaCO_3$, also was independently developed by Lemmens et al. at the Philips Laboratories in Holland as the "L" cathode (31). In 1945, in the United States at the M.I.T. Radiation Laboratory, Coomes and Forsbergh (32), endeavoring to improve oxide cathodes for use in magnetrons, developed a cathode in which Ni powder was mixed with the alkaline-earth carbonates to produce a "molded Ni cathode." Because of the limited space available, only the extension of development of these latter two cathodes (Philips "L," "molded Ni") will be discussed here,† along with some brief descriptions of recent advances in other adaptions of matrix cathodes.

W-Matrix Cathodes (Philips Type)

The first W-matrix cathode, announced by the Philips Laboratories, was designated the "L" cathode (31) and is shown in Fig. 2.‡ This is composed of a W frame on top of which is attached a porous tungsten cap prepared by powder metallurgy techniques. Behind

*To avoid ambiguity between these and other types of cathodes, the term "matrix" rather than "dispenser" is preferred here since the dispensing action of all the various forms of these cathodes is not entirely clear at present (e.g., some do not appear to dispense active material much differently than oxide cathodes would diffuse donors to the surface after temporary oxygen poisoning).

†For a further discussion of matrix cathodes, see Refs. 33-35.

‡Only indirectly heated, gun-type cathodes are described here. For further information concerning other geometries see, for example, Refs. 2, 33, and 34.

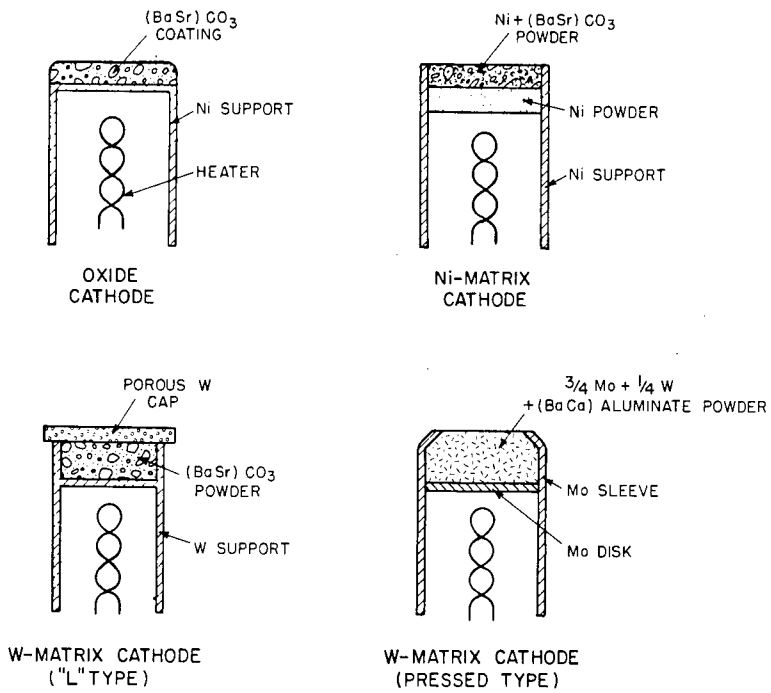

Fig. 2 - Sectional views of various end-fire cathodes

the tungsten cap, in a vapor-tight enclosure, is a pellet of (Ba Sr) carbonate. Upon heating to 1000°C,* this is decomposed to yield the oxide which is then reduced by the tungsten to give (36)

$$2\,BaO + 1/3\,W \rightarrow 1/3\,Ba_3WO_6 + Ba.$$

The free barium then diffuses through the pores of the tungsten cap by migration over internal pore walls and by Knudsen flow of the vapor. On reaching the surface, the barium spreads from each pore, the resulting surface being very nearly a monolayer of barium on oxygen-on-tungsten.† The surface dipole which is formed as a result of this adsorbed layer decreases the electron barrier of the surface by more than two electron volts, giving an effective work function $(\phi_o + \alpha T)$ of $1.68 + 3.24 \cdot 10^{-4}\,T$ (36).

*This temperature is rather well defined since heating below 1000°C would cause excessively long activation times; heating the cathode much above 1000°C would cause the reduction of the $BaCO_3$ by the W, resulting in a wasteful reaction producing barium tungstate rather than barium oxide (36).

†The oxygen which is always adsorbed on the tungsten under these vacuum conditions serves to hold the Ba more tightly and also further decreases the work function by increasing the surface dipole (36).

Since continuous evaporation of Ba takes place, the end of life of this cathode occurs when the above BaO-W has gone to completion and the following chemical reaction takes over

$$2/3\,Ba_3WO_6 + 1/3\,W \rightarrow BaWO_4 + Ba,$$

which is accompanied by the release of an oxygen-bearing poisoning agent (36).

The emission characteristics of this cathode are shown in Fig. 1. Normal operating temperatures are in the vicinity of 1400°K, and at these temperatures emission densities of the order of an amp/cm^2 can be maintained for several thousand hours.

In order to overcome difficulties of fabricating a vapor-tight enclosure, a new cathode was developed by Levi (37) called the "impregnated, Type A" cathode, which consists of a tungsten matrix which is impregnated in vacuum by a melt of barium aluminate. Since the carbonates are not used, very little gas is given off, thereby increasing the speed of activation as well as eliminating the unwanted reaction of $BaCO_3$ with W. For this cathode, the barium dispensing mechanism is thought to be given by

$$2/3\,Ba_3Al_2O_6 + 1/3\,W \rightarrow 1/3\,BaWO_4 + 2/3\,BaAl_2O_4 + Ba$$

which results in a surface having an effective work function of $1.53 + 5.78 \cdot 10^{-4}T$ (38). While this has eliminated the need for a vapor-tight enclosure, as well as decreasing the critical nature of activation, the resulting emission is about one fifth that of the "L" cathode.

A later version of this cathode called the "impregnated, Type B" cathode uses the addition of calcium aluminate which gives an effective work function of $1.67 + 3.2 \cdot 10^{-4}\,T$, or an increase in emission of a factor of 4 over the type-A cathode (39). Furthermore, the rate of Ba evaporation has been reduced to nearly one-eighth, thereby significantly improving life.

Rittner et al. (38) suggest that the difference in emission between the type A and B cathodes is due to the release of the poisoning agent, which is counteracted by the calcium aluminate of the type-B cathode. Brodie and Jenkins (39a), on the other hand, propose that the difference might be caused by the contribution in emission of the impregnant at the end of the pores. For the type-A cathode this contribution is relatively small, whereas for the type-B cathode a Ba-activated CaO surface forms at the end of the pores, giving an appreciable increase in emission.

Cuppola and Hughes (40) describe a variant of the impregnated cathode, called the "Pressed Cathode" (Fig. 2), which is more suitable for production processing. The step of impregnating the sintered metal matrix with molten BaCa aluminate is eliminated by starting with a prescribed mixture of metal powder and BaCa aluminate powder. This is then pressed and sintered as a mixture to form a coherent strong mass. The metal powder is 75 percent Mo and 25 percent W by weight and comprises 90 percent of the total weight of the mixture, the remainder being composed of the aluminate.

This mixture of refractory metal alloy and Ba source was specifically chosen to ensure a low rate of Ba evaporation and, therefore, give good life properties. The emission characteristics of this cathode are somewhat similar to those of the original L cathode and the impregnated, type-B cathode, the effective work function being $1.7 + 3.62 \cdot 10^{-4}T$.

Another variation of the impregnated cathode called the "type S" cathode has been recently developed by Semicon Associates; this is claimed to give more uniform (from cathode to cathode) and slightly larger emission than the type-B impregnated cathode. However, no published information concerning the process of fabrication or the impregnant used is yet available.

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While the construction and exact nature of the impregnant might vary between the different types of cathodes just mentioned, they are all considered diffusion cathodes which dispense an activating compound from the interior, giving a surface of barium on oxygen-on-tungsten, as was described for the case of the L cathode. Furthermore, they all have similar emission characteristics (within a factor of about five) and their lives are measured in terms of thousands of hours at emission levels of the order of one amp/cm^2. This life time, which might be somewhat shorter than that attainable with oxide cathodes, is largely the result of the increased temperature (about 250° to 300°C higher) at which these W-matrix cathodes must operate to give a comparable level of emission.

Several investigators (41,42) have studied the poisoning effects of various gases on these cathodes and have found that for temperatures in the region of 1100°C, it is necessary to maintain the pressure of $O_2 < 10^{-7}$, $H_2O < 3 \cdot 10^{-7}$, $CO_2 < 10^{-6}$, and air $< 5 \cdot 10^{-6}$ mm Hg in order to avoid poisoning. Other gases which can poison the cathode are metal vapors such as Hg, Pt, Pd, Ti, and Zr (43). Gases like N_2, H_2, or CO are relatively harmless, except in their ability to cause sputtering.

