

# The Influence of the Core Material on the Thermionic Emission of Oxide Cathodes\*

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**Summary**—The influence of the core material on the thermionic emission of oxide cathodes was investigated. Alloys of nickel with 4.8 per cent Mn, 4.0 per cent Al, 0.38 per cent Mg, and 3.5 per cent W were used as cores, with pure electrolytic nickel as a core being used as a control. The experiments showed that both the dc and pulsed emission of oxide cathodes are dependent on the core to a marked degree.

## INTRODUCTION

THE EFFECT of the core material on the thermionic emission of oxide cathodes was early discounted by the work of Deinninger.<sup>1</sup> Lowry<sup>2</sup> and Beese<sup>3</sup> reopened the question in the 1930's, and Benjamin<sup>4</sup> contributed to it in 1935. Since 1939, however, the problem of the influence of the core material has received increasing attention.<sup>5-12</sup>

To date, the only work on the effect of the more common impurities found in commercial, cathode-type nickel on the thermionic emission of nickel-base oxide cathodes is that of Benjamin.<sup>4</sup>

Among other materials, the effect of which was studied by Benjamin, were 0.07-per cent Mg-, 0.34-per cent Mn-, and 2-per cent Al-nickel alloys, used as core material for oxide cathodes. His work, however, is open to several criticisms. The most serious of these is his measurement of saturation currents at such high temperatures as 1,020° K under dc conditions. Such measurements are subject to the following errors:

- (a) Poisoning by evolution of gases from the anode.
- (b) Poisoning by evolution of gases produced by the decomposition of anode deposits.<sup>13,14</sup>
- (c) Heating of the coating by the  $I^2R$  loss in the coating itself, caused by the resistance of the coating. This is a serious criticism of Benjamin's work since he made the assumption that the "brightness temperature would depend only on the watts supplied to the filament." Thus, it is difficult to say what part of the differences in emission noted by Benjamin were due to, or were masked by, differences in  $I^2R$  loss in the coating.

Moreover, the use of two cathodes in one envelope is open to question because of the possibilities of affecting the emission of one cathode by the gases given off by the other cathode.

## DISCUSSION OF METHODS

### A. Vacuum Systems

The system was pumped with a three-stage, glass-fractionation pump, using Octoil-S. The vacuum was measured with a distillation products, VG-1A ionization tube. A trap was located between the diffusion pump and the manifold. This trap was baked to 400° C each time the manifold was baked to 450° C. With this system, the pressure as measured at the gauge was consistently lower than  $1 \times 10^{-7}$  mm Hg, and generally  $6 \times 10^{-8}$  mm at tipoff.

### B. Description of the Tube

The tube used in these experiments was the "Coomes Diode,"<sup>15</sup> which was developed by the Radiation Laboratory at M.I.T. The tube is illustrated in Fig. 1. The anode and leads are made of kovar. The tube is so designed as to permit the anode to be water cooled. The anode can then be operated at low temperatures, even for a relatively high anode dissipation. The design is also such as to allow the tube to be sealed with a minimum oxidation of the tube parts.

In order to measure cathode temperatures below 800° C, a thermocouple was added to the tube. The

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<sup>1</sup> F. Deinninger, "On the emission of oxides," *Ann. Phys.* (Lpz), vol. 25, p. 285; 1908.

<sup>2</sup> E. Lowry, "The role of core metal in oxide cathodes," *Phys. Rev.*, vol. 35, p. 1367; 1930.

<sup>3</sup> N. Beese, "Ba-Ni alloy core for oxide cathodes," *Phys. Rev.*, vol. 36, p. 1309; 1930.

<sup>4</sup> M. Benjamin, "The influence of metallic impurities in the core of oxide cathodes," *Phil. Mag.*, vol. 20, p. 1; 1935.

<sup>5</sup> W. Liebold, "Dissertation," University of Berlin, Berlin, Germany; 1941.

<sup>6</sup> A. Fineman and A. Eisenstein, "Studies of the interface of oxide cathodes," *Jour. Appl. Phys.*, vol. 17, p. 663; August, 1946.

<sup>7</sup> H. Jacobs and G. Hees, "Variations in the constants of Richardson's equation as a function of life for the case of oxide coated cathodes on nickel," *Phys. Rev.*, vol. 72, p. 174; July, 1947.

<sup>8</sup> W. Mutter, "Rectification characteristics of an oxide cathode interface," *Phys. Rev.*, vol. 72, p. 531; September, 1947.

<sup>9</sup> D. Wright, "Oxide cathodes, the effect of coating-core interface on conductivity and emission," *Proc. Roy. Soc. A*, vol. 190, p. 394; 1947.

<sup>10</sup> J. Acker, "A.S.T.M. committee work—factory tests on cathode Ni," *Proc. I.R.E.*, vol. 36, p. 376; March, 1948.

