THERMIONIC EMISSION STUDIES OF ACTIVATION
SINTERED ALLOYS

By

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The object of the present work was to investigate new alloy emitters using an activation sintering method for their preparation. It was also desired to study the effect of porosity on thermionic emission.

Alloys of W-Pd, W-Ni, W-Co and W-Cu were chosen because Palladium and Nickel strongly promote sintering whereas Cobalt and Copper have a much lower activating power, although they are otherwise closely related transition elements.

The emitters were impregnated with optimum concentration of metal salts, reduced and sintered in hydrogen tube furnace. The technique results in an effectively monatomic emitting layer around each tungsten particle.

The results show the reduction in work function of the emitters e.g. W-Pd (0.25 ev); W-Ni (0.20 ev); W-Co (0.40 ev) and W-Cu (0.30 ev).

Presintered (porous) emitters have ten times more emission than fully sintered emitters, and their thermionic curves are heterogenous consisting of three steps in the saturation region. Porous emitters are characterized by a surface which consists of protuberances and cavities, and the heterogenous nature of emission is assumed to be associated with different depths of the cavities.

Decay in saturation emission (with a rate coefficient of between 0.4 - 0.55) has been observed in emitters which are sintering during emission; this phenomenon is not obtained in fully sintered materials and porous tungsten.
A new correlation has been proposed to connect the work function of both elemental and duplex emitters with the number of electrons in the outershell of the component atoms. This correlation explains qualitatively the values of work function of most emitting surfaces. An attempt has also been made to quantitize the correlation by reference to the spectroscopically determined promotion energies of the s-p-d electronic states used in the hypothesis.
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II. LITERATURE SURVEY.

II.1. Introduction.

The literature survey has been divided into three sections (i) deals with the types of cathodes hitherto developed, in (ii) the techniques of preparations are described, while (iii) is an account of the physical electronics of cathodes. In section (i) the cathodes are classified according to the materials used in their preparation viz;

(1) oxide coated cathodes
(2) thin film emitters.
(3) compound emitters.
(4) pure metal emitters.
(5) alloy emitters.

All of these cathodes are described along with their thermionic properties and uses. The recent developments, and wherever possible, further direction of improvements are also indicated. In section (ii) the various techniques used for the preparation of cathodes are described. Section (iii) includes the old and recent theories of thermionic emission, the study of effect of metallurgical variables, and the evaluation of thermionic constants.

The main characteristics considered in the first part are expressed in terms of the constants of the basic Richardson equation:

\[ J_s = A T^2 \exp \left( \frac{-\phi}{kT} \right) \]  

(1)

where \( A \) is the Richardson constant
\( \phi \) is the work function.

These concepts are then discussed in further detail in later parts of the literature survey.
II.2. Classification and Development of Cathodes

II.2.1. Oxide-Coated Cathodes

These cathodes consist of a layer of Barium, Strontium or Calcium oxides on a metal base. A mixture of alkaline earth carbonate is used and thermally decomposed in vacuum to obtain the thermionically active oxide surface.

A more mechanically and electrically stable version of these cathodes are the so-called Matrix cathodes, in which the active material is dispersed through a metal matrix (usually Nickel).

Dispenser type cathodes (L-cathode) \(^{(1)}\) consists of porous tungsten at the bottom of which, exists a Barium-Strontium carbonate enclosure. After thermal decomposition and reduction, free Barium diffuses over the surface which reduces the work function of the cathode. Two other modifications of the dispenser type cathodes are impregnated cathodes, \(^{(2)}\) and pressed cathodes \(^{(3)}\). In these cathodes the enclosure is eliminated and instead, the active material is adsorbed in pores or incorporated during the pressing of powder manufacture.

Further development of these cathodes has been in the direction of changing both the base material and the active material. At the same time, a study of the activation mechanism and physico-chemical phenomena associated with these additional components has provided a better understanding of cathode electronics.

In studies of matrices of Mo, Re, Re-Mo with or without their compounds (i.e., carbides, borides and silicides), \(^{(4,5)}\) it has been found that some of the matrices specially of Re are
mechanically more stable and possess a high water cycle resistance.

Rare-earth oxides (6) when used as impregnant produce cathodes which can withstand exposure to air and possess good high temperature mechanical properties.

It has been found that if L-cathodes are coated with Osmium, the emission is increased by one order of magnitude. The reduction in work function by the high work function adsorbant is anomalous and was not explained (7).

A very recently developed cathode is the so-called "Tungstate cathode" (8) which employs Ba₅Sr(WO₆)₂ as an activator. An emission of 5-10 amps/cm² can easily be drawn continuously at 950-1000°C. Different metallic coatings can be used on the surface to protect the surface against evaporation and poisoning of the environment, but no coatings were found which could improve the emission and in many cases it deteriorated. In the case of Osmium, which reduces the work function of a normal dispenser cathode, the work function is increased by the amount it decreased in normal dispenser cathodes.

Bondarenko (10) has reported thermionic investigations of the Tantalates, Hafniates, and Rheniates of alkali metals. Different Ba:MeOₓ have been investigated, in the case of Ba:WOₓ composition the best results are obtained by Ba₃WO₆, which turns out to be the most stable. The replacement of W as base metal by Ta yields even better results. Rheniates and especially the Hafniates of Barium are better than Tungstate and Tantalates. Other alkali metal compounds have inferior emission properties than Barium. Zhaden (11) has used Irridium as base metal, and his results show better thermionic properties than Tungstates. The thermionic properties of Ba:MeOₓ cathodes are listed in Table 1.b.
In order to obtain additional information of the physical electronics of oxide cathodes, many new experiments with (Ba-Sr) oxides or (Ba-Sr-Ca) oxides \(^{(12)}\) have been performed. Sr has been identified as the donor in double oxides, while Ca is the donor in triplex oxides.
**TABLE I.a** The effective work function of the various cathodes with the range of temperature.