Like oxide cathodes, these cathodes also generally have a lower dc emission than pulsed emission because of gases liberated at the anode, but since they are thin-film-type emitters rather than semiconductors, they would not be expected to suffer from donor depletion effects. On the other hand, since the active surface is just a monolayer thick, they are very susceptible to ion-bombardment stripping of this active surface (44).

Their ability to recover from severe poisoning effects is generally better than that for oxide cathodes because of their ability to repeatedly provide a new surface by diffusing barium from within the matrix; however, it is noted that for these cases the time for reactivation becomes progressively longer. This is especially true in demountable vacuum systems (23,45) where the cathode is opened to air and then has to be reactivated. Furthermore, if the anode or other tube parts in close proximity to the cathode cannot be cleaned after each air exposure, the cathode will deteriorate much more rapidly than oxide cathodes in similar applications (23,45). This is the result of the higher evaporation rate of these W-matrix cathodes, which causes a larger quantity of cathode evaporation products (e.g., Ba) to be deposited on the anode than is the case for oxide cathodes. While these evaporation products might not be harmful in themselves, they pick up water and oxygen upon air exposure, which are later desorbed by electron bombardment to poison the cathode.*

Ni-Matrix Cathodes

Thermionic properties of a cathode similar to the one originally described by Coomes and Forsbergh (32) were first published by McNair et al. (46) under the name "molded cathodes." Further studies on this general-type cathode have also been carried out by various investigators under the names of "B.N." (Bariated Ni) cathode (34,47), "sintered Ni matrix" cathode (48,49), "extended interface cathode" (50), and "M" cathode (51,52).

The method of fabrication varies slightly with different investigators, but, in general, this type of cathode is composed of a mixture of Ni powder and alkaline-earth carbonate powder. This mixture is then pressed in suitably shaped dies, sintered, and, finally, machined to any given configuration.

The nickel powder is usually carbonyl Ni in the size range of 1 to 10 microns. This is mixed with the triple carbonate powder so that the weight of the Ni is from 60 to 80 percent that of the total mixture. In order to insure a rapid activation, a reducing agent such as zirconium hydride (34,53), B (49), C (45,48), Al (46), or Th (54) is generally added in the concentration of 0.1 to 1 percent of the total weight. The powder is then ball milled and thoroughly mixed, whereupon it is pressed in steel dies at about 80 tons/sq in. pressure. After pressing, the cathode is ready for mounting in the tube. For large cathodes, Beck (34) finds that it is better to press the powdered mixture first only to 10 tons/sq in.

and then hydrogen-fire it for 20 minutes at 650°C. This provides a partial sintering which produces a stronger matrix that can now be pressed at the full 80 tons/sq in. These cathodes are called "presintered" cathodes. Since breakdown of the carbonates occurs when the cathode is heated, it is desirable to control the atmosphere during and after this step so that excessive flaking and poisoning will not occur (45). Elaborate firing schedules have been developed, some using various ambient gases for different temperature ranges (53); however, nearly all techniques employ a maximum temperature in the region of 1100°C and recommend leaving the cathode at this point for about 30 minutes.

Several variations in the fabrication of this cathode have been devised wherein the metal matrix is first constructed by pressing and sintering the Ni powder and the alkaline-earth compounds are then impregnated into this matrix. This eliminates the unavoidable conversion of these alkaline-earth compounds while sintering. For this technique, coarser Ni powder is used (50 to 100 μ), and the resulting matrix is somewhat more porous ($\sim$50 percent). Balas et al. (55) employed a method of impregnating the matrix with a saturated solution of (BaSr) acetate which was then converted to the carbonates by immersion in $(NH_4)_2CO_3$. Apelbaum (56) accomplished the impregnation by placing the Ni matrix in contact with melted $Ba(OH)_2$, whereas Arshanskaia et al. (54) used a combination cataphoretic and mechanical method for introducing the carbonates. When large Ni particle sizes are used, fine Ni powder ($<1\,\mu$) in concentrations up to 10 percent can also be added to the carbonates to reduce the possibility of arcing (54).

Special precautions are necessary in the manner in which the matrix is mounted in the tube. As a rule, the bonding to a supporting sleeve is made by actually pressing the powder together with the sleeve in the die. It has also been found that not all materials make good sleeves, Kovar and Ni-iron being especially deleterious to the emission properties (34). In order to obtain a good bond between the sleeve and the matrix, a number of investigators (34,46,48,53) use pure Ni powder in the region where the bond is made, using the alkaline-earth Ni mixture just in the vicinity of the emitting surface, as shown in Fig. 2.

The emission characteristics of this cathode are given in Fig. 1, and exhibit an effective work function in the region of about $1.2 + 5 \cdot 10^{-4}T$ (34,45,55,56). It is noteworthy that this value which is independent of the various different methods of fabrication has essentially the same temperature independent component (ϕ_o) of the work function as was observed with oxide cathodes. The temperature dependent component α is somewhat higher, making this emitter operate nearly an order of magnitude below most oxide cathodes (Fig. 1). The similarity in ϕ_o indicates that, on the basis of the interpretation using Eq. (5), the majority of the emission comes from areas that exhibit the same semiconducting properties (χ and E_D) as was the case for oxide cathodes. Two factors undoubtedly contribute to a higher value of the temperature coefficient, the first being a decrease in the average donor density (cf. Eq. (4)) due to a less efficient activation process. The second is an apparent increase in α caused by using the total cathode area in computing J rather than the actual emission area (which is just the sum of all the pore areas containing the alkaline-earth oxides exposed to the surface).

*All of the W-matrix cathodes described here are commercially available from Semicon Associates, P. O. Box 832, Lexington, Ky., and, with the exception of the type S cathode, also from Philips Electronics, Inc., Irvington-on-Hudson, New York.

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It is true that the part of the surface which is comprised of the Ni grains will also have a monolayer of BaO adsorbed on it, as was the case with the tungsten-matrix cathodes. However, since the work function of a monolayer of BaO on Ni is $1.84 + 1.35 \cdot 10^{-4}$ T (57), the emission from these regions is nearly two orders of magnitude less than that from an equal-size oxide grain and is, therefore, relatively insignificant. This fact is born out by the manner in which not only the work function of Ni-matrix cathodes but also their pulse-emission decay phenomena exhibit characteristics indigenous to bulk oxide rather than to thin-film behavior (34).

Consequently, the Ni-matrix cathode is not a diffusion-type cathode which derives most of its emission from a continually replenished monolayer of BaO on a metal substrate, as was the case with the tungsten-matrix cathodes. Rather, it is essentially a patchy oxide cathode which has the structural advantages of a metallic matrix support. It therefore has been found to withstand mechanical shock and vibration, as well as electrical sparking and ion bombardment, much better than oxide cathodes. It also has the advantage of being machined to intricate shapes and close tolerances. On the other hand, it suffers the same losses of emission such as are caused by donor migration (34), gas poisoning (34,52),* heating without drawing current (48), and flaking of the coating (45), as was the case with the oxide cathode. Furthermore, it has the additional disadvantage of being more difficult to fabricate and harder to activate than the oxide cathode.†

Special-Matrix Cathodes

Many variations of the W and Ni matrix cathodes previously discussed have been investigated for applications, such as in high-power magnetrons, and some are described in Table 1.‡ It is seen that not only were different matrix metals used (e.g., Mo, Pt, Re, Cb) but also various carbides, borides, and silicides. New impregnants were also tried, such as the silicates and the beryllides of the alkaline earths, as well as thorium§ and the oxides of the rare earths.

The Re-matrix cathodes were chiefly developed because of the high recrystallized ductility, high water-cycle resistance, lack of carbide formation, and improved strength properties of Re over other matrix compounds. Pt was used to overcome some of the noise problems in matrix cathodes, and the rare-earth oxides were employed because they are unaffected by air exposure, have good high-temperature mechanical properties, and can be operated at temperatures substantially lower than the thoria-type cathodes while still giving comparable emission. The various characteristics of thoria and the rare-earth oxides will be discussed later.

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*Added in proof: A recent study by Jenkins and Trodden (103) shows that O_2, H_2O, and CO_2 will poison matrix cathodes at pressures above 10^{-7} mm Hg, whereas N_2, H_2, and CO have little or no effect at pressures up to 10^{-4} mm Hg.

†Unlike the W-matrix cathodes, the Ni-matrix cathodes are not available as stock items; they can, however, be obtained by special order from Semicon Associates or Westinghouse Electric Corporation, Elmira, New York.

‡Table 1 includes Refs. 58 to 64.

§These cathodes are fabricated in a manner similar to the W-matrix cathodes and are not to be confused with thoriated cathodes where the Th content is of the order of 1 percent or less.