<sup>11</sup> H. Jacobs, G. Hees, and W. Crossley, "Thermionic emission of oxide coated filaments," *Bull. Amer. Phys. Soc.*, vol. 23, p. 12; 1948.

<sup>12</sup> R. McCormack, "A standard diode for radio-tube-cathode core material approval tests," *Proc. I.R.E.*, vol. 36, p. 376; March, 1948.

<sup>13</sup> H. Jacobs, "Dissociation energies of surface films of various oxides as determined by emission measurements of oxide cathodes," *Phys. Rev.*, vol. 69, p. 692; 1946. Also, *Jour. Appl. Phys.*, vol. 17, p. 596; July, 1946.

<sup>14</sup> H. Bruining, H. Hamaker, and A. Alten, Jr., "On the activation of oxide cathodes," *Philips Res. Rep.*, vol. 2, p. 171; 1947.

<sup>15</sup> E. Coomes, J. Buck, A. Eisenstein, and A. Fineman, "Alkaline Earth Oxide Cathodes for Pulsed Tubes," N.D.R.C., Div. 14, OEMsr 262, Report 933; March 30, 1946. (Publ. No. PB 55739, Office of Technical Services, U. S. Dept. of Commerce.)

couple was composed of an extremely fine, 0.002-inch diameter molybdenum wire, which was welded onto the cathode sleeve immediately adjacent to the coating.

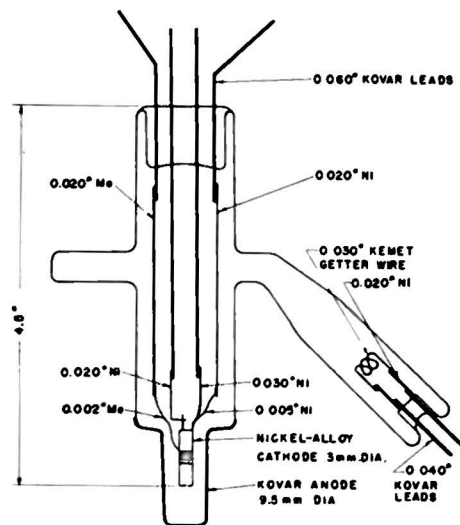


Fig. 1.—Diode construction.

To minimize end effects, only the center 4 mm of the 14-mm long cathode were coated. Before tipoff, all tubes were gettered by flashing an iron-clad barium getter, which had been carefully degassed before cathode activation.

### C. Techniques and Processing

The utmost attention was paid to the adherence of a uniform processing technique for all the tubes. The processing techniques<sup>15</sup> developed by the M.I.T. Radiation Laboratory were taken as the basis for this work, with the following exceptions: Al-, Mg-, and Mn-nickel-alloy cathodes were only vacuum fired, not hydrogen fired; Mn-nickel alloy cathodes were vacuum flashed at 950° C instead of 1,000° C because of the volatility of the manganese; and all the tubes were continuously flushed with dry nitrogen during sealing to minimize oxidation of the leads.

The salient points of the processing technique may be briefly enumerated. The kovar anode is outgassed by electron bombardment at 1,500 volts from a dummy tungsten filament. The central portion of the anode is heated to 800° C (brightness temperature) until the pressure is  $5 \times 10^{-7}$  mm. The cathodes are vacuum fired in a separate envelope. Each is flashed at 1,000° C for 5 minutes, and held at 850° C until the pressure is  $2 \times 10^{-7}$  mm. The fired cathodes are sprayed with an equimolecular mixture of barium and strontium carbonates in a nitrocellulose binder to a controlled coating weight of from 9 to 12 mg/cm<sup>2</sup>. When the sprayed cathodes are ready for mounting, the diodes are carefully opened with a hot wire and the sprayed cathode is

mounted in place of the tungsten filament that was used to bombard the anode. The technique is such that the processed parts are exposed to the air only for the irreducible time necessary for spraying, mounting, and sealing.

### D. Emission Measurement

The most direct method of approach is to use direct-current measurements at the normal operating temperatures of from 700 to 900° C, and to increase the plate voltage until the plate current begins to saturate. To consider this current as the temperature-limited emission of the cathode for that temperature, and hence as a measure of the cathode emission, is a serious error.

The primary faults are the following:

1. *The Anode Effect*—It is extremely difficult, if not impossible, to construct and sufficiently outgas an anode so that it will not liberate gases when saturation currents are drawn from the cathode. This is primarily because the saturation currents of oxide cathodes are so high and oxide cathodes are readily poisoned by minute amounts of gases that will react with free barium.

2. *I<sup>2</sup>R Heating and Coating Changes*—In drawing currents in the neighborhood of saturation, the *I<sup>2</sup>R* loss in the coating itself becomes comparable to the heater input.