<table>
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<tr>
<th>Base</th>
<th>Activator</th>
<th>Effective Work Function</th>
<th>T(°K)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>W</td>
<td>(BaSr)Co&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.68+3.24x10&lt;sup&gt;-14&lt;/sup&gt;T</td>
<td>1230-1470</td>
<td>1</td>
</tr>
<tr>
<td>&quot;</td>
<td>BaAl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2.3 +1.6x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>BaSi&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.81 + 4.7 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ni</td>
<td>(BaSr)Co&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.2 + 5 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mo</td>
<td>Ba Al&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.1 + 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>BaSi&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.23+1.3x10&lt;sup&gt;-3&lt;/sup&gt; &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>Ta</td>
<td>BaSi&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.93 + 1x10&lt;sup&gt;-4&lt;/sup&gt; &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>(BaCa)Si&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.26+7.7x10&lt;sup&gt;-4&lt;/sup&gt; &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>Re</td>
<td>(BaCa)Al&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.2 + 7 &quot;</td>
<td>1230-1430</td>
<td>5</td>
</tr>
<tr>
<td>WC</td>
<td>BaAl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2.27 + 2.1 &quot;</td>
<td>900-1400</td>
<td>4</td>
</tr>
<tr>
<td>&quot;</td>
<td>BaSi&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.71 + 4.6 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>MoC</td>
<td>BaSi&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.76 + 7.8 &quot;</td>
<td>&quot;</td>
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<tr>
<td>TaC</td>
<td>&quot;</td>
<td>1.79 + 3.5 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;5&lt;/sub&gt;</td>
<td>&quot;</td>
<td>2.3 + 4.3 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>2.69 + 6.2 &quot;</td>
<td>&quot;</td>
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<tr>
<td>Ta&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>1.88 + 3.9 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W Si&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>2.25 + 1.1 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>MoSi&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>2.22 + 3.1 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>TaSi&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>1.92 + 4.0 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1/2Re-1/2Mo</td>
<td>(BaCa)Al&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.7 + 4.67 &quot;</td>
<td>1230-1430</td>
<td>5</td>
</tr>
<tr>
<td>1/2Re-1/W</td>
<td>&quot;</td>
<td>1.4 + 6.6 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W</td>
<td>La&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.6</td>
<td>1573</td>
<td>6</td>
</tr>
<tr>
<td>&quot;</td>
<td>Nd&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.76</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.97</td>
<td>1673</td>
<td>&quot;</td>
</tr>
<tr>
<td>W</td>
<td>OS/(BaSr)Co&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.60</td>
<td>&quot;</td>
<td>7</td>
</tr>
<tr>
<td>W</td>
<td>Ba&lt;sub&gt;5&lt;/sub&gt;Sr(Wo6)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.14+5.6x10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>1023-1173</td>
<td>8</td>
</tr>
<tr>
<td>W</td>
<td>&quot;</td>
<td>1.79</td>
<td>2.379</td>
<td>1175-1223</td>
</tr>
</tbody>
</table>

*Note: Base Activator Effective Work Function T(°K) Ref."
### TABLE I.b. (10,11) The effective work function and the
temperature range of various Tungstate, Hafniates and
Rheniakes Cathodes.

<table>
<thead>
<tr>
<th>Emitting Surface</th>
<th>Effective work function(ev)</th>
<th>T(°k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_3$WO$_6$/W</td>
<td>1.25</td>
<td>1000 - 1550</td>
</tr>
<tr>
<td>Ba$_5$Ta$<em>2$O$</em>{10}$/W</td>
<td>2.72</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ba$_3$WO$_6$/Ta</td>
<td>1.18</td>
<td>950 - 1400</td>
</tr>
<tr>
<td>Ba$_3$Ta$<em>2$O$</em>{10}$/Ta</td>
<td>2.15</td>
<td>840 - 1230</td>
</tr>
<tr>
<td>2Ba OHfO$_2$/W</td>
<td>2.2</td>
<td>1200°k</td>
</tr>
<tr>
<td>7Ba O Re$_2$O$_7$/W</td>
<td>2.38</td>
<td>&quot;</td>
</tr>
<tr>
<td>5Ba$_5$ Ta O$_5$/W</td>
<td>2.31</td>
<td>&quot;</td>
</tr>
<tr>
<td>3Ba O WO$_3$/W</td>
<td>2.61</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ba$_3$WO$_6$/W</td>
<td>2.42</td>
<td>1100°k</td>
</tr>
<tr>
<td>Sr$_3$WO$_6$/W</td>
<td>3.19</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ca$_3$WO$_6$/W</td>
<td>3.36</td>
<td>&quot;</td>
</tr>
<tr>
<td>(Ba-Sr)WO$_6$/W</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>(Ba-Ca)WO$_6$/W</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>(Ba-Ca-Sr)WO$_6$/W</td>
<td>2.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ba-Tungstate/W</td>
<td>2.08</td>
<td>1000°k</td>
</tr>
<tr>
<td>Ba-Tungstate/Ir</td>
<td>1.82</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Monolayers of alkali metals, when adsorbed on the base metal, reduce the work function of the cathodes. The first emitter of this type was developed by Langmuir in 1923. He found that the emission can be increased many orders of magnitude higher than the pure metals if the substrate is covered by a monolayer of alkali metals (e.g., Cs, Ba, Th). In the case of cesiated surfaces, the emission depends on both operating temperature as well as on the pressure of Cs vapour. These cathodes are widely used in the energy conversion field.

Intensive work has also been done on thoriated cathodes. Current densities of 0.3—29 amp/cm² are obtainable at 1700—2000°C. These cathodes are more reliable in stability and have a low evaporation rate than oxide cathodes. Physical studies of these surfaces have been important in understanding of the patch effect (due to nonuniformity of the surfaces). Different base materials e.g., Mo, Ta, Re (14, 15, 16) have been used to improve the stability and emission properties of these cathodes. (Table II)

Recently more complicated surfaces which have an additional component either in the substrate or in the adsorbate have been investigated. Tsarev (17, 18) has studied the cesiated surfaces with the separate addition of Fluorine and Hydrogen. He found that Fluorine systems are thermally more stable than a single oxide system and are better in emission properties. Similarly the use of hydrogen results in enhanced emission. These results are shown in Table (II).

Instead of using a single alkali vapour, such as Cesium multi-alkali vapours have been tried and vapours of Li, Ba, Sr, and CsF have been used in conjunction with Cs. The results are shown in Table II. The addition of Lithium
Psarouthakis (20) obtained very important and useful results in achieving higher efficiencies for Cs-converters by the introduction of Ba or Sr vapours. R. Langpape (21) has studied the effect of CsF on the work function of the metals and on the optimum pressure of the Cesium. The idea was to increase the work function of the substrate and consequently a reduction in the electrode work function and operating pressure of Cesium.

In thoriated cathodes a further reduction in work function can be obtained by the use of Iodine film on the substrate (22). The resultant work function is found to be smaller than for W-Th or W-O-Th systems.
### TABLE II
The effective work function of different film emitters.

<table>
<thead>
<tr>
<th>Emitting Surface</th>
<th>Effective work function (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W - Cs</td>
<td>1.7</td>
<td>13.a</td>
</tr>
<tr>
<td>Mo - Cs</td>
<td>1.68</td>
<td>14</td>
</tr>
<tr>
<td>W - Th</td>
<td>$2.6 \pm 3.2 \times 10^{-4}$</td>
<td>13.b</td>
</tr>
<tr>
<td>Re - Th</td>
<td>$2.58 \pm 3.86 \times 10^{-4}$</td>
<td>16</td>
</tr>
<tr>
<td>Mo - F - Cs</td>
<td>1.30</td>
<td>17</td>
</tr>
<tr>
<td>Mo - H - Cs</td>
<td>1.32 - 1.4</td>
<td>18</td>
</tr>
<tr>
<td>W - Li</td>
<td>2.18</td>
<td>19</td>
</tr>
<tr>
<td>W - Li - Cs</td>
<td>1.61</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mo - Ba - Cs</td>
<td>1.82</td>
<td>20</td>
</tr>
<tr>
<td>Mo - Sr - Cs</td>
<td>1.74</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mo + CsF =</td>
<td>4.75</td>
<td>21</td>
</tr>
<tr>
<td>Re + CsF =</td>
<td>5.40</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mo + CsF + Cs =</td>
<td>3.15</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re + CsF + Cs =</td>
<td>3.10</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
II.2.3. Compound Emitters

Compound emitters generally operate at higher temperatures, and are physically more rugged than the oxide coated cathodes. These consist of hexaborides and oxides of rare earth elements, or carbides, nitrides, and borides of refractory metals.