Table 1
Effective Work Functions and Temperature Range of Measurements for Various Matrix Cathodes. The Value of the Zero Field Current Was Determined by the Following Methods: P - Pulsed; Sch - Schottky Plot; SCL - Space-Charge-Limited; OV - Zero Field.

Matrix	Impregnant and Percentage of Total Weight	Reference Number	J-From:	Effective Work Function	Temperature Range of Measurement (°K)
W (L-type)	(BaSr) CO_3	36	P-Sch	$1.68 + 3.24 \cdot 10^{-4}T$	1230-1470
Ni (molded)	20%-40% (BaSrCa) CO_3	45 55,34	P-Sch P-SCL	$1.2 + 5 \cdot 10^{-4}T$	~900-1300
Re	10% (BaCa) Aluminate	58	P-Sch	$1.2 + 7 \cdot 10^{-4}T$	1230-1430
1/3 Mo, 1/3 Re, 1/3 W	10% (BaCa) Aluminate	58	P-Sch	$1.2 + 7.2 \cdot 10^{-4}T$	1230-1430
3/4 Re, 1/4 W	10% (BaCa) Aluminate	58	P-Sch	$1.4 + 6.6 \cdot 10^{-4}T$	1230-1430
1/2 Re, 1/2 Mo	10% (BaCa) Aluminate	58	P-Sch	$1.7 + 4.67 \cdot 10^{-4}T$	1230-1430
W*	10% $BaAl_4$	59	dc-OV	$2.3 + 1.6 \cdot 10^{-4}T$	~900-1400
W	10% $BaSi_4$	59	dc-OV	$1.81 + 4.7 \cdot 10^{-4}T$	~900-1400
WC*	10% $BaAl_4$	59	dc-OV	$2.27 + 2.10 \cdot 10^{-4}T$	~900-1400
WC	10% $BaSi_4$	59	dc-OV	$1.71 + 4.6 \cdot 10^{-4}T$	~900-1400
W_2C*	10% $BaAl_4$	59	dc-OV	$1.91 + 6.0 \cdot 10^{-4}T$	~900-1400
W_2C	10% $BaSi_4$	59	dc-OV	$2.0 + 2.24 \cdot 10^{-4}T$	~900-1400
W_2B_5*	10% $BaAl_4$	59	dc-OV	$2.0 + 6 \cdot 10^{-4}T$	~900-1400
W_2B_5	10% $BaSi_4$	59	dc-OV	$2.3 + 4.3 \cdot 10^{-4}T$	~900-1400
WSi_2*	10% $BaAl_4$	59	dc-OV	$2.16 + 1.7 \cdot 10^{-4}T$	~900-1400
WSi_2	10% $BaSi_4$	59	dc-OV	$2.25 + 1.1 \cdot 10^{-4}T$	~900-1400
TaB_2	10% $BaSi_4$	59	dc-OV	$1.88 + 3.9 \cdot 10^{-4}T$†	~900-1400
TaC	10% $BaSi_4$	59	dc-OV	$1.79 + 3.5 \cdot 10^{-4}T$†	~900-1400
$TaSi_2$	10% $BaSi_4$	59	dc-OV	$1.92 + 4 \cdot 10^{-4}T$†	~900-1400
MoC*	10% $BaSi_4$	59	dc-OV	$1.76 + 7.8 \cdot 10^{-4}T$	~900-1400
Mo_2B	10% $BaSi_4$	59	dc-OV	$2.69 + 6.2 \cdot 10^{-4}T$†	~900-1400
$MoSi_2$*	10% $BaSi_4$	59	dc-OV	$2.22 + 3.1 \cdot 10^{-4}T$	~900-1400
Ta*	10% $BaSi_4$	59	dc-OV	$1.93 + 10^{-4}T$	~900-1400
Mo	10% $BaAl_4$	59	dc-OV	$1.1 + 10^{-3}T$	~900-1400
Mo	10% $BaSi_4$	59	dc-OV	$1.23 + 1.3 \cdot 10^{-3}T$	~900-1400
W*	10% (BaCa) Si_4	59	dc-OV	$2.0 + 3 \cdot 10^{-4}T$	~900-1400
TaC*	10% (BaCa) Si_4	59	dc-OV	$2.01 + 3.5 \cdot 10^{-4}T$	~900-1400
Ta*	10% (BaCa) Si_4	59	dc-OV	$1.26 + 7.7 \cdot 10^{-4}T$	~900-1400
W*	9.5% Ba_2SiO_4 0.5% Al	59	dc-OV	$1.81 + 3.2 \cdot 10^{-4}T$	~900-1400
Ta*	9.5% Ba_2SiO_4 0.5% Al	59	dc-OV	$1.94 + 7.3 \cdot 10^{-4}$	~900-1400
W*	9.5% Ba_2TiO_4 0.5% Al	59	dc-OV	$1.78 + 3.4 \cdot 10^{-4}$	~900-1400
Ta*	9.5% Ba_2TiO_4 0.5% Al	59	dc-OV	$2.15 + 5.8 \cdot 10^{-5}$	~900-1400

*These emitters were not included in the original review article either because the information was not available at that time or there were space limitations.

†More recent values than previously quoted.

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Table 1 (Continued)
Effective Work Functions and Temperature Range of Measurements for Various Matrix Cathodes. The Value of the Zero Field Current Was Determined by the Following Methods: P - Pulsed; Sch - Schottky Plot; SCL - Space-Charge-Limited; OV - Zero Field.

Matrix	Impregnant and Percentage of Total Weight	Reference Number	J-From:	Effective Work Function	Temperature Range of Measurement (°K)
WC*	10% (BaSr) Si_4	59	dc-OV	$1.69 + 4.65 \cdot 10^{-4}$	~900-1400
W_2C*	10% (BaSr) Si_4	59	dc-OV	$1.49 + 6.6 \cdot 10^{-4}$	~900-1400
W_2B_5*	10% (BaSr) Si_4	59	dc-OV	$1.3 + 1.35 \cdot 10^{-3}$	~900-1400
W, 10% WC	Thorium	60	dc-SCL	~3.2	~1800-2000
Pt	~30% (BaSr) CO_3	61	dc-Sch	$1.15 + 7.3 \cdot 10^{-4} T$	~800-1000
Ni with Pt surface layer	~30% (BaSr) CO_3	61	dc-Sch	$\sim 1.23 + 5.5 \cdot 10^{-4}$	~800-1000
W	La_2O_3	62	dc	~2.6	1573
W	30% Nd_2O_3	62	dc	~2.76	1573
W	30% Gd_2O_3	62	dc	~2.97	1673
W	22% Gd_2O_3 7% La_2O_3	62	dc	~2.87	1673
W	Th	30	P-SCL	~2.83	1550-1750
W	BaBe	30	P-SCL	~1.75	1100-1170
Mo	BaBe	30	P-SCL	~1.67	1060-1110
W	$BaCO_3$ + Si	30	P-SCL	~1.83	1100-1200
85-100% N 0-15% Ti	BaSrO	35	P	~1.67	1023
50-100% W 0-50% Zr	ThO_2	35	P	~2.8	1773
W	67% ThO_2	63	P-Sch	$2.97 + 2.58 \cdot 10^{-5}$	1070-1820
Ta	20% Th	64	dc-Sch	$2.52 + 2.12 \cdot 10^{-4} T$	~1500-2000
Cb	20% Th	64	dc-Sch	$2.42 + 2 \cdot 10^{-4} T$	~1500-2000
Re*	50% ThO_2	64	dc-Sch	$2.83 + 2 \cdot 10^{-4} T$	1450-2100
W*	50% ThO_2	64	dc-Sch	$3.18 + 2.12 \cdot 10^{-4} T$	1600-2300
Ni (cast)*	1.5% Ba	64	dc-Sch	$1.84 + 2.43 \cdot 10^{-4} T$	~1100-1350
Ni*	5% Ba	64	dc-Sch	$2.62 - 0.8 \cdot 10^{-4} T$	~1100-1350
Ni*	3% Ba, 4% Cr	64	dc-Sch	$2.64 - 0.55 \cdot 10^{-4} T$	~1100-1350
Ni*	2.1% Ba, 1.4% Sr 0.75% Cr, 0.75% Zr	64	dc-Sch	$2.58 - 0.63 \cdot 10^{-4} T$	~1100-1350
Fe*	2.5% Ba	64	dc-Sch	2.58	1323
Cu* (cast)	2.2% Ba	64	dc-Sch	$1.7 + 1.2 \cdot 10^{-4} T$	~1100
Cu*	3% Ba, 2% Sr	64	dc-Sch	$2.07 + 1.1 \cdot 10^{-4} T$	~1100-1400
Pt* (cast)	1% Ba	64	dc-Sch	$3.1 - 1.1 \cdot 10^{-4} T$	~1100-1400
Ni* (cast)	1.5% Ba + (BaSr) O Surface coating	64	dc-Sch	$1.24 + 3.32 \cdot 10^{-4} T$	~1000-1100
Cu* (cast)	2.2% Ba + (BaSr) O Surface coating	64	dc-Sch	$1.19 + 3.17 \cdot 10^{-4} T$	~1000-1100
W*	9.5% BaCa tungstate, 0.5% Al	96	dc-SCL	~2.1	1250-1300

*These emitters were not included in the original review article either because the information was not available at that time or there were space limitations.