For these reasons, in order to measure reliably the cathode-emission ability, it is necessary to take measurements at much reduced temperatures and currents, i.e., at from 150 to 400° C,  $10^{-10}$ – $10^{-6}$  a/cm<sup>2</sup>. Under these conditions the anode dissipation, and hence the gas liberation from the anode, is kept at an absolute minimum; furthermore, the passage of current through the cathode is kept exceedingly small so as to cause a minimum of disturbance to the existing physico-chemical makeup of the cathode.

In an effort to overcome the anode limitation, efforts were made as early as 1930 by Thomson,<sup>16</sup> and later by Maddock,<sup>17</sup> Heinze,<sup>18</sup> and Patai,<sup>19</sup> to draw emission current in pulses. In this manner, high peak currents could be drawn at operating temperatures of from 700 to 900° C at low anode temperatures, and hence at low poisoning levels. Thomson was able to reach peak currents as high as 3a/cm<sup>2</sup> in this manner.

Within recent years, by use of microsecond pulses, it was found that oxide cathodes could deliver up to 100 a/cm<sup>2</sup>, space-charge limited,<sup>16,20</sup> and up to 150 a/cm<sup>2</sup>,

<sup>16</sup> B. Thomson, "High efficiency emission from oxide-coated filaments," *Phys. Rev.*, vol. 36, p. 1415; 1930.

<sup>17</sup> A. Maddock, "Activation of oxide cathodes," *Phil. Mag.*, vol. 19, p. 422; 1935.

<sup>18</sup> W. Heinze, "Calorimetric determination of work function for oxide cathodes," *Ann. Phys. (Lpz)*, vol. 16, p. 41; 1933.

<sup>19</sup> E. Patai and G. Frank, "Emission constants of oxide cathodes," *Z. techn. Phys.*, vol. 16, p. 254; 1935.

<sup>20</sup> E. Coomes, "Pulsed properties of oxide cathodes," *Jour. Appl. Phys.*, vol. 17, p. 647; August, 1946.

space-charge limited,<sup>21,22</sup> when an auxiliary dc current was simultaneously drawn.

Our emission measurements were made by measurement at low temperatures and low current drain, and by pulse testing at 1 microsecond and at a low repetition rate, such as 60 cycles.

In addition to the gases given off from the anode as a result of excessive heating, it has been shown, by Jacobs<sup>13</sup> and Bruining,<sup>14</sup> that cathodes may be poisoned by the dissociation of oxide deposits on the anode. Where cathodes contain appreciable quantities of impurities, for example, magnesium, silicon, manganese, and the like, we may also expect to find their oxides on the anode. These compounds will be decomposed, as Jacobs has shown, at critical potentials, corresponding to the heats of formation. If the anode voltages are kept below this level, no dissociation of the anode deposit occurs, and hence there is no gas liberation and consequent emission decay.

For this reason the anode potentials on all the dc, low-temperature measurements have been restricted below 6 volts. Since a contact potential of at least 1 volt is generally present, in effect, only 5 volts remain to produce dissociation. This potential is below that corresponding to the critical potentials for any of the compounds likely to be deposited on the anode. Proof of this statement is the fact that in our measurements, up to 6 volts, absolutely no emission decay could be noted.

1. *Low-Temperature, dc Measurements:* Currents in the range of  $10^{-6}$ – $10^{-11}$  amperes were measured with a dc amplifier, and cathode temperatures below 700° C were measured by means of a thermocouple, formed by spot welding 0.002-inch molybdenum wire to the cathode immediately adjacent to the coating.

2. *Pulsed Measurements:* The pulsed measurements were made with a standard, Link Model-4 modulator, which was triggered at 60 cycles by a standard P4 Browning synchroscope.

The emission current was determined by measuring the drop of potential across a noninductive resistor, and the potential was measured by means of a capacity potential divider.

### E. Calibration

For the cathode-thermocouple calibration, special vacuum tubes, 2 feet in length, were constructed so that the one end containing the cathode could be kept in an oven, while the other end could be maintained at a fixed temperature. The temperature in the oven was measured by a chromel-alumel thermocouple immediately adjacent to the outside of the 2-foot tube and at the

level of the cathode. The chromel-alumel thermocouple, in turn, was calibrated against three fixed points: the boiling point of water, the melting point of tin, and the melting point of zinc.

### RESULTS

By measuring the dc emission at low temperatures and at low current levels, and by measuring pulsed emission at normal operating temperatures, significant differences in emission, which can be attributed to the core,<sup>23</sup> were found. The results are tabulated in Table I.