(i) Hexaborides

Lafferty (23) was the first to investigate the thermionic properties of the hexaborides of Y, La, Ce, Rb, Nd, Gd, Dy and Ho. These cathodes are prepared by pressing and sintering hexaborides powders. On heating the crystals, a monolayer of the metal is formed on the surface. These cathodes can be used in demountable systems and provide very high current. The LaB$_6$ cathode has become the most important example of this group in practice.

It has been found that in hexaborides cathodes the slow destruction of the Boron matrix can be avoided by carburizing the Ta wire on which the hexaborides are coated (24).

(ii) Rare-Earth-Oxides

The oxides of rare earth are applied by the technique of either brushing or cataphoresis on to a base, to obtain low work function surfaces. These cathodes operate at high temperature and have the advantages of quick activation and mechanical strength. In most of the cathodes the activation requires heating to 1500°C. Among the whole series of rare earth oxides, the Gd$_2$O$_3$ and Y$_2$O$_3$ have received much attention (25). Their thermionic properties are better than the Thoria cathodes. Mo, Re, Ni and Ta (26,27,28) have also been used as base metals. The effective
work function of rare earth oxides varies from ~3.0 to 3.5 ev at 1600\(^{\circ}\)k and is listed in Table III. 

(iii) Carbides, Nitrides and Borides 

Many carbides e.g. UC, ZrC, ThC, Mo\(_2\)C \((29,30,31)\) have been investigated for their thermionic properties. Uranium Carbide has become more important owing to its use in conversion of nuclear heat energy into electrical energy.

G.A. Hass\(^{(32)}\) has also investigated other compounds of Uranium such as UO\(_2\), UN, UB\(_2\), WSi\(_2\) and UC - ZrC. He reports that the emission of active state can be described within a factor of 2 or 3 for all compounds by the empirical constant \(\phi = 3.00\) ev; \(A = 10\) Amp/cm\(^2\)deg\(^2\) and considered that electron emission comes from a Uranium film on the surface. The Nitrides and Borides of Zr, Ti, U, Ta and Mo\(^{(33)}\) have also been investigated. The results are shown in Table III.
<table>
<thead>
<tr>
<th>Emitter</th>
<th>Effective work function (eV)</th>
<th>Temperature $°K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeB$_6$</td>
<td>$2.59 + 3.0 \times 10^{-4}$</td>
<td>140 - 1370</td>
<td>23</td>
</tr>
<tr>
<td>BaB$_6$</td>
<td>$3.45 + 1.74$</td>
<td>1250 - 1650</td>
<td>&quot;</td>
</tr>
<tr>
<td>ThB$_6$</td>
<td>$2.92 + 4.72$</td>
<td>1150 - 1600</td>
<td>&quot;</td>
</tr>
<tr>
<td>LaB$_6$</td>
<td>$2.66 + 1.22$</td>
<td>1080 - 1300</td>
<td>&quot;</td>
</tr>
<tr>
<td>YB$_6$</td>
<td>$2.2 \pm 1.8$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>PrB$_6$</td>
<td>$3.46 - 7.9$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>NdB$_6$</td>
<td>$3.97 - 1.08$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>GdB$_6$</td>
<td>$2.05 + 4.28$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>DyB$_6$</td>
<td>$3.53 + 1.37$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>HoB$_6$</td>
<td>$3.42 + 1.86$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>La oxide/W</td>
<td>$3.0 \pm 0.75 \times 10^{-4}$</td>
<td>1000 - 1100</td>
<td>25</td>
</tr>
<tr>
<td>Ce</td>
<td>$2.3 \pm 4.1$</td>
<td>1200 - 2000</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pr</td>
<td>$2.8 \pm 5.4$</td>
<td>1400 - 1600</td>
<td>&quot;</td>
</tr>
<tr>
<td>Nd</td>
<td>$2.3 \pm 4.1$</td>
<td>1400 - 1600</td>
<td>&quot;</td>
</tr>
<tr>
<td>Gd</td>
<td>$2.1 \pm 4.5$</td>
<td>1100 - 1600</td>
<td>&quot;</td>
</tr>
<tr>
<td>Lu</td>
<td>$2.3 \pm 6.0$</td>
<td>1500 - 1700</td>
<td>&quot;</td>
</tr>
<tr>
<td>Y</td>
<td>$2.0 \pm 2.64$</td>
<td>1350 - 1500</td>
<td>&quot;</td>
</tr>
<tr>
<td>Th</td>
<td>$2.6 \pm 2.4$</td>
<td>1300 - 2200</td>
<td>25</td>
</tr>
<tr>
<td>ThC on W</td>
<td>$3.2 \pm 1.16$</td>
<td>1500 - 2000</td>
<td>30</td>
</tr>
<tr>
<td>ZrC</td>
<td>$2.18 \pm 5.1$</td>
<td>1173 - 2073</td>
<td>30</td>
</tr>
<tr>
<td>UC</td>
<td>$2.94 \pm 1.1$</td>
<td>1200 - 2100</td>
<td>29</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>$4.75 \pm 0.05$</td>
<td>1400 - 1600</td>
<td>31</td>
</tr>
<tr>
<td>10%UC-ZrC</td>
<td>$2.9 + 2.3 \times 10^{-4}$</td>
<td>$1800^°K$</td>
<td>32</td>
</tr>
<tr>
<td>ZrN on W</td>
<td>$3.96$</td>
<td>2000</td>
<td>33</td>
</tr>
<tr>
<td>TiN</td>
<td>$3.96$</td>
<td>2000</td>
<td>&quot;</td>
</tr>
<tr>
<td>UN</td>
<td>$3.1 + 2.14 \times 10^{-4}$</td>
<td>1350 - 2100</td>
<td>32</td>
</tr>
<tr>
<td>TaB$_2$</td>
<td>$2.89 + 2.14$</td>
<td>1400 - 2100</td>
<td>33</td>
</tr>
<tr>
<td>ZrB$_2$</td>
<td>$4.48 - 4.76$</td>
<td>1500 - 2100</td>
<td>&quot;</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>$4.80 - 1.17$</td>
<td>1350 - 1850</td>
<td>33.a</td>
</tr>
<tr>
<td>MoB$_2$</td>
<td>$3.05 + 4.1$</td>
<td>1550 - 2050</td>
<td>&quot;</td>
</tr>
<tr>
<td>W B$_2$ on W</td>
<td>3.3</td>
<td>1300 - 2100</td>
<td>32</td>
</tr>
</tbody>
</table>
II.2.4. Pure Metal Emitters

Thermionic emission properties of the metals have been investigated by many workers. But the only metal cathodes which are used in practice are those of W, Mo, Ta, Re, or Nb owing to their requirement of a high melting point. These emitters have many advantages over the other type of cathodes. They can withstand mechanical shock and ion bombardment, and are immune to gas poisoning. Since no active materials are used, a longer life is characteristic of these emitters.