Although many of these cathodes appear to have emission properties comparable to or better than the commercially available matrix cathodes, most of them are still in the developmental state, and not too much information is yet available regarding long-term reliability and life characteristics. Furthermore, none as yet can be purchased as a stock item.

REFRACTORY-COATED CATHODES

The refractory-coated cathodes were developed for the purpose of providing a more rugged cathode than the oxide cathode but yet not resorting to the complications of fabricating a metal-matrix cathode. These cathodes, having higher work functions than the oxide cathode, are normally operated at higher temperatures and, therefore, have inherent disadvantages, such as heater failure and evaporation. They do, on the other hand, have the general advantage of being physically more rugged and less damaged by sparking and ion bombardment than oxide cathodes, as well as being chemically more stable in air. This latter property provides the advantage of being able to handle the cathode in its final emissive form, thereby eliminating the conversion procedure (i.e., carbonate to oxide) of oxide cathodes.

Thoria Cathodes (Thorium Oxide)

The development of the thoria cathodes was one of the earlier steps in improving on the capabilities of the oxide cathode by utilizing a coated-type cathode rather than a matrix type, and was motivated to a large extent by magnetron applications, as well as some special requirements of rectifiers, power tetrodes, and ion gages. While self-supporting thoria sleeves were first used, methods of painting, spraying, and cataphoresis have been developed (65-68). The coating is applied to a thickness of about 20 mg/cm^2, and the cathode is activated by heating to 2200 °K, which essentially precludes the use of indirectly heated cathodes.

A currently accepted model of this cathode is one in which a thin film of thorium on the surface of the thoria provides the low-work-function surface. This film is furnished by the electrolytic decomposition of the thoria (69). The emission characteristics, like those of oxide cathodes, are different under dc and pulsed conditions, the latter thermionic data giving an effective work function of about $2.6 + 2.4 \cdot 10^{-4} T$ (65-67).

Beside the general advantages of the refractory-coated cathodes, this cathode activates much more easily than the oxide cathode. It also has a lower electrical resistance and does not form a high-resistance interface layer with the base metal (W or Ta). These latter characteristics make this cathode especially less prone to sparking.

Hexaboride Cathodes

Hexaboride cathodes, which were principally investigated by Lafferty (70) at the General Electric Research Laboratory, were developed for reasons similar to the thoria cathodes, with the same advantages in mind.

The hexaborides are somewhat unusual in their crystallographic properties. The small boron atoms form a three-dimensional cage-like structure around the metal atoms but do not form any valence bonds with them. The valence electrons of the metal are therefore free, giving a metallic behavior to the solid. The strong binding forces between the boron atoms in the cage structure, on the other hand, lead to very refractory compounds with melting points above 2100°C. These high melting points are characteristic of the boron cage structure rather than of the metal atom since the variation in melting point is less than 4 percent between the various different hexaborides tested.

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When the crystal is heated, a monolayer of the metal atoms forms on the surface, resulting in a low-work-function emitter. The metal atoms that are evaporated or otherwise lost at the surface are immediately replaced by diffusion of metal atoms from the interior. Consequently, the hexaboride crystal acts in a manner similar to a matrix cathode, being composed of a boron-matrix structure which contains either alkaline-earth or rare-earth metal atoms as impregnants.

The cathodes are prepared by pressing the hexaboride powder into the desired shapes and then sintering them at 1375°C for 15 minutes. This results in a material which is soft enough to permit machining. A further sintering at 1800°C for 15 minutes results in the finished, hard, refractory material.

Activation is accomplished automatically when the cathode is heated in vacuum at 1500° to 1600°C for a few minutes for outgassing purposes; it is then ready for use. Emission properties for the various cathodes tested are given in Table 2.*

The hexaborides are useful in applications involving high currents and, because of their resistance to positive-ion bombardment, are also suitable for high-voltage applications. In addition, because they are stable in air and activate easily, they are particularly useful in demountable vacuum systems.

The major disadvantage of these cathodes is the strong tendency of the boron atoms to diffuse into interstices of the base metal. This causes a collapse of the boron cage structure and results in the rapid evaporation of the metal atoms. Two methods to obviate this are (a) the use of a base metal in which boron diffuses slowly and (b) prefilling the interstices. For directly heated filaments, a Ta wire that has had its surface carbonized appeared to have good mechanical properties with no evidence of B diffusion into it when coated with the hexaboride (70).

Rare-Earth-Oxide Cathodes

The oxides of the rare earths have in the past been available only in limited abundance and purity. However, recent advances in techniques of ion exchange and chromatography have permitted the employment of chemical separation methods, that result in highly pure samples whose use is economically feasible.

Rare-earth-oxide cathodes, similar to thoria cathodes, have the properties of good high-temperature mechanical strength, quick activation, ease of degassing, and freedom from arcing. This makes them highly desirable in high-power or magnetron-type applications where cathode ruggedness is important.

The cathodes are coated by brushing or by using cataphoretic techniques (71-74). Spraying is also possible but results in too much waste of the material (74). Since the rare-earth oxides are relatively stable in air, it is not necessary to convert them in vacuum to the oxide from some other more stable form. Therefore, only activation is necessary and this is accomplished by heating them in vacuum. Upon heating, the oxides discolor, turning either dark grey or black. When the temperature reaches ~1150° to 1200°C they again return to their normal color (72). This is quite likely due to the formation of carbon from the organic binder, as is also noticed in oxide cathodes. Upon reaching 1500°C the majority of the rare-earth oxides are completely activated and ready for use; erbium oxide and holmium oxide, on the other hand, require temperatures about 400° higher than this for their activation (71).

*Table 2 contains Refs. 96-103.

Table 2
Effective Work Functions and Temperature Range of Measurements for Various Refractory-Coated Cathodes. The Value of the Zero Field Current Was Determined by the Following Methods. P - Pulsed; Sch - Schottky Plot; SCL - Space-Charge-Limited; OV - Zero Field.

Emissive Material	Base Metal	Reference Number	J-From:	Effective Work Function	Temperature Range of Measurement (°K)
Oxides of:					
Th	W, Ta, Mo	66,67	P-Sch	$\sim 2.6 + 2.4 \cdot 10^{-4}T$	~1300-2200
Hf*	W	97		$2.82 + 4.72 \cdot 10^{-4}T$	1300-1950
Zr*		16		3.9	2000
Ti*		16		3.7	2000
Sc*	W	97		$3.66 + 2.2 \cdot 10^{-4}T$	1300-2000
Y	W	71	Sch	$2.0 + 4.64 \cdot 10^{-4}T$	1300-1500
La*	Ni	72	Sch	$3.0 + 0.075 \cdot 10^{-4}T$	~1000-1100
Ce*		16		$2.3 + 4.1 \cdot 10^{-4}T$	~1800-2000
Pr*	W	71	Sch	$2.8 + 5.4 \cdot 10^{-4}T$	~1400-1600
Nd*	W	71	Sch	$2.3 + 4.1 \cdot 10^{-4}T$	~1400-1600
Sm*	W	71	Sch	$2.8 + 5.1 \cdot 10^{-4}T$	~1700-1900
Eu*	W	71	Sch	$2.6 + 6 \cdot 10^{-4}T$	~1400-1600
Gd	W	71	Sch	$2.1 + 4.5 \cdot 10^{-4}T$	1100-1600
Tb*	W	71	Sch	$2.1 + 5.4 \cdot 10^{-4}T$	1400-1600
Dy	W	71	Sch	$2.1 + 4.16 \cdot 10^{-4}T$	1100-1600
Ho*	W	71	Sch	$2.3 + 5.1 \cdot 10^{-4}T$	1350-1950
Er*	W	71	Sch	$2.4 + 4.35 \cdot 10^{-4}T$	~1700-1900
Yb*	W	71	Sch	$2.7 + 2.85 \cdot 10^{-4}T$	1500-1900
Lu*	W	71	Sch	$2.3 + 6 \cdot 10^{-4}T$	~1500-1700
U*	W	77	P-Sch	$\sim 3.1 + 2.1 \cdot 10^{-4}T$	1350-2100
Hexaborides of:					
Ca	None	70	dc	$2.86 + 3.3 \cdot 10^{-4}T$	1100-1400
Sr	None	70	dc	$2.67 + 5.82 \cdot 10^{-4}T$	1250-1450
Ba	None	70	dc	$3.45 + 1.74 \cdot 10^{-4}T$	1250-1650
Th	None	70	dc	$2.92 + 4.72 \cdot 10^{-4}T$	1150-1600
Y*	Ta	98	Sch	$2.2 + 1.8 \cdot 10^{-4}T$	
La	None	70	dc	$2.66 + 1.22 \cdot 10^{-4}T$	1080-1300
Ce	None	70	dc	$2.59 + 3.0 \cdot 10^{-4}T$	1140-1370
Pr*	Ta	98	Sch	$3.46 - 7.9 \cdot 10^{-5}T$	
Nd*	Ta	98	Sch	$3.97 - 1.08 \cdot 10^{-4}T$	
Gd*	Ta	98	Sch	$2.05 + 4.28 \cdot 10^{-4}T$	
Dy*	Ta	98	Sch	$3.53 + 1.37 \cdot 10^{-4}T$	
Ho*	Ta	98	Sch	$3.42 + 1.86 \cdot 10^{-4}T$	

*These emitters were not included in the original review article either because the information was not available at that time or there were space limitations.