TABLE I  
TABULATED RESULTS

Core	Tube No.	Zero-Field Current at 230° C $\times 10^{-9}$ a/cm <sup>2</sup>	Sparking Current at 880° C a/cm <sup>2</sup>
3.5% W-Ni alloy	38	385	51
	27	395	40
	25	520	52
	73	525	61
		$460 \pm 66^*$	$51 \pm 7$
Electrolytic nickel	56	195	31
	31	245	37
	51	250	38
	66	240	45
		$230 \pm 22$	$38 \pm 5$
0.38% Mg-Ni alloy	37	46	28
	33	57	—
	48	79	35
	70	78	26
		$65 \pm 14$	$30 \pm 3$
4.0% Al-Ni alloy	35	42	27
	36	26	—
	58	42	23
		$37 \pm 7$	$25 \pm 2$
4.8% Mn-Ni alloy	26	1.8	14
	67	1.4	11
	34	8.0	19
	71	4.1	22
		$4 \pm 3$	$17 \pm 4$

\* Standard deviation.

The dc, low-temperature emission readings were taken in the range from 150 to 400° C and  $10^{-10}$ – $10^{-6}$  a/cm<sup>2</sup>. A typical set of data, illustrating the effect of the core material, is shown in Fig. 2. Tubes #73 and #34 are identical in every respect, except the core material. At a 10-degree higher temperature, however, the emission of the 4.8-per cent Mn-Ni cathode is only one-hundredth that of the 3.5-per cent W-Ni alloy.

To obtain the zero-field currents tabulated in Table I, the saturation currents were extrapolated to zero-field by the use of the Schottky equation,<sup>24</sup>  $\log I/I_0 = K/T\sqrt{E}$  where  $I$  is the saturation current at the anode potential  $E$ ,  $I_0$  is the saturation current when the field at the

<sup>23</sup> Chemical analysis of the cores is given in Tables II and III, Appendix.

<sup>24</sup> W. Schottky, "Ueber den Einfluss der Bildkraefte," *Phys. Z.*, vol. 15, p. 872; 1914.

The Schottky equation is derived from, and strictly applies only to, the emission of homogeneous metal surfaces. It is used for composite emitters, such as oxide cathodes, in lieu of an equation strictly applicable to composite cathodes. When so used, it is found that the slope is different from that given by the Schottky equation.

<sup>21</sup> W. Ramsey, "Sparking of Oxide Cathodes," N.D.R.C., Div. 14, OEMsr 358, Report 294; July 15, 1944. (Publ. No. PB12136, Office of Technical Services, U. S. Dept. of Commerce.)

<sup>22</sup> W. Ramsey, "General Survey of Sparking in H. V. Thermionic Tubes," N.D.R.C., Div. 14, OEMsr 358, Report 516, Oct. 31, 1945, 91p PB12128, Office of Technical Services, U. S. Dept. of Commerce.

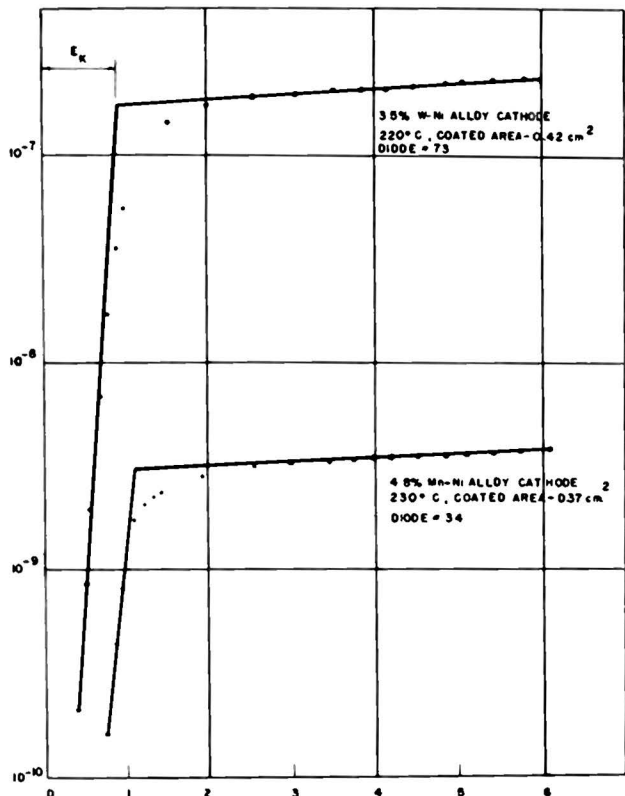


Fig. 2—Effect of the core material on the dc-emission characteristics of diodes at low temperatures. Ordinate is current in amperes; abscissa is applied anode potential in volts.  $E_K$  is the contact potential.

cathode is zero,  $T$  is the temperature, and  $K$  is a constant. Fig. 3 shows the extrapolation of the saturation