Tantalum and Molybdenum are easier to fabricate than Tungsten owing to their better ductility. Rhenium \(^{(5)}\) is becoming more important owing to its capability of resistance against "water cycle" reaction. Tungsten is not as good as Rhenium in the atmosphere of water traces. Niobium has a lower neutron cross section and hence, is used in nuclear heat energy conversion.

Current research in the thermionic studies of the metal is in the direction of (i) re-investigating the thermionic values under very clean condition, (ii) determining the work function of different crystal faces and (iii) exploring different technique to measure the work function.

Wilson\(^{(34)}\) has measured the thermionic work functions of Nb, Mo, Ta, W, Re, Os, Ir, Be, Ti, Cr, Fe, Ni, Cu and Pt. in vacuum (and in Cs) using a cup collector system. His measurement covers a wide range of temperature. In many cases his results deviate from the older reported values. An explanation of the discrepancies have been provided in terms of the different temperature range, heat treatment, crystal orientation and melting points. Some of his results, along with old values are retabulated in Table IV.a.
Hopkins (35) has developed a method of determining the work function of the metals which consists of depositing a thick layer of metal on glass or sheets of other metals. It is shown that the thermionic values obtained on glass substrates do not differ appreciably from the reported values of polycrystalline specimens in literature. The dissimilarities in the work function values with sheet metals has been explained by the growth of expitaxial with the (100) and (111,112) faces of tungsten and tantalum. In glass the structure of deposited film has been identified as polycrystalline. The results are shown in Table IV.b.
**TABLE IV.a. (34)** The work function of the pure metal emitters

<table>
<thead>
<tr>
<th>Metals</th>
<th>Work function (ev)</th>
<th>Work function (old values) ev</th>
<th>Temperature °k.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>3.67</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>4.3 ~ 3.73</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>3.9</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.2 ~ 4.6</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>$6.27 - 1.04 \times 10^{-3} T$</td>
<td>4.6</td>
<td>1380&lt;T&lt;1500</td>
</tr>
<tr>
<td></td>
<td>$4.41 \pm 0.02 \times 10^{-3} T$</td>
<td>-</td>
<td>1170&lt;T&lt;1250</td>
</tr>
<tr>
<td>Cu</td>
<td>4.41 ± 0.02</td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>5.79; 5.03 + 4.2 \times 10^{-4}</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>4.19</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>4.12</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.17</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>4.25</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>4.54</td>
<td>4.54</td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>4.96</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>4.84 - (5.9 - 3.9 \times 10^{-4})</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>5.27 $\pm$ 1111</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Polycrystalline Sheet material</td>
<td>Thick multilayer deposited in vacuum</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
<td>-------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>Sheet Tungsten</td>
</tr>
<tr>
<td>Ag</td>
<td>$4.29 \pm 0.02$</td>
<td>$4.3 \pm 0.02$</td>
<td>$4.32 \pm 0.03$</td>
</tr>
<tr>
<td>Al</td>
<td>$4.19 \pm 0.03$</td>
<td>$4.24 \pm 0.03$</td>
<td>$-$</td>
</tr>
<tr>
<td>Au</td>
<td>$4.71 \pm 0.02$</td>
<td>$4.71 \pm 0.004$</td>
<td>$4.97 \pm 0.02$</td>
</tr>
<tr>
<td>Ba</td>
<td>$2.35 \pm 0.03$</td>
<td>$2.42 \pm 0.05$</td>
<td>$2.66 \pm 0.01$</td>
</tr>
<tr>
<td>Cd</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Cs</td>
<td>$-$</td>
<td>$1.84 \pm 0.01$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mo</td>
<td>$4.20 \pm 0.03$</td>
<td>$4.21 \pm 0.04$</td>
<td>$-$</td>
</tr>
<tr>
<td>Nb</td>
<td>$4.37 \pm 0.03$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Ta</td>
<td>$4.22 \pm 0.02$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Th</td>
<td>$3.71 \pm 0.01$</td>
<td>$-$</td>
<td>$3.44 \pm 0.01$</td>
</tr>
<tr>
<td>U</td>
<td>$3.19 \pm 0.01$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>W</td>
<td>$4.54 \pm 0.05$</td>
<td>$4.55 \pm 0.02$</td>
<td>$-$</td>
</tr>
</tbody>
</table>
B.C. Dyubuya (36-39) seems to be the principal investigator of the thermionic studies of alloys. He has studied many alloys of Hf, Re, Th, La, Nb as the common additive to different alloying components covering a wide range of temperature and composition. The minimum value of the work function is associated to the composition that corresponds to a single mono-layer.

The work function of Hafnium alloys with Nb, Ta, W, Re (36) has been found to be less than that of pure Hf. The alloy of Hf with Nb and Ta yields $\phi = 3.4 \sim 3.7$ while with that of W or Re reduced to 3.7 ev. Similar results are obtained with Zr alloys.

A solid solution of Tungsten in Rhenium gives $\phi = 4.85$ ev while Rhenium solution in Tungsten produces $\phi = 4.54$ ev. The Rhenium in Tungsten does not increase the work function of tungsten which seems to be anomalous (36). In the case of Nb-Ta, Ti-Re, Ta-Re alloys (37) the values of the work function are approximately equal to 4-4.2 ev. However, 1% Ti-Re alloys reduces the work function as low as 2.85 ev. When 2% Thorium is alloyed with Os, Re, Pt, or Ir (38) the work function becomes practically equal to that of a monolayer of a Thorium in the case of Os and Re, while for Pt and Ir alloys it is 3.9-4.0 ev. Lanthanum alloys with Ir and Os (39) reduce the work function even lower than that of pure Lanthanum. However a La-Pt alloy results in a higher value i.e. 4.01 ev. The lower values of the work function of the alloys with Th or La are ascribed to the formation of monolayer on the alloy surface.

Atta (40) has investigated the thermionic properties of binary alloys of rare earth metals with tungsten, which did not show any marked improvement until an additional third
metal (i.e. Zr, Th, etc.) was added. It was concluded that the presence of third metal increases the value of Richardson constant, while the work function is determined by the alloy additives. The results are explained by a mobilising action of the third metal. The rare earth metals do not wet the tungsten, and in the molten state reach the surface only by evaporation. The mobiliser (third metal) wets the tungsten and hence the molten alloys rise to the surface by capillary action. (Fig.1). The results are shown in Table V.

Recently Rozhkov studied Re-rare-earth metal alloys. The work function of the alloys have been found to stay approximately constant i.e. 2.9~3.0 ev which is 0.2 ev less than that of corresponding rare-earth metals. The Re-Lu is an exception, with a slightly higher work function. The similarity in the work function of the alloys has been attributed to the similarity in electronic structure of all the rare earth metals. The closeness between the work function of rare earth metals and their alloys has been associated with the nature of the formation of distributive type thin films on the surface. The results are shown in Table V.