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Table 2 (Continued)
Effective Work Functions and Temperature Range of Measurements for Various Refractory-Coated Cathodes. The Value of the Zero Field Current Was Determined by the Following Methods. P - Pulsed; Sch - Schottky Plot; SCL - Space-Charge-Limited; OV - Zero Field.

Emissive Material	Base Metal	Reference Number	J-From:	Effective Work Function	Temperature Range of Measurement (°K)
(Continued) Hexaborides of:					
Er*	Ta	98	Sch	$3.37 + 2.15 \cdot 10^{-4}T$	
Yb*	Ta	98	Sch	$3.13 + 3.32 \cdot 10^{-4}T$	
Lu*	Ta	98	Sch	$3.0 + 5 \cdot 10^{-4}T$	
Carbides of:					
Ta	W	75	P-Sch	$3.14 + 5.2 \cdot 10^{-4}T$	1400-2300
Th	Ta	16	P-Sch	$3.2 + 0.16 \cdot 10^{-4}T$	~1500-2000
	W	75	P-Sch	$3.5 - 1.32 \cdot 10^{-4}T$	
Ti	W	75	P-Sch	$3.35 + 1.35 \cdot 10^{-4}T$	1400-2300
Zr	W	75	P-Sch	$2.18 + 5.1 \cdot 10^{-4}T$	1173-2073
U	W	76	P-Sch	$2.94 + 1.1 \cdot 10^{-4}T$	1200-2100
Diborides of:					
Ta	W	75	P-Sch	$2.89 + 2.14 \cdot 10^{-4}T$	1400-2100
Zr	W	75	P-Sch	$4.48 - 4.76 \cdot 10^{-4}T$	1500-2100
Ti*	None	99	dc-Sch	$4.6 - 1.17 \cdot 10^{-4}T$	1350-1850
V*	None	99	dc-Sch	$4.2 + 6.1 \cdot 10^{-4}T$	1450-1800
Nb*	None	99	dc-Sch	$4.0 + 3.65 \cdot 10^{-4}T$	1500-2000
Cr*	None	99	dc-Sch	$4.1 + 3.55 \cdot 10^{-4}T$	1450-1900
Mo*	None	99	dc-Sch	$3.85 + 4.9 \cdot 10^{-4}T$	1550-2050
U*	W	77	P-Sch	~3.3	1300-2100
Nitrides of:					
Zr	W	75	P-Sch	3.96	2000
B	W	75	P-Sch	4.0	2000
Ti	W	75	P-Sch	3.96	2000
U	W	77	P-Sch	$\sim 3.1 + 2.14 \cdot 10^{-4}T$	1350-2100
Basic Tungstate of:					
Ba*	W, Mo	100	dc	$0.64 + 1.7 \cdot 10^{-3}T$	800-1000
	W	101	dc	$1.25 + 1.3 \cdot 10^{-3}$	1000-1550
	Ta	101	dc	$1.1 + 1.21 \cdot 10^{-3}T$	950-1400
Basic Tantalate of:					
Ba*	Ta	101	dc	$1.22 + 1.04 \cdot 10^{-4}T$	840-1230
	Ta	102	dc	2.39	1200
Sr*	Ta	102	dc	2.82	1200
Ca*	Ta	102	dc	2.98	1200
Basic Niobate of:					
Ba*	Ta	102	dc	2.42	1200

*These emitters were not included in the original review article either because the information was not available at that time or there were space limitations.

Thermionic measurements are not too abundant; only two references are presently available for the work functions of the majority of the rare-earth oxides (71,73), and these provide agreement to only about 10 to 30 percent. For example, in the case of Gd_2O_3, which has been investigated most extensively, the emission level at 1400°C is found to be 0.4 and 0.5 amp/cm^2 for W-matrix (62) and Re-base (74) cathodes, respectively, while for pure W a value as high as 0.87 amp/cm^2 is reported (71). On the other hand, emission values as low as 0.0025 (extrapolated), 0.1, and 0.14 are claimed for Ni (72), Ta (72), and Mo (73) substrates, respectively. Undoubtedly, some of this discrepancy might arise from the different base metals employed as well as slight variations in the purity of the various samples used.

It is agreed, however, that yttrium oxide,* gadolinium oxide, and dysprosium oxide appear to have not only better emission properties than thoria, but also seem superior or at least comparable to thoria in their evaporation rate. The thermionic properties of these are given in Table 2. The effective work function of the oxides of the other rare earths measured (La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Yb, Lu) ranged between ~3 and 3.5 ev at 1600°K (71,73), as compared to the corresponding value for thoria $\phi \simeq 3$ ev, and had evaporation rates slightly larger than that for thoria.

Refractory Carbides, Borides, and Nitrides

Refractory carbides, borides, and nitrides were also developed for application at high temperatures. They are fabricated by either painting or cataphoretically coating a W (75-77) or Ta (16) directly heated filament. Activation essentially consists of heating the filament to about 1500°C for several minutes to an hour.

It is seen from Table 2 that in the region of 2000°K only the emission from the carbides of Zr, Th, and U appear to be competitive to that obtainable with thoria. On the other hand, it is noted by some investigators (75) that, unlike thoria, the carbides give substantially the same dc emission as pulsed, which would make some of them useful in applications of heavy dc loads.

The carbide which has received much attention recently is the carbide of uranium. With its good thermionic properties, as well as its ability to be fission heated, it is presently one of the more promising electron sources in the field of thermionic energy conversion concerned with the transformation of nuclear heat directly to electrical energy.

THORIATED CATHODES

The earliest cathode of the thoriated type, the thoriated-W cathode, was discovered quite by accident. It was noted that when 0.5 to 2 percent thoria was added to the tungsten for the purpose of reducing crystal growth in filaments (thus decreasing the burnout rate), the emission would increase nearly 3 orders of magnitude.

This technique of providing a low-work-function surface for the metal is not to be confused with the similar type of matrix emitters where larger percentages of the "impregnant" or active material were used and in which diffusion took place largely by Knudsen flow of the vapor through the voids in the relatively coarse matrix. In the case of thoriated cathodes, the active material (ThO_2) is dispersed in a much smaller concentration in a denser metallic enclosure, diffusion taking place principally through lattice imperfections and grain boundaries. Because of this, the temperature of activation is

*While yttrium and lanthanum are, strictly speaking, not true rare earths, they are often classified with them.

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much higher than was the case with the matrix cathode, thereby limiting the use of indirectly heated cathodes. However, since neither large pores nor areas where appreciable agglomerates of the active materials exist on the surface, the lattice can (as could the hexaborides) be taken to temperatures higher than the melting temperature of the active material without excessive evaporation. This is because of the much higher adsorptive forces that hold a monolayer of thorium to the (probably oxidized) metal substrate compared to those forces which hold the surface atoms on a solid piece of thorium. Consequently, the thoriated cathodes can be operated at much higher temperatures than matrix cathodes and, since they do not evaporate so readily, have long stable and reliable life characteristics. Values of 30,000 hours are not uncommon for the thoriated-W cathode. The emission level for these cathodes, however, is somewhat less than those of the matrix type.

Thoriated-Tungsten Cathode

Next to the oxide cathode, the thoriated-tungsten cathode is probably the most widely used cathode in present-day commercial tubes. It has been thoroughly investigated and served to elucidate many of the physical problems of nonuniform (patchy) emitters (78-81). While the early emitters were made by merely adding a small mixture of thoria to the tungsten, present-day emitters are further "carburized" at the surface in order to decrease the rate of throium evaporation (82).