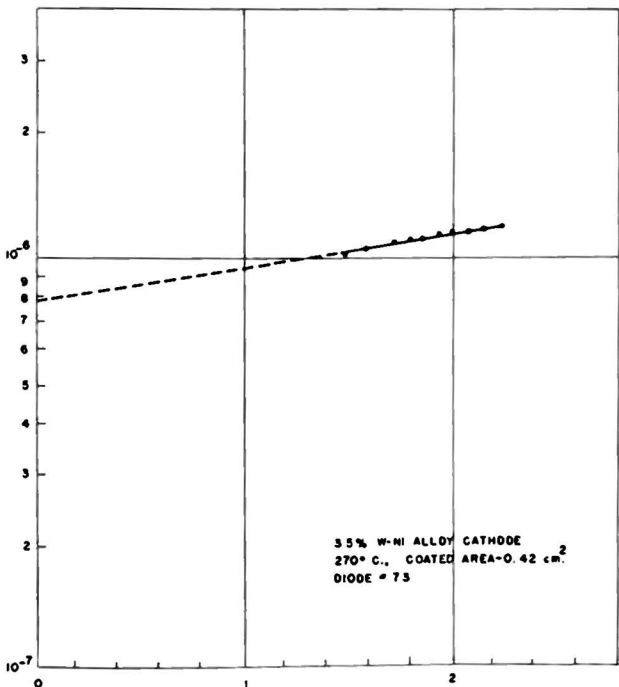


Fig. 3—Determination of the zero-field emission current extrapolation from the Schottky  $\sqrt{E}$  characteristic. Ordinate is current in amperes. Abscissa is  $\sqrt{E_A - E_K}$ , where  $E_A$  is the applied anode potential and  $E_K$  is the contact potential; unit is  $\sqrt{\text{volts}}$ .

currents to zero-field, using the Schottky relation. Account has been taken here of the contact potential, which must be added algebraically to the applied voltage to obtain the voltage that appears in Schottky's relation. The contact potential is given to a sufficient degree of accuracy by the interaction<sup>25,26</sup> of the initial and the saturation-current lines (Fig. 2).

The saturation currents for each cathode were measured for at least three different temperatures. The zero-field currents were determined, and were plotted against temperature. A typical set of data is shown in Fig. 4.

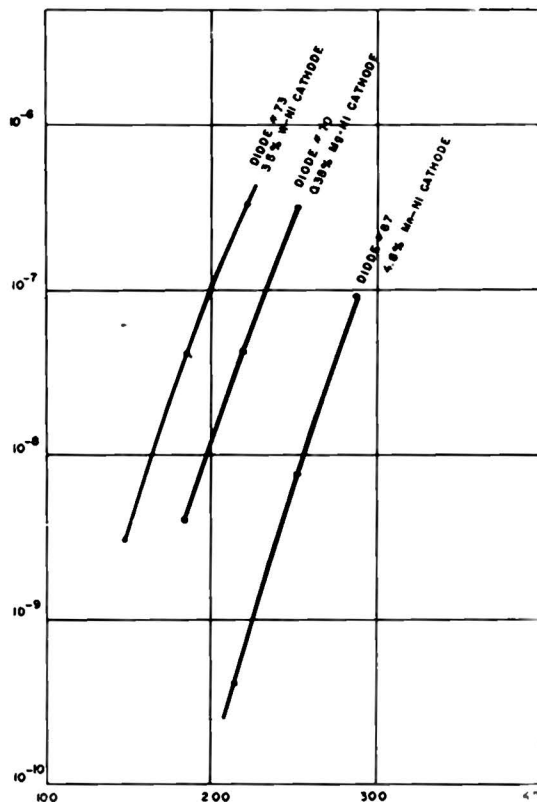


Fig. 4—Effect of the core material on the emission current of oxide cathodes. Ordinate is zero-field emission current in amperes per square centimeter; abscissa is temperature in degrees centigrade.

The comparative zero-field emission currents, shown in Table I, were taken from these graphs at the arbitrary temperature of 230° C. As noted earlier, the tubes were seasoned on the pumps. The emission measurements were made shortly after the tubes were taken off the vacuum system. The dc test was made first, the tubes being aged 10 minutes at 850° C (brightness) and 250 ma/cm<sup>2</sup> before the test. The tubes were retested after one hour dc operation at 850° C (brightness) and 250 ma/cm<sup>2</sup>, with satisfactory agreement.

The sparking currents are significant because they limit the maximum current that can be drawn from a cathode. There is evidence<sup>15,21,22</sup> that sparking is initiated by a metallic vapor, but whether this vapor is

<sup>25</sup> H. Rothe, "Austrittsarbeit und Kontaktpotential," *Z. techn. Phys.*, vol. 6, p. 633; 1925.

<sup>26</sup> W. Heinze and S. Wagener, "Variations of emission constants of oxide cathodes during activation," *Z. Phys.*, vol. 110, p. 164; 1938.

produced by a dielectric breakdown or by an  $I^2R$  heating of the interface is not as yet clear.