Jones has studied the work function changes of different layers of Copper deposited on Tungsten. In case of type I layer the work function rises from 4.52 ev to 4.83, while the type II layer decreases to 4.2 ev. The type III layer slightly increases it to 4.3 ev. The type I, II, III layers have been assumed to be one, two and three atomic thick. The results are shown in Table V and illustrated in Fig 2.
Fig. 1a: Transport of adatoms via evaporation.

Fig. 1b: Rise of molten alloy on surface by capillary action.

Fig. 2: Change in work function with amount of Copper deposited on Tungsten tip surface.
TABLE V  The work function of different alloy emitters with the range of temperature and the values of $A_R$ (from Ref. 40)

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Work function (ev)</th>
<th>Temperature $^\circ K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf-Nb</td>
<td>3.4-3.7</td>
<td>1300-1700</td>
<td>36</td>
</tr>
<tr>
<td>Hf-Ta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf-W</td>
<td>~ 3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf-Re</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Hf-Re</td>
<td></td>
<td>1200-2000</td>
<td></td>
</tr>
<tr>
<td>1% Zr-Re</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Re-Hf</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Re-Zr</td>
<td>~ 4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-Re</td>
<td>4.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re-W</td>
<td>4.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-Ta</td>
<td>4.0-4.1</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>Ti-Re</td>
<td>4.1-4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta-Re</td>
<td>4.15-4.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Ti-Re</td>
<td>~ 2.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os-2%Th</td>
<td>3.08</td>
<td>1600</td>
<td>38</td>
</tr>
<tr>
<td>Re- &quot;</td>
<td>3.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt- &quot;</td>
<td>4.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir- &quot;</td>
<td>3.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir-0.5%La</td>
<td>2.69</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>Os- &quot;</td>
<td>2.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt- &quot;</td>
<td>4.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# TABLE V (contd)

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Work Function</th>
<th>&quot;A_R&quot;</th>
<th>Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-La</td>
<td>2.45</td>
<td>1.39</td>
<td>1600-1900</td>
<td>40</td>
</tr>
<tr>
<td>W-La-Zr</td>
<td>2.56</td>
<td>8.80</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-La-Hf</td>
<td>2.52</td>
<td>5.30</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Gd-Zr</td>
<td>2.50</td>
<td>4.90</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Y-Zr</td>
<td>2.71</td>
<td>4.65</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Th</td>
<td>2.66</td>
<td>2.52</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Th-Zr</td>
<td>2.70</td>
<td>11.01</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Th-Hf</td>
<td>2.69</td>
<td>12.24</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Y</td>
<td>2.98</td>
<td>-</td>
<td>1300</td>
<td>41</td>
</tr>
<tr>
<td>Re-Gd</td>
<td>2.90</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Tb</td>
<td>2.95</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Dy</td>
<td>2.90</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Ho</td>
<td>2.95</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Er</td>
<td>3.00</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Tu</td>
<td>2.05</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Re-Lu</td>
<td>3.20</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>W-Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I Layer</td>
<td>4.83</td>
<td>-</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>&quot; II &quot;</td>
<td>4.20</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot; III &quot;</td>
<td>4.30</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* amps/cm² deg²
II. 2.6. Techniques of Preparation.

Various techniques are used to produce duplex cathodes. The most widely used methods are as follows:

II. 2.6.1. Painting, dipping or dragging.

In these techniques the emitting paste is either painted on the core metal or the latter is dipped or dragged through the paste. Oxide coated cathodes (43), thoria cathodes and cathodes of refractory carbides, nitrides and borides (30) are prepared by these techniques.

II. 2.6.2. Spraying.

Here the active material is sprayed on the substrate. The type of cathodes produced normally by this method are oxide-coated cathodes (43), thoria cathodes (44) and rare earth oxides cathodes (27).

II. 2.6.3. Electrophoretic.

The deposition of the emitting material is obtained electrophoretically by immersing the core metal and a second electrode into an emission paste and by applying a potential between these cathodes.

This technique is being applied in the preparation of various types of cathodes e.g. oxide coated cathodes (43), thoria cathodes (44); rare earth oxide cathodes (25, 27) and cathodes of refractory carbides, borides and nitrides (30).

II. 2.6.4. Impregnation.

In this method the base matrix is impregnated in vacuum by a melt of active material (Ba Al₄). The impregnated L - cathodes (45) are produced by this technique.
II. 2.6.5. **Pressing.**

This technique consists of pressing and sintering the mixture of the powders of base metal and active material. Cathodes prepared in this way are pressed - L - cathodes \((3)\); Hexaboride cathodes \((23)\); thorium-tungsten (Cermet type) cathode \((46)\), and alloy emitters \((37,40)\).

II. 2.6.6. **Deposition of Powder.**

The powdered form of the metal is deposited in vacuum on the substrate. This process is used in the preparation of W-W powder or W-Mo powder cathodes \((47)\) and cathodes of various metals on different substrates \((35)\).

II. 2.6.7. **Alloying.**

Straightforward alloying of the components in a vacuum are furnace (in Helium or Argon atmosphere). The alloy emitters \((36-39)\) have usually been prepared by this method.

II. 2.6.8. **Activated sintering.**

Sintering may be considered as welding together of particles caused by heat; the temperature used is normally at least \(2/3\) melting point. In order to accelerate the sintering process the use of various activators can be made \((48,49,50)\).

The activation is termed as gaseous, liquid, and solid activation according to the state of the phase responsible for the acceleration of the process.

Mechanisms for metallic activation have been suggested by Brophy \((51)\), Toth \((52)\) and Samsonov \((53)\). According to Brophy the activating
element forms a "carrier phase" layer on the tungsten particle surface. Tungsten dissolves preferentially into the layer at points of particle contact and diffuses "outward" in the interfaces between the carrier phase layer and the particle. The Toth model also uses a similar "modified" surface but it is suggested that diffusion takes place towards the points of contact. Samsonov has explained the metallic activation on the basis of stable configuration of localised electrons (see sec. II.5.3).

It is suggested that the decrease in the amount of free energy, during the transfer of electrons from the activator to the tungsten, (which takes place in order to increase the statistical weight of the stable configurations of tungsten and activator), is responsible for the metallic activation.

Metal additives have been used as activators by many workers \(^{51,52,53}\) in the sintering of tungsten powder. The optimum concentration of the additive has been found such as to give a monolayer around each particle of tungsten. Brophy \(^{51}\) has suggested that nickel remains on the surface of tungsten particles during the early stages of sintering, and is then located at grain boundaries during the final stages.

A common technique used for adding the activators is to impregnate the tungsten in metal salt solution which is followed by reduction and sintering (see section III.3). It is this technique which has been used for the preparation of the emitters of the present work.
II.2.7. General Conclusions on Type of Emitters

(1) The recent trend in the development of the cathodes have been directed towards the replacement of base metal and the use of additional components either in the active material or in base material. The purpose being (i) to prolong the life of the cathode by reducing the evaporation rate of the active material, (ii) to achieve mechanical stability, (iii) and to increase the current densities.

(2) The replacement of traditional base metals, in film type and composite cathodes, and its effect on the thermionic properties are quite marked, but a systematic study of the work function changes with different substrate has not been currently formulated.