This step is accomplished by heat treatment of the Th-W filaments in a hydrocarbon atmosphere of benzene, acetylene, napthalene, or xylene vapors. At temperatures in the vicinity of 2200°K, the hydrocarbons are decomposed by the hot metal, forming a layer of tungsten carbide at the surface. The carburization must be carefully controlled because, though a thick layer is desired, embrittlement of the filament will occur if it is carburized too deeply. If the carburizing temperature is too high, the wire becomes too rich with carbon. This produces an excess amount of thorium carbide, which is a poorer emitter than a monolayer of thorium and also plugs the surface so that less diffusion of thorium takes place from within the metal.

The thoriated-tungsten wire is activated by first flashing it in a vacuum to 2500°K for about one minute. This serves to reduce some of the thoria in the interior, as well as providing a clean metallic surface since any thorium which reaches the surface is immediately evaporated. Lowering the temperature then to 2100°K for about half an hour will allow the thorium to diffuse from the interior and form a monatomic film on the surface. The filament is then operated in the temperature range of 1800° to 2000°K. If anything should poison the surface or strip it of thorium, the cathode is reactivated by merely repeating this same activation procedure.

Under normal operation, the small amount of thorium that is evaporated from the filament is replaced by diffusion from the interior. The tungsten-carbide surface layer effectively controls this diffusion rate so that excessive thorium evaporation does not occur. The end of useful life takes place when the thorium supply has been diminished to the extent that the rate of arrival of thorium to the surface is no longer sufficient to keep up with the rate of loss from it.

The thermionic constants of this surface vary with the degree of thorium coverage, which is a function of temperature and length of activation time. For a fully activated surface this value is $2.6 + 3.2 \cdot 10^{-4}\,T$ (16).

Thorium-Tungsten-Cermet Cathode

This is one of the variations of the thoriated-tungsten cathode in which neither thoria is used nor does carburization take place. Furthermore, designs have been tested using an indirectly heated cathode, the heating being accomplished by electron bombardment and by radiation (83,84).

The cathode is fabricated (84) by making a powdered mixture of 89.5 percent (by weight) of tungsten, 10 percent ditungsten carbide, and 0.5 thorium hydride.* The powdered mixture is pressed into a tabular shape by steel dies and is then sintered to 2400°C. Accurate dimensions are maintained by slipping this sleeve over a slighly tapering pin so that when it is sintered, it shrinks to a predetermined diameter. After sintering, the taper helps remove the sleeve and the proper length is obtained by diamond-honing the ends. The cermet is then brazed onto a Mo sleeve backing with a heater inserted in it and is then mounted in the assembled tube.

During the sintering, the thorium hydride is thought to lose its hydrogen and start alloying with the tungsten, at the same time forming the carbide as a result of its reaction with the tungsten carbide.

When heated in vacuum to operating temperatures of 1200° to 1600°C the thorium coverage on the surface is supplied by the thermal breakdown of the thorium carbide (84). It is believed that this source of thorium holds the evaporation rate to a smaller value than if thorium diffusion were the only rate-limiting process (84).

While no data are yet available regarding the thermionic emission values of this cathode, over 10,000 of them have already been used successfully in the Westinghouse type 6249A magnetrons.

Thoriated-Rhenium Cathode

Because of the similarity in the metallic properties of W and Re, it was of interest to also investigate the effects of thoriation of this metal (85).

Various percentages of ThO_2 were tried and it was found that 2.28 percent ThO_2 gave the best results. It was also observed that the Th-Re cathodes activated at temperatures as low as 1300° to 1450°K, which is about 400° below that required for Th-W cathodes. Furthermore, the emission level is slightly higher than that reported for the Th-W surface, the effective work function being $2.58 + 3.86 \cdot 10^{-4} T$ (85).

One disadvantage observed with this emitter is that since the activation temperature is lower, the temperature at which thorium evaporation becomes excessive is also lower.

THIN-FILM EMITTERS

The thin-film emitters, which are comprised simply of a thin film (usually monatomic) of some adsorbant (i.e., Th, Ba, and Cs) on a metal substrate, have been investigated largely from an academic standpoint or in the development of low-work-function surfaces for matrix cathodes. Because of the short lifetime of the adsorbed film, these emitters offer little as a potential cathode unless there is some way of continually replenishing this film, such as is the case, for example, of the W-matrix cathode or the thoriated-W cathode which have already been discussed.

*This is obtained by firing thorium powder in dry hydrogen to 800°-1000°C, slowly cooling, and then flushing it with an inert gas before air exposure.

A thin-film cathode receiving increasing attention is one which was studied in the nineteen twenties by Langmuir, Becker, and some of their contemporaries (86-88). Here, the metal substrate is tungsten and the adsorbed film is cesium condensed on to it from a surrounding cesium atmosphere. The cesium film is continually maintained on this surface, the extent of coverage depending on an equilibrium condition established between the arrival rate from the vapor phase and the evaporation rate from the metal. Since the former is a function of the ambient cesium vapor pressure and the latter is a function of the filament temperature, it is seen that the electron emission, which depends on the degree of surface coverage, will also be a function of both of these.

Taylor and Langmuir (88) have calculated how the emission from such a surface should vary as a function of temperature and cesium vapor pressure (here given in terms of cesium bath temperatures). The results of their curves are shown in Fig. 3. At low temperatures the tungsten surface is covered with many layers of cesium. As the tungsten temperature is increased for a given bath temperature, more and more of the cesium layers desorb until the most active surface is reached, which is $\phi \simeq 1.7$ ev and corresponds to slightly less than a monolayer of Cs on W (88). Upon further heating the tungsten, the rate of cesium evaporation increases and a correspondingly lower net amount will remain in equilibrium on the surface, thereby causing the emission to decrease with increasing temperature. When a temperature is reached so that no more cesium can remain in equilibrium on the surface, the emission again increases with temperature, finally reaching the emission characteristic of clean tungsten. At higher cesium bath temperatures, a correspondingly higher cesium evaporation rate from the metal is required for the same surface equilibrium conditions, therefore shifting the curve to a higher temperature range.

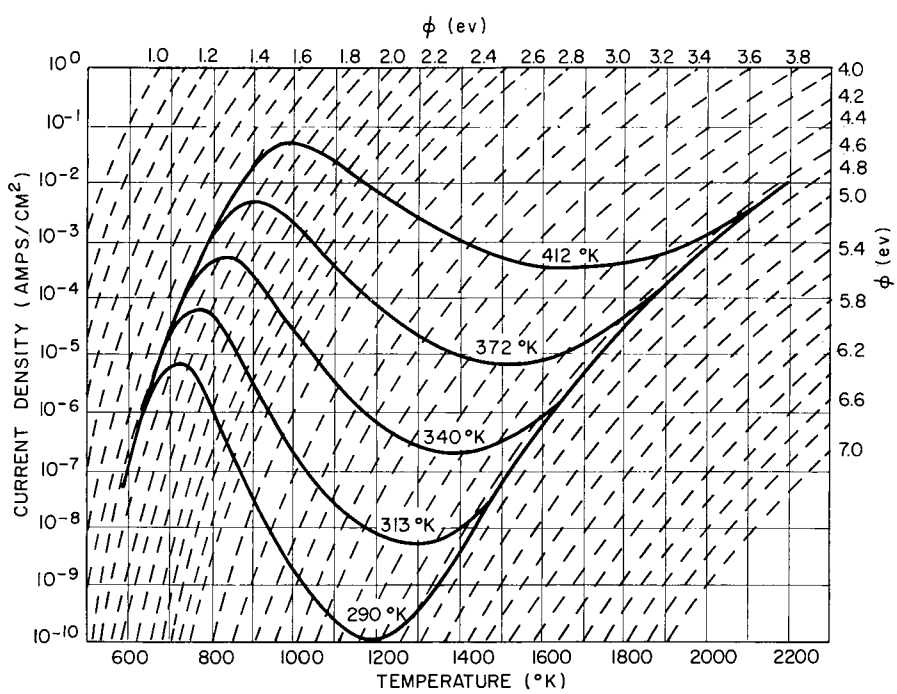

Fig. 3 - Emission characteristics of a surface of cesium on tungsten for various temperatures of the ambient saturated cesium vapor (replotted from the data of J. B. Taylor and I. Langmuir, Phys. Rev. 44:423, 1933)

The application of this electron emitter is in the field of thermionic energy conversion where cesium vapor is introduced into a diode to help neutralize the space charge (89). Since the voltage output of the converter depends on a high-work-function hot cathode and a low-work-function cool anode (89), it is evident from Fig. 3 that this is automatically obtained for such a system by the equilibrium film adsorbed on these surfaces. Furthermore, in order to maximize the converter efficiency it is possible to manipulate the work function of the surfaces by varying the surface temperatures and cesium bath temperatures.

METAL CATHODES

While pure-metal emitters generally have a much lower emission level for a comparable temperature than most of the other cathodes described here, they have inherent advantages that often make them preferable over any other type cathode.