A typical set of data illustrating the effect of core material on pulsed emission is shown in Fig. 5. The data

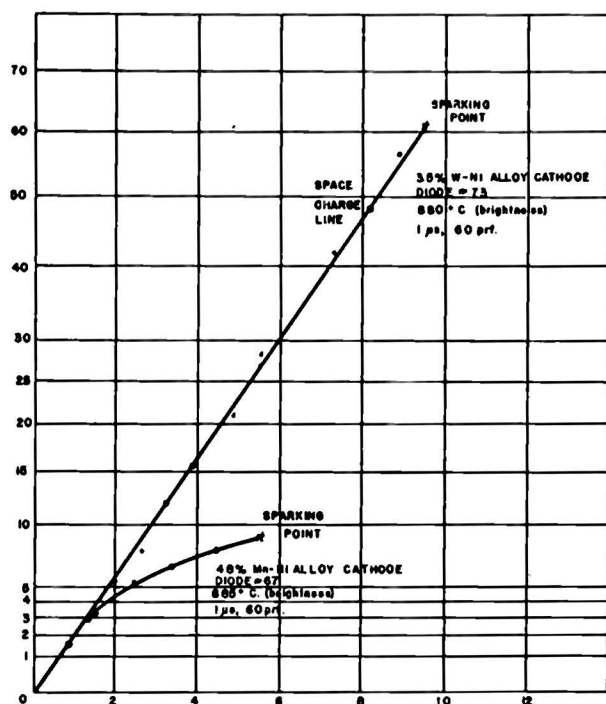


Fig. 5—Effect of the core material on the pulsed emission characteristics of experimental diodes. Ordinate is current in amperes per square centimeter; abscissa is applied anode potential in kilovolts. Draw on  $\frac{1}{2}$ -power paper.

was taken at 880° C., 1  $\mu$ s, 60 prf. The emission characteristic of the 3.5-per cent W-Ni core tube is typical of that of a good emitter. No falling off of emission from the space-charge limited line could be determined, the emission being limited by sparking. The emission characteristic of the 4.8-per cent Mn-Ni tube is characteristic of a poor emitter. The emission falls away from the space-charge curve at low values, and is ultimately limited by sparking.

The accuracy of the low-temperature dc measurements is limited by the accuracy with which the cathode temperature could be measured. Uncertainty in determining the temperature of the cold junction of the thermocouple limits temperature measurements to  $\pm 4$  per cent. The emission-current measurements were made to  $\pm 3$  per cent, and the voltage measurements to within  $\pm 2$  per cent. Pulse measurements are within  $\pm 5$  per cent. The temperature, when expressed as "brightness" temperature, could be measured to  $\pm 2$  per cent.

#### DISCUSSION OF RESULTS

The data of Table I show that the core material exerts a marked influence on the thermionic emission of oxide cathodes. The observed influence is in con-

formity with already published theories, as will be shown.

The work of Becker<sup>27</sup> and other<sup>28</sup> has shown that the oxide coating behaves as an impurity semiconductor, small amounts (in the order of 0.2 per cent) of free alkaline-earth metals furnishing the impurity. Furthermore, Prescott and Morrison<sup>29</sup> have shown that the emission of an oxide cathode is dependent on the amount of free barium present in the coating. They found that the thermionic emission increases with the barium content up to a concentration of 30  $\mu$ g<sup>30</sup> of barium per cm<sup>2</sup> of superficial area. Free barium, however, can be produced by reaction of the core material with the oxide coating, such as



where Ke represents the core metal.

Benjamin<sup>4</sup> advanced the thesis that the emission of nickel-alloy base oxide cathodes was related to the reducing power of the additive alloyed with the nickel. He used the heats of formation of the most likely formed oxides as a measure of the reducing power. In this manner he was able to explain the emission of 2-per cent Al-Ni, 0.07-per cent Mg-Ni, and 0.34-per cent Mn-Ni alloys. The emission of pure nickel, however, was out of place in this scheme, and Benjamin attributed this to small traces of reducing elements in the pure nickel, in spite of the fact that the other alloys were made using the same pure nickel as base.

In an investigation of the thermionic emission of oxide cathodes using eleven different core materials, Liebold found<sup>5,28</sup> that his results could not all be explained by the theory of Benjamin. He proposed a modified theory, into which the experimental data obtained here fits.

Benjamin divided the core materials into two groups: (a) those core materials for which the most probably formed interface oxides have a dissociation pressure, or a vapor pressure, higher than that existing in the tube (about  $10^{-6}$  mm), at the operating temperatures; and (b) those core materials for which the dissociation pressure and vapor pressure of the most probably formed interface oxides are lower than the pressure existing in the tube.

In the first group, the interface compounds that are formed do not persist. As soon as they are formed, they decompose, giving off oxygen, or they are evaporated away. Hence, no interface is formed. For these cores, basing Ba formation on the reduction of BaO by the core, Liebold concludes that the thermionic emission should increase with the reducing power of the core. To

<sup>27</sup> J. Becker, "Phenomena in oxide-coated filaments," *Phys. Rev.*, vol. 34, p. 1323; 1929.

<sup>28</sup> G. Herrmann and S. Wagener, "Die Oxydkathode," Johann Barth, Leipzig, Germany; 1943.