(3) Only a few alloy emitters have been studied. In the investigation of alloy emitters, a wide range of composition and temperature can be covered, which is useful in providing additional thermionic data with which a general thermionic model or correlation can be developed.
II.3. GENERAL CATHODE ELECTRONICS.

Introduction.

In order to determine the physical phenomena of electron emission, two approaches have been used. One is the hitherto developed old semi-classical approach which considers the electrons as "free" in the form of an electron gas inside the metal, while in the other approach the electrons are viewed as occupying "localised" orbits.

The importance of metallurgical aspects (e.g. grain size, microstructure and porosity etc) of the substrate in thermionic emission is discussed in section (II.7), while the relationship between the current, temperature and work function, and methods to determine the thermionic constants are discussed in section (II.8).

II.4. The Semiclassical Approach.

In this approach it is assumed that "free electrons" exist in the form of an electron gas inside the metal (54), in which case a force field \( f(x) \) is necessary to prevent them coming out of the surface (Fig.3). In order to take an electron out of the metal, work has to be done against this force (or barrier), and the least energy imparted to the electron at \( T = 0^\circ K \) to remove it from the surface is equal to the work function of the surface

\[
W = f(x) \, dx \quad (2)
\]

Sommerfeld (55) modified this theory by pointing out that since at \( T = 0^\circ K \) the electrons have a range of energies from zero to a maximum \( (W_i) \) and not only zero, the magnitude of the work function should be
Wa - Wi = -Emax \tag{3}

where $Wa$ is external work function equal to the depth of the potential box, $Wi$ is the maximum energy of the electron (which is equal to Fermi energy). $Emax$ is the energy difference, and the work function will then be equal to the energy of the uppermost electron at $T = 0^\circ K$.

FIG.3. Energy scheme of electron emission from a conduction band.

When electrons leave the metal, a negatively charged electrical layer is formed near the surface, while excess positive charges form another layer under this surface. Thus a double layer is formed whose field retards the electrons passing through it. The work function is determined quantitatively by the potential drop across this double layer plus the interior work function. Thus

$$\phi = x + D \tag{4}$$

where $x$ is the interior work function and $D$ is the strength of double layer barrier.

The main deficiency in the Sommerfeld model is that a real metal cannot be represented by a potential box with a flat bottom i.e. $U \neq \text{const.}$ and the field
inside it must vary with the co-ordinates of structure of lattice and the detailed state of the electrons.

Many other modifications have therefore been carried in the model by other workers, a review of which is provided by Herring and Nichols (56). Further modifications are related with other minor factors taken into account e.g. polarizability; patches etc.

II.4.1. The Work function of Composite surfaces.

When foreign atoms are adsorbed on the substrate metal, they induce negative charges on the surface and thus form an additional double layer, which changes the strength of the ordinary surface double layers. The magnitude of this force (ΔD) has been given by Langmuir (57) as:

$$ΔD = 2πεσM$$

where $M$ is the dipole moment of each adsorbed atom, and $σ$ is the number of ions per unit area.

Rasor and Warner (58) have extended the Langmuir theory (especially for Cs surfaces) assuming two adsorbed species, i.e. atoms and ions with different charges, instead of assuming only one state for adsorbed Cs (see Fig:4). Each state of the Cs particle i.e. ion or atom will then have a different dipole moment.
This theory leads to the further consequences that the ions with their induced negative charges form an additional double layer, which changes the strength of the double layer at the surface. The amount of change is the measure of changes in the work function of the surface. Assumptions made in this treatment include:

(i) That the electronic structure of the substrate metal is not affected by the adsorbate particles.

(ii) That the ratio of the ionic coverage ($\theta_i$) and atomic coverage $\theta_a$ is given by the

$$\frac{\theta_a}{\theta_i} = 2 \exp \left(-\frac{E}{kT}\right) \quad (6)$$

where $T$ is the surface temperature; and $\theta_a + \theta_i = \theta$ (total coverage).

By virtue of these assumptions the final expression for $\Delta \phi$ is given as:

$$\Delta \phi = 2 \tilde{A} \sum_{i=1}^{n=2} \phi_i M_i \quad (7)$$

where $\phi_i$ is the population of each type of distribution and $M_i$ is the dipole moment of Cs ion (the dipole moment of the atomic species is taken as being equal to zero).
and of \( \text{Mi} \) (from \( \text{Mi} = 2e \text{ri} \); \( \text{ri} \) being the ionic radius) will then provide the magnitude of work function changes. This theory can explain experimental results satisfactorily at low coverage (\( \Theta = 3/4 \)).

Gyptopoulos and Levine (59) have used the concept of electronegativity due to Pauling (60) in developing their theory for the work function changes of composite surfaces. The dipole moment of surface molecules is here related to the electronegativities of the two constituents atoms. In this model the adsorbed atom (classically Cs) is assumed to be present on the surface in only one state and its interaction, such as overlap charge (\( q \)) between adsorbate particles, overlap charges (\( Q_{\perp} \)) between adsorbate and substrate particles and a charge transfer (\( F \)) between substrate and adsorbate are then examined. \( F \) and \( Q \) determine the change in electronegativity and hence \( \Delta \phi \).

Major assumptions of this model are:

(i) The electronegativity of the surface is a function of coverage (\( \Theta \)). At \( \Theta = 0 \), it is equal to that of pure substrate.

(ii) The dipole moment is in turn a function of "\( \Theta \)".

(iii) The adsorbate (Cs) atom forms four bonds with four atoms of substrate and gives rise to four dipole moments per adsorbate atom.

(iv) The dipole barrier is formed from polarised adatom-substrate molecules.

An estimation of \( \Delta i \) which is determined experimentally,
The effective work function consists of two superimposed barriers, i.e., electronegativity barrier $E(\theta)$ and dipole barrier $d(\theta)$ i.e.  
$$\phi(\theta) = E(\theta) + d(\theta) \quad (8)$$

$E(\theta)$ can be determined from Pauling's electronegativity concept and $d(\theta)$ from the relation  
$$d(\theta) = 4 \kappa e_0 \sigma M e(\theta)$$

where $M e(\theta)$ is the first moment of Cs atom.

This is the only theory which relates $\phi$ with coverage $(\theta)$ and satisfactorially explains results even at $\theta = 1$.

II. 5. General Comments on more recent approaches.

The trend in recent approaches is clearly to incorporate some measure of "localisation of electrons" so that the metals bear a closer resemblance to the structure of free atoms. Thus "spin orbitals" are considered localised around individual atoms (Gyftopoulos) (61), stable localised configuration have been proposed by Samsonov (63), and alloy structures have been reviewed in terms of spectroscopic energy levels (Engel and Brewer) (68).

Many physical, chemical and metallurgical properties of elements and compounds can be described with these new models although, in general, different models have been used for each group of properties.

Only the models which seem to be relevant to the discussion of the present work (see section VI) are reviewed in this section.
II. 5.1. **Localized Electron Orbitals.**

Gyftopoulos and Steiner (61) introduced the idea of localized electron orbitals which have a quantum thermodynamical foundation. They assign to each electron a "spin orbital" which is localized around a lattice site. For these spin orbitals the ionisation and excitation energies and electron affinity can be precisely defined; the crystal structure is also describable in terms of these spin orbitals.