Because of their mechanical ruggedness they are least affected by mechanical shock or ion bombardment; furthermore, they require no activation and are relatively immune to gas poisoning, making them useful in gas-filled and demountable systems, such as electron microscopes. Their low vapor pressure provides them with exceptionally long life characteristics and allows them to be used in ultraclean devices. Since anode contamination and other effects such as donor migration and heating due to high-resistance coatings are essentially eliminated, they do not suffer from emission decay effects and, therefore, can be used in dc as well as pulsed applications.

The near-Maxwellian behavior of their emitted electrons and their availability in single crystal form makes them especially useful in application where the energy distribution must be well defined. The high temperature to which they (especially W, Ta, Mo, and Re) can be heated allows them to be thoroughly outgassed, which results in a clean surface having a highly reproducible emission level. This has made it possible to use them to indicate very small partial pressures of various gases by first flashing at a high temperature and then observing the effect on their emission properties at lower temperatures as gases slowly adsorb on the surface.

The usefulness of a metallic emitter depends largely on its ability to provide a sufficient density of electrons without evaporating too many atoms. In Fig. 1, therefore, the emission characteristics are given for only those metals that can provide at least 1/10 amp/cm^2 while having a vapor pressure below 10^{-5} mm Hg. However, iridium is included since it is not damaged when exposed to air while at high temperatures; this makes it especially attractive in the use of ionization gages.

Of the other metals noted, W, Ta, and Mo are the most common refractory metals available, with W being generally preferred because of its high melting point (~3670°K). Tantalum is sometimes chosen over tungsten because its high ductility makes it more easily formed into many shapes; however, high cost has somewhat restricted its usefulness. Another disadvantage of tantalum is its reactivity with gases at high temperature, which prevents it from being hydrogen fired. Molybdenum, which does not have this problem, is also more ductile than tungsten although not quite as much as tantalum. It is much less expensive than either tungsten or tantalum, but because of its low melting point (~2900°K), it is not as often used as an electron source.

Some of the other metals mentioned are becoming more readily available and show promise in many applications. Rhenium, which has been intensively investigated at Battelle Memorial Institute (85), is found to have properties very similar to tungsten, yet it possesses a strong resistance to the "water cycle" reaction, which is so detrimental to tungsten filaments when operated in the presence of traces of water vapor. Niobium has

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characteristics very similar to tantalum, but because of its lower density it is much more useful in cases where shock and vibration are likely to cause failure. Furthermore, because of its much lower neutron cross section, it is one of the metals being investigated for nuclear-heat to electrical-energy converter cathodes.

LOW-TEMPERATURE EMITTERS

There are several advantages in developing a surface that has a fairly low electron barrier at low temperatures. Such a surface would be very applicable, for example, as an electron emitter in low-noise devices, for applications where heater sources are limited, and more recently as used for the low-work-function collector in thermionic energy converters.

These surfaces, which comprise the lowest work function surfaces so far developed, were originally designed for use as photoemitters with the hope of suppressing the thermionic emission. However, a few cases in the literature are reported in which their properties as thermionic cathodes have been stressed. Examples of recently investigated surfaces are the [Ag] - Cs_2O, Ag, Cs (90) cathode and the Bi-Ag-Cs (91) cathode, which were studied in the 300° to 400°K temperature range. Results from the former showed that a maximum thermionic activity was obtained just prior to the point where the excess Cs in the tube would react with adsorbed oxygen on the walls to form a Cs_2O "short" between cathode and anode. The effective work function for this surface was found to be $\phi \simeq 0.8 + 6.55 \cdot 10^{-4}$ T. The Bi-Ag-Cs cathode showed maximum thermionic activity ($\phi \simeq 0.9 + 8 \cdot 10^{-4}$T) when the photoactivity was "oxygen poisoned."

The disadvantages in the use of these cathodes are the difficulty of fabrication, the critical activation procedures, and the lack of chemical and mechanical stability.

HOT-ELECTRON EMITTERS

Under the category of hot-electron emitters comes a number of different surfaces such as MgO, Al_2O_3, BeO (92-94), and also cesiated Ge and Si crystals (95) which, it has been recently observed, are capable of giving self-sustained electron emission at room temperature without resorting to high fields (as would be necessary for field emission).

The emission process for this type of emitter occurs by letting the electron gain sufficient energy from an internal field in the crystal so that upon reaching the surface it has sufficient kinetic energy to surmount the electron barrier and be emitted. This field can either be caused by an external field, by a self-induced field as might exist from a p-n junction at the surface, or a combination effect whereby a surface charge is developed.

The energy gained by the electron is much higher than the thermal energy given to it from lattice vibrations; hence, it appears "hotter" (higher in energy) than the corresponding lattice from which it came. However, since the electron is no longer in equilibrium with the lattice, it cannot be interpreted by the same laws of thermionics as mentioned in the Introduction which are based on an electron kinetic energy corresponding to a given lattice temperature.

An audio amplifier has been demonstrated whose pentode output tube uses an MgO cold cathode rather than a conventional oxide cathode (93). Once the emission is started (using ultraviolet light, Tesla coil, radioactivity, etc.) it is sustained by keeping the collector at least 300 volts positive with respect to the cathode. This tube is capable of providing 900 milliwatts of audio power with less than 3 percent distortion (93). The life characteristics seem particularly promising since these surfaces are not subject to continuous evaporation of active material as are oxide cathodes. Meager life data available so far indicate no change in emission at 14,000 hours at a dc current density of 2.9 ma/cm^2.

REFERENCES

1. Herring, C., and Nichols, M.H., Revs. Modern Phys. 21:185 (1949)
2. Herrmann, G., and Wagener, S., "The Oxide Coated Cathode," Vols. I and II, London: Chapman and Hall Ltd., 1951
3. Huber, H., and Freytag, J.P., Le Vide 15:234 (1960)
4. Electronic Industr. 18(No. 4):53 (1959)
5. Varadi, P.F., Doolittle, H.D.D., and Ettre, K., Proc. 5th Nat'l Conf. on Tube Tech., New York, 1960
6. Benjamin, M., Huck, R.J., and Jenkins, R.O., Proc. Phys. Soc. (London) 50:345 (1938)
7. Hensley, E.B., Report on the 15th Annual Conference on Physical Electr., Mass. Inst. of Tech., Cambridge, 1955, p. 18
8. Ortusi, J., Le Vide 9:100 (1954)
9. Nergaard, L.S., RCA Rev. 13:464 (1952)
10. Moore, G.E., Wooten, L.A., and Morrison, J., J. Appl. Phys. 26:943 (1955)
11. Plumlee, R.H., J. Appl. Phys. 27:659 (1956)
12. Hamaker, H.C., Bruining, H., and Aten, A.H.W., Jr., Philips Res. Rep. 2:171 (1947)
13. Metson, G.H., Proc. Phys. Soc. (London) B 62:589 (1949)
14. Wargo, P., and Shepherd, W.G., Phys. Rev. 106:694 (1957)
15. Haas, G.A., J. Appl. Phys. 28:1486 (1957)
16. Wright, D.A., Proc. Inst. Elect. Engrs. 100(Pt 3):125 (1953)
17. Sproull, R.L., Phys. Rev. 67:166 (1945)
18. Hung, C.S., J. Appl. Phys. 21:37 (1950)
19. Metson, G.H., Proc. Inst. Elect. Engrs. 102B:657 (1955)
20. Wooten, L.A., Ruehle, A.E., and Moore, G.E., J. Appl. Phys. 26:44 (1955)
21. Caldwell, C.W., Proc. 5th Nat'l Conf. on Tube Tech., New York (1960)
22. Coomes, E.A., J. Appl. Phys. 17:647 (1946)
23. Haas, G.A., and Jensen, J.T., Jr., Rev. Sci. Inst. 28:1007 (1957)
24. Herrmann, G., and Krieg, O., Ann. der Physik 4:441 (1949)

UNCLASSIFIED

25. Metson, G.H., "Advances in Electronics," Vol. 8, p. 403, New York:Academic Press, Inc., 1956

26. Nienhold, J., German Patent 403209 (1920-1924)

27. Pirani, M., and Ewest, H., German Patent 529392 (1928-1931)

28. Espe, W., and Evers, F., German Patent 567909 (1927-1934)

29. Hull, A.W., Phys. Rev. 56:86 (1939)

30. Katz, H., J. Appl. Phys. 24:597 (1953)

31. Lemmens, H.J., Jansen, M.J., and Loosjes, R., Philips Tech. Rev. 11:341 (1950)

32. Coomes, E.A., and Forsbergh, P.W., Jr., U.S. Patent 2,543,439

33. Kohl, W.H., "Materials and Techniques for Electron Tubes," New York:Reinhold Publishing Corp., 1960

34. Beck, A.H.W., Proc. Inst. of Elect. Engrs. B106:372 (1959)

35. Stout, V.L., Proc. 4th Nat'l Conference on Tube Tech. (1958), New York:New York Univ. Press, p. 178, 1959

36. Rittner, E.S., Ahlert, R.H., and Rutledge, W.C., J. Appl. Phys. 28:156 (1957); Rutledge, W.C., and Rittner, E.S., J. Appl. Phys. 28:167 (1957)