<sup>29</sup> C. Prescott and J. Morrison, "The oxide-coated filament," *Jour. Amer. Chem. Soc.*, vol. 60, p. 3047; 1938.

<sup>30</sup> Per 1 mg BaO, 1 mg SrO of coating.

this extent Liebold's theory is the same as Benjamin's. Indeed, Liebold found that the thermionic emission of Au, Pt, Pd, Cu, and Ni increased with the heats of formation<sup>31</sup> of the oxides most probably formed at the interface. These oxides all have dissociation pressures above  $3 \times 10^{-6}$  mm.

For the second group, an interface compound is formed that persists. This interface, by its interposition, retards the reduction by the core metal of BaO to Ba, and does so to a larger degree as it grows in thickness. Indeed, Liebold found that for W, Mo, Ta, Cr, and Zr, the emission decreased as the heats of formation of the most probably formed oxides increased. The dissociation and vapor pressures of all these oxides are considerably below  $10^{-6}$  mm.

Finally, Liebold explains the high thermionic activity of pure, nickel-base oxide cathodes. According to Liebold, the heat of formation of the nickel oxide is just large enough to supply a sufficient reduction of BaO to Ba, without, at the same time, the dissociation pressure of NiO ( $3 \times 10^{-6}$  mm at  $950^\circ$  C) being so low as to permit an appreciable interface formation. Finally, the dissociation pressure is not so large that the oxygen liberated by the dissociation of NiO is too much for the getter to handle; otherwise, the cathode would soon be poisoned by oxygen.

The results that were obtained for the 3.5-per cent W-Ni alloy may at first seem to be a contradiction because Liebold, in testing the emission of pure tungsten core oxide cathodes, found their emission to be inferior, and noted the presence of an interface formation, which he concluded was probably  $WO_2$ . However, this contradiction is resolved when we remember that a large part of the interface formation takes place during the breakdown of the carbonate to the oxide, as a result of the thermal dissociation of  $2CO_2$  to  $O_2$  and  $2CO$ , and with the subsequent oxidation of the W core by the  $O_2$ . However, since the core is a 96.5-per cent Ni-3.5-per cent W alloy, instead of pure tungsten, not as much tungsten is accessible to the oxygen during the brief (3 to 4 minutes) carbonate-to-oxide breakdown procedure. As a result, a relatively smaller interface is formed. Furthermore, if it can be assumed that the tungsten alloyed in the core gradually diffuses to the surface where it is removed by combination with the oxygen of the BaO to form Ba (noting that the heats of formation indicate that W is more active in reducing BaO to Ba than Ni), it becomes understandable that the 3.5-per cent W-Ni alloy, when used as the base of an oxide cathode, yields a more efficient emitter than pure

nickel. The sparking-current data for the 3.5-per cent W-Ni alloy supports this view.

The results obtained with a 0.38-per cent Mg-Ni alloy, when used as core, show thermionic emissions inferior to that of pure nickel. Rooksby<sup>32</sup> has noted that an interface compound is formed when nickel containing small amounts of magnesium is used as the core for oxide cathodes, and he analyzed this interface to be MgO. It will be assumed that an MgO interface also is formed in the Mg-Ni cathodes tested here. The low values of sparking current obtained for 0.38-per cent Mg-Ni give further indication of the formation of an interface. Decreased emission of the 0.38-per cent Mg-Ni alloy core oxide cathodes, therefore, is probably due to the formation of an MgO interface which persists and retards the action of the Mg of the core in its reduction of the BaO.

The improved emission reported by Benjamin<sup>4</sup> with 0.07-per cent Mg-Ni as core, and the general use by the Germans of 0.07-per cent Mg-Ni for oxide cathodes during World War II,<sup>33</sup> can be explained by reasoning similar to that applied to the 3.5-per cent W-Ni core. As a result of the small amount of magnesium in the core, the interface formation during conversion of the carbonate to oxide is reduced. The interface that is formed is not sufficient to impede the reducing action of the magnesium in the core.

The results with 4.0-per cent Al-Ni show a reduced emission relative to the use of pure nickel as core. Rooksby<sup>32</sup> has analyzed the interface formed on 2-per cent Al-Ni core oxide cathodes, and found it to be  $BaO \cdot Al_2O_3$ . Unfortunately, data on the dissociation and vapor pressures of this compound are not available. The presence of an interface in the cathodes analyzed by Rooksby, however, indicates that the vapor pressure and the dissociation pressure are below that of normal tube operation. It will be assumed that  $BaO \cdot Al_2O_3$  is the interface formed in our 4.0-per cent Al-Ni cathodes. That an interface is formed also is indicated by the low sparking currents obtained for 4.0-per cent Al-Ni cathodes (Table I).