In particular, electrons localized around surface lattice sites are thought of as a separate class of surface atoms and it is from these surface atoms that thermal electrons are thought to originate.

On the basis of the above model, the value of the chemical potential ($\mu_c$), electronegativity ($\chi$) and work function are rederived and their interrelation demonstrated.

The energy $E(q)$ of the surface atoms is expressed as a function of the continuous variable "$q" which is the statistical measure of the charge in a valence spin orbital. All quantities are first derived in terms of "$q" and then correlated. The quantum thermodynamically derived relationships for $\mu_c$, $\chi$ and $\phi$ of electron in spin orbital are as follows:

(a) **Chemical potential** ($\mu_c$)

$$\mu_c = -\frac{dE(q)}{dq} \text{ at constant entropy} \quad (9)$$

For small temperature the above equation can be reduced to
\[ M_c = \frac{I + A}{2e} \] for \( q = 0 \) (neutral atom) \hspace{1cm} (9a)

\[ M_c = \infty \] for \( q = +e \) (positive ion) \hspace{1cm} (9b)

\[ M_c = -\infty \] for \( q = -e \) (negative ion) \hspace{1cm} (9c)

\( I \) and \( A \) are the ionisation potential and electron affinity respectively of the valence electron in the localised spin orbital.

(b) **Orbital Electronegativity** \( (x) \).

\[ x(q) \] is defined as

\[ x(q) = \frac{dB(q)}{dq} \] at constant entropy \hspace{1cm} (10)

which is equal to \(-M_c\)

and the neutral orbital electronegativity will be

\[ x(0) = \frac{I + A}{2e} \] for \( q = 0 \) \hspace{1cm} (11)

(c) **Work function** \( (\phi) \).

Since electrons originate from valence orbitals of surface atoms, the work function must be equal to the neutral orbital electronegativity of the valence electron i.e.

\[ \phi = x(0) = \frac{I + A}{2e} \] \hspace{1cm} (12)

(d) **Role of Spin orbitals in composite surfaces.**

The theory of the work function of composite surfaces on the basis of the spin orbital model is developed very much on the same lines as the earlier Gyftopoulos theories. In the newer approach all the assumptions are similar to the previous theory (see Sec. II.4.) except that they are redefined and refined in the light of spin orbitals concept.
II.5.2. Activated Surface atom theory.

J. Bohdansky (62) has proposed a theory of thermionic emission which involves an activation process of surface atoms and derived a new formula for thermionic emission. His interpretation is based on the model of spin orbitals localised around lattice sites introduced by Gyftopoulos (61).

By assuming that electrons are emitted from atoms at and on the surface, and considering the emission as a transition process of a localised electron configuration in the solid structure, he derived the following equation:

\[ J = e n_0 \tau_0 \frac{e^{-\phi/T}} {T} \]  \hspace{1cm} (13)

where \( J \) = current density  
\( e \) = charge of electron  
\( n_0 \) = no. of surface particles per unit area  
\( \tau_0 \) = characteristic lattice frequency  
\( \phi \) = electronegativity  
\( T \) = Temperature (expressed in units of energy)

This derivation has been shown not to be in contradiction with the Richardson equation as derived by the Carnot cycle.

A comparison of the measured "A" (Richardson Constant) with \( e n_0 \tau_0 / T^2 \) is shown in TABLE VI which shows good agreement.
It has also been concluded that since electronegativity has previously been equated with \( \phi \) it follows that \( \phi \) should be equal to \( \phi' \) in this analysis.

Bohdansky has also discussed the two generally used approaches of thermionic emission from cesiated surfaces (see Section II.4) and has theoretically calculated the minimum work function values based on his interpretation (see Table VII). The results are close to the experimental values.

**TABLE VI.**

Comparison of the Emission Constants \( (T_0 = 1800^\circ k) \)

<table>
<thead>
<tr>
<th>Material</th>
<th>predicted ( &quot;A&quot; )</th>
<th>measured ( &quot;A&quot; )</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>260</td>
<td>30 - 200</td>
</tr>
<tr>
<td>Mo</td>
<td>310</td>
<td>20 - 300</td>
</tr>
<tr>
<td>Ta</td>
<td>210</td>
<td>10 - 100</td>
</tr>
</tbody>
</table>
TABLE VII.
Calculated Minimum Work Function Values.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bare $\phi$ (ev)</th>
<th>$\phi$ min (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>4.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Ta</td>
<td>4.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Nb</td>
<td>4.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Mo</td>
<td>4.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Re</td>
<td>4.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Ir</td>
<td>5.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Os</td>
<td>5.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

II. 5.3. Stable configuration of localised electrons.

In Samsonov's model (63) electrons exist in both localised "stable configurations", or remain in an unlocalised state during the initial formation of the crystalline solid. Stable, less stable or even unstable states exist in dynamic equilibrium together with unlocalised electrons.

The most likely stable configuration are described as follows:-

(1) The energetically most stable configuration based on quantum mechanical foundations are
(ii) The stability of the "s" and "sp" configuration decreases with increase of principal quantum number while that of "d" and "f" increases.

(iii) d^5 and f^7 configurations are more energetically stable than d^{10} and f^{14} respectively.

(iv) The tendency of electrons in a crystal to form a localised state, and the statistical weight of such states, increases as the number of electrons increases in a given atomic shell.

Many of the properties of elements and compounds e.g. melting points, resistivity, crystallisation, compound formation (63); magnides (64); aluminides (65); and sintering (66) etc., have been explained on the basis of these stable configurations. For example -

(a) melting points can be related with the statistical weight of the stable configuration. Higher statistical weight of configuration results in higher melting points.

(b) Resistivity of the substance depends upon the population of the unlocalised electrons. It decreases with the decrease in number of unlocalised electrons (i.e. with increase in statistical weight of stable configuration).

II. 5.4. Engel-Brewer theories of Crystal structure.

Engel (67) has empirically correlated the structure of crystal with the outermost electronic structure of the separated atoms. Brewer (68) further developed this approach, and showed that the structure and composition
range of the various intermetallic phases can also be predicted. The binding energies and cohesive energies are shown to be related with the number of electrons in the outermost shell. The relation between the different energies in question is shown in Figure 5.

Promotion energy

atomic ground state

Heat of atomization

Final state (i.e. solid)

Fig. 5. The relationship between the Promotion energy, Binding energy and Heat of atomization.

The main conclusion of the Engel-Brewer correlation is that the crystal structure of the solid is correlated with the number of s and p outer electrons as follows:

\[ d^{n-1}s = 1 = B.C.C. \]
\[ d^{n-2}sp = 2 = H.C.P. \]
\[ d^{n-3}sp^2 = 3 = F.C.C. \]

The correlation obtained holds quite well for transition elements (Fig.6) and this indicates

Fig. 6. Relative energies of the \( d^{n-1}s \) and \( d^{n-2}sp \) electronic configuration for gaseous atoms of the second transition series.
that discrete promoted states play an important role even in the bulk material. At the surface such states can be expected to be even more prominent, as the surface is intermediate in character between the solid state and the free atomic configuration. The promotion energies used by Brewer-Engel are further discussed in relation to the present work in Section VI.