37. Levi, R., J. Appl. Phys. 24:233 (1953)

38. Rittner, E.S., Rutledge, W.C., and Ahlert, R.H., J. Appl. Phys. 28:1468 (1957)

39. Levi, R., J. Appl. Phys. 26:639 (1955)

39a. Brodie, I., and Jenkins, R.O., Brit. J. Appl. Phys. 8:27 (1957)

40. Coppola, P.P., and Hughes, R.C., Proc. IRE 44:351 (1956)

41. Jenkins, R.O., and Trodden, W.G., J. Electr. and Contr. 7:393 (1959)

42. Popov, B.N., and Gugnin, A.A., Radiotekhnika i Elektronika 3:1024 (1958)

43. Espersen, G.A., IRE Trans. ED-6:115 (1959)

44. Brodie, I., Proc. Phys. Soc. (London) B 68:1146 (1955)

45. Haas, G.A., and Jensen, J.T., Jr., Proc. Third Nat'l Conf. on Tube Tech. (1956), New York Univ. Press, p. 60, 1958

46. MacNair, D., Lynch, R.T., and Hannay, N.B., J. Appl. Phys. 24:1335 (1953)

47. Beck, A.H., Cutting, A.B., Brisbane, A.D., and King, G., Le Vide 9:302 (1954)

48. Mesnard, G., and Uzan, R., Le Vide 9:1492 (1954)

49. Fane, R.W., Brit. J. Appl. Phys. 9:149 (1958)

50. Stout, V.L., and Gibbons, M.D., Proc. 17th Nat'l Conf. on Phys. Elect., M.I.T., Cambridge, Mass., 1957

51. Thien-Chi, Nguyen, and Dussaussoy, Pierre, Le Vide 9:297 (1954)

52. Richardson, J.F., Brit. J. Appl. Phys. 8:361 (1957)

53. Hadley, C.P., Rudy, W.G., and Stoeckert, A.J., J. Electrochem. Soc. 105:395 (1958)

54. Arshanskaia, N.G., Parkhomenko, V.S., and Raskina, N.I., Radiotekhnika i Elektronika 3:1058 (1958)

55. Balas, W., Dempsey, J., and Rexer, E.F., J. Appl. Phys. 26:1163 (1955)

56. Apelbaum, J., Proc. Third Nat'l Conf. on Tube Tech. (1956), New York Univ. Press, p. 56, 1958

57. Russell, P.N., and Eisenstein, A.S., J. Appl. Phys. 25:954 (1954)

58. Baker, J.B., and Gaines, G.B., Proc. 5th Nat'l Conf. on Tube Tech., 1960

59. Affleck, J.H., Proc. 5th Nat'l Conf. on Tube Tech., 1960
Ibid, General Electric Co. Sci. Reports No. 6-12, "Investigation of Various Activator-Refractory Substrate Combinations," Contract AF 19 (604)-4093, Dec. 14, 1959 - May 25, 1961

60. Goldwater, D.L., and Danforth, W.E., Proc. 4th Nat'l Conf. on Tube Tech. (1958), p. 190, New York: New York Univ. Press, 1959

61. Sackinger, J.P., Westinghouse Electric Corp. 4th Quarterly Interim Report, "Low Temperature Cathodes for Crossed-Field Devices," USN BuShips contract NObsr 77640, Aug. 1960

62. Dudley, K., and Lesensky, L., Proc. 5th Nat'l Conf. on Tube Tech., 1960

63. Fan, H.Y., J. Appl. Phys. 20,682 (1949)

64. Espersen, G.A., Farnsworth, H.E., Levi, R., and Lun, M.J., Philips Lab., Inc., Tech. Report #23 "Fundamental Research in Cathode Emitters," ONR Contract N6ONR261 T.O. 1, 1949

65. Weinreich, O., Rev. Gén'l Élec. 54:243 (1945)

66. Wright, D.A., Nature 160:129 (1947)

67. Hanley, T.E., J. Appl. Phys. 19:583 (1948)

68. Mesnard, G., and Uzan, R., Le Vide 5:769 (1950)

69. Goldwater, D.L., and Danforth, W.E., Proc. Third Nat'l Conf. on Tube Tech. (1956), p. 66, New York:New York Univ. Press, 1958

70. Lafferty, J.M., J. Appl. Phys. 22:299 (1951)

71. Kulvarskaya, B.S., Marchenko, V.B., and Stepanov, G.V., Radiotekhnika i Elektronika 3:1005 (1958)

UNCLASSIFIED

72. RCA Quarterly Report #3, "Thermionic Emission Studies," Contract DA36-039-SC-78155, June 30, 1959

73. Cronin, L.J., and Apelbaum, J.H., IRE National Convention Record, Part 3, p. 120 March 1957

74. Gaines, G.B., Battelle Memorial Institute 1st and 2nd Scientific Report, "Investigations of Rare-Earth Oxide Cathodes," Contract AF19(604)-5691, Dec. 1959

75. Goldwater, D.L., and Haddad, R.E., J. Appl. Phys. 22:70 (1951)

76. Haas, G.A., and Jensen, J.T., Jr., J. Appl. Phys. 31:1231 (1960)

77. Preliminary data by the author (unpublished)

78. Langmuir, I., Phys. Rev. 22:357 (1923)

79. Brattain, W.H., and Becker, J.A., Phys. Rev. 43:428 (1933)

80. Becker, J.A., Revs. Modern Phys. 7:95 (1935)

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

82. Schneider, P., J. Chem. Phys. 28:675 (1958)

83. Lea-Wilson, C.P., J. of Electr. 1:529 (1956)

84. Sackinger, J.P., and Foreman, R.J., Military Systems Design, Nov.-Dec., p. 310, 1959

85. Maykuth, D.J., Gaines, G.B., Root, G.S., Baker, J.B., Jaffee, R.I., and Peet, C.S., "Investigation of Rhenium for Electron Tube Applications," Battelle Memorial Institute Final Report, Contract AF 19(604)-1741, March 1960

86. Langmuir, J., and Kingdon, K.H., Science 57:58 (1923)

87. Becker, J.A., Phys. Rev. 28:341 (1926)

88. Taylor, J.B., and Langmuir, I., Phys. Rev. 44:423 (1933)

89. Nottingham, W.B., "General Theory of the Plasma Diode Energy Converter," 20th Annual Conference on Physical Electronics, M.I.T. (1960); also, Thermo Electro. Engr. Corp. Tech. Report #TEE-7002-5, Sept. 1960

90. Davey, J.E., J. Appl. Phys. 28:1031 (1957)

91. Mostovskii, A.A., Vorob'eva, O.B., and Maiskaya, K.A., Soviet Phys.-Solid State 1:585 (1959)

92. Dobischek, D., Schweitzer, J.A., and Ward, P.T., U.S. Patent 2,873,218 (Feb. 10, 1959)

93. Skellett, A.M., Firth, B.G., and Mayer, D.W., Proc. IRE 47:1704 (1959)

94. Mayer, D.W., Proc. 5th Nat'l Conf. on Tube Tech., 1960

95. Investigations in this area are presently being conducted by RCA under Contract DA-36039 SC 78155 and by Nuclear Corp. of America under Contract NObsr 77591

96. Mel'nikov, A.I., Morozov, A.V., Popov, B.N., and Maklakov, A.A., Radiotekhnika i Elektronika 3:322 (1958)

97. Bondarenko, B.V., and Tsarev, B.M., Radiotekhnika i Elektronika 4:1060 (1959)

98. Kudintseva, G.A., and Tsarev, B.M., Radiotekhnika i Elektronika 3:428 (1958)

99. Steinitz, R., Final Report, "Research on Thermionic Emission of Borides," Contract AF 18(600)-1504 Div File 20-20, American Electro Metal Division of Firth Sterling, Inc., Yonkers, N.Y.

100. Kapitsa, M.L., Mel'nikov, A.I., Morozov, A.V., Popov, B.N., Sobolevskaya, R.B., Tsarev, B.M., and Shul'man, A.R., Radiotekhnika i Elektronika 3:1010 (1958)

101. Bondarenko, B.V., Ostapchenko, E.P., and Tsarev, B.M., Radiotekhnika i Elektronika 5:1246 (1960)

102. Bondarenko, B.V., Ermakov, S.V., and Tsarev, B.M., Radiotekhnika i Elektronika 5:1553 (1960)

103. Jenkins, R.O., and Trodden, W.G., J. Elect. and Control 10:81 (1961)

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