The thermionic emission, therefore, is reduced for the 4.0-per cent Al-Ni cathodes for the reasons already outlined for the 0.38-per cent Mg-Ni alloy. The emission in this case is inferior to that obtained by Benjamin because of the increased aluminum content, the discussion being similar to that given for 0.38-per cent Mg.

Finally, the emission of 4.8-per cent Mn-Ni alloy was found to be considerably inferior to that of pure nickel. Benjamin<sup>4</sup> in his work with 0.34-per cent Mn also found it to be the worst of 0.07-per cent Mg-Ni, 2-per cent Fe-Ni, 2-per cent Al-Ni, and 0.2-per cent Th-Ni. No data on the interface compound of an Mn-Ni alloy oxide cathodes is available. In a manner

<sup>32</sup> H. Rooksby, "Application of X-ray technique to individual laboratory problems," *Jour. Roy. Soc. A.*, vol. 88, p. 308; 1940.

<sup>33</sup> T. Briggs, "European practices in the manufacture of cathodes," *Proc. I.R.E.*, vol. 36, p. 376; March, 1948.

<sup>31</sup> It is to be noted that, strictly speaking, the heats of formation cannot be used as a guide to the reducing power of an element, but rather it is the free energy of the reaction that is the determining factor. Heats of formation, when used as a guide of reducing power, will give the correct result only when the entropies involved are the same for all the reactions compared. Furthermore, the values of the thermodynamic constants at the temperatures of the reaction should be taken, and not the values for room temperatures, as is so commonly done. Finally, it should be pointed out that the free energies in a reaction do not determine the rate of the reaction.

similar to the other alloys, an interface compound probably is formed, reducing the emission for the reasons discussed for the 0.38-per cent Mg-Ni and 4.0-per cent Al-Ni alloys. The pulsed-emission data for the 4.8-per cent Mn-Ni alloy given in Table I are the lowest for all the alloys tested. The emission of the 4.8-per cent Mn-Ni alloy base oxide cathodes, however, is so reduced that it seems likely that another factor is at work. One such factor might be the formation of an interface compound that can oxidize barium.

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## APPENDIX

TABLE II

QUANTITATIVE CHEMICAL ANALYSIS OF THE NICKEL ALLOYS\*

Type	INCO melt No.	Si	Mg	C	Mn	Fe	Cu	S	Ni+Co	Other	Ni	Co
Grade A	—	0.20% max.	—	0.20% max.	0.35% max.	0.30% max.	0.25% max.	0.008% max.	99.00 min.	—	—	—
Electrolytic Ni	12808	0.03%	0.027%	0.012%	—	—	—	—	—	—	Remainder 0.76%	
0.38% Mg-Ni	12811	0.03%	—	0.012%	—	—	—	—	—	0.38% Mg	Remainder 0.76%	
4.0% Al-Ni	12827	0.03%	0.027%	0.012%	—	—	—	—	—	4.01% Al	Remainder 0.76%	
4.8% Mn-Ni	12888	0.03%	0.027%	0.012%	—	—	—	—	—	4.83% Mn	Remainder 0.76%	
3.5% W-Ni	12890	0.03%	0.027%	0.012%	—	—	—	—	—	3.48% W	Remainder 0.76%	

\* A qualitative spectrochemical analysis is given in Table III.

† This special series of nickel melts, together with the analyses, was kindly supplied by the International Nickel Company, through the courtesy of Mr. E. M. Wise. Melt No. 12808 is the base melt to which Al, Mn, Mg, and W are added to obtain the other nickel alloys. The analysis is for the ingot.

TABLE III.

SPECTROCHEMICAL QUALITATIVE ANALYSIS\* OF THE NICKEL ALLOYS AND OF THE EMISSION MIXTURE

	Estimated range	Electrolytic nickel	0.38% Mg-Ni alloy	4.0% Al-Ni alloy	4.8% Mn-Ni alloy	3.5% W-Ni alloy	Raytheon emission mixture C-51-2
Principal component	>10%	Ni	Ni	Ni	Ni	Ni	Ba, Sr
Major component	> 1%	—	—	Al	Mn	W	—
Minor component	0.1-3%	Co	Co, Mg	Co	Co	Co	Ca, Na
Impurities	0.01-0.3%	Fe, Mn, Si, Mg	Fe, Mn, Si, Ca	Fe, Mn, Si, Mg, Pb, Na	Fe, Cr, Si	Fe, Mn, Si, Zn	Mg
Traces	<0.03%	Ca, Cu, Na	Cu, Na, Pb	Ca, Cu, Cr, Zn	Ca, Cu, Na, Pb, Mg	Cu, Na, Pb, Mg, Ca, Cr	Pb
Faint traces	—	—	—	—	—	—	Al, Bi, Cu, Fe, Mn, Ni, Si

\* Furnished through the courtesy of Dr. L. A. Wooten; analysis by Mr. W. Hartmann, Bell Telephone Laboratories. Analysis is for the rolled nickel sheet from which the cathodes were formed.