(1) In the semiclassical approaches variation in $\Delta \phi$ is explained by the theories of Rasor and Gyftopoulos. In both theories the same quantity (dipole moment of the surface double layer) is investigated but with different approaches. Rasor and Warner use the dipole layer concept and assume two states of the adsorbed particles (i.e. atom and ion). This theory does not take into account bonds between the particles and is not applicable at high coverage. In Gyftopoulos and Levin's model the concept of electronegativity is used and related to the dipole moment of the molecule. The $\Delta \phi$ is shown as dependent of coverage and has the advantage that it explains results at $\theta = 1$ satisfactorily. In the latest approach of Gyftopoulos, though the calculations are based on a spin orbital model, the numerical results are not markedly changed.

(2) There are some difficulties related to defining the state of the Cs particle in these models as it has not been possible to conceive an experiment to confirm the presence of two kinds of adsorbed species (i.e. atoms and ions). Also in the Gyftopoulos model, the quantities
F and Q are so closely related that no means are available to determine them independently.

Thus for their derivation both theories rely upon heavy approximation and, in particular, consider the effect of substrate as insignificant.

(3) These theories have been developed specially for Cs (Ba, Th) and are not really applicable to other systems e.g. complex and alloy emitters, either because the required parameters cannot be determined, or because the model is too far removed from the rest system.

(4) The basic idea behind the alternative recent approaches is to consider a proportion of the electrons in essentially localised orbits and correlate the thermionic and other properties of matter with the ratio of localised and delocalised electrons. These concepts can be further extended to provide the basis for proposing a general correlation for the work function with the number of electrons in orbits and such a correlation is developed in Section (VI) and used to explain the results of present work.

Metallurgical variables such as crystal orientation, microstructure, grain size and porosity play an important role in the evaluation of thermionic parameters and as well as in understanding the physical electronics of the cathode. Inclusion of these factors is relatively recent, and a model for thermionic emission has yet to be found which includes all such structural features of the substrate metal.


Many investigators have found that different faces of a crystal have different values of the work function. Some metals such as W, Ta, Mo, Ni (69) have been studied extensively in this respect.

G.N. Shuppe (70) has made a very detailed study of the work function of different crystal faces of W, Mo, and Ta with or without contaminants (e.g. Ba, Th, Cs). The average work function is found to lie nearer to the minimum values. The average work function for B.C.C. metals is approximately equal to the work function of [100] face. It is inferred that a prediction can be made for the average $\phi$ of other B.C.C. metal e.g. Niobium.

The values of Richardson constant for different faces of Tungsten and Molybdenum are near to the theoretically expected value. The value for Tantalum is an exception and remained unexplained.

In the case of Tungsten covered with Barium \([hkl = 110, 112, 100, 111, 116]\) the emission current
increases monotonically with the degree of coverage, which is in agreement with Levine and Gyftopoulos theories.

Barium and Thorium are adsorbed primarily on the faces with low intrinsic work function while Cs adsorption is favoured by higher work function faces. The results of the investigations are shown in Table VIII.

TABLE VIII. The work function and Richardson constants of various faces of W, Mo and Ta.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Work function (eV)</th>
<th>Richardson Constant (A degree$^{-2}$cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>110</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>5.35 ± 0.05</td>
<td>4.8 ± 0.05</td>
</tr>
<tr>
<td>Mo</td>
<td>5.0 ± 0.05</td>
<td>4.55 ± 0.05</td>
</tr>
<tr>
<td>Ta</td>
<td>4.8 ± 0.02</td>
<td>4.3 ± 4.4</td>
</tr>
<tr>
<td></td>
<td>125 ± 15</td>
<td>100 ± 10</td>
</tr>
<tr>
<td></td>
<td>30 ± 10</td>
<td>-</td>
</tr>
</tbody>
</table>
It seems that a correlation of work function with grain size or microstructure has only been considered by very few investigators.

Yang (71) has suggested a possible effect of grain boundary diffusion on emission in his work. His results also include the effect of heat treatment of the material on the emission. Pidd et al. (72) have pointed out the possibility of a relation between the Richardson constant and the grain size. A detailed investigation of the effect of grain size and microstructure on the work function has also been carried out by A.O. Jenson (73). The important conclusions can be summarised as follows:

(i) Different grain sizes have different work function and Richardson constant.
(ii) Since grain grows with time and temperature, the surface of the crystal changes and the emission from the surface varies.
(iii) Electron emission is constant if the microstructure remains constant.

II. 7.3. Porosity

Porosity plays an important role in determining the thermionic properties of both bare and covered surfaces. The current evaluation of the surface area of a porous solid requires a detailed knowledge of the nature and percentage porosity of the emitter.

In a porous emitter there may be both external and internal emitting surfaces; very fine powders have a
large external surface area and a small or even negligible internal surface area, while porous solids are characterised by internal surface area of many order of magnitude greater than the external surface area.

The porosity of an emitter can also control the diffusion rate, migration and activation mechanism of activating materials. Consequently it has effects on the life of the emitter. A different shape to the whole thermionic curve can be expected from porous emitters owing to the nonsaturated emission from heterogeneous surfaces.

Dewsberry (74) has studied the emission properties of porous oxide cathodes on the basis of the potential distribution and space charge within the pores oxides. His results exhibit a curvature of Richardson plot at high temperature. (Figure 7.)

The results are interpreted, partly in terms of "pore limitation theory" (75) which relate the diameter of pore to the thermionic parameters and partly by adsorption effect.

**Fig. 7. Richardson plots of porous emitter.**
Bondarenko (76) has found interesting results from a study of porous W and powdered W and Mo deposited on a metallic ribbon. Lower work function values have been obtained in the case of porous, powdered surfaces, (rough).

However the work function steadily increases as the operating temperature increases, and ultimately attains the value of solid tungsten. This change is correlated satisfactorily with the sintering rate of the powder.

Similar results have been obtained for Molybdenum powder, the only difference being that Mo powder sinters at lower temperatures (1500-1600°C).

The results on W are shown in Table IX.

<table>
<thead>
<tr>
<th>Emitter.</th>
<th>Work function (ev)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous W (used for impregnated cathodes)</td>
<td>3.8 ± 0.05</td>
<td>1300-1500°K</td>
</tr>
<tr>
<td>W - Ribbon.</td>
<td>4.61; 4.55</td>
<td>1900°K</td>
</tr>
<tr>
<td>&quot; &amp; W powder</td>
<td>3.82, 3.88</td>
<td>1900°K</td>
</tr>
</tbody>
</table>

A thermionic equation which includes the term for porosity has also been provided as:

\[ J = \varphi f (1-\bar{R})\varepsilon T^2 \exp \frac{e\phi_{\text{eff}}}{kT} \]  

where \( \varphi \) = surface roughness coefficient.

\( f \) = porosity.

\( \bar{R} \) = reflection coefficient.
Other factors have the usual significance in thermionic emission.

Some of the results predicted by the equation are as:

**TABLE X.**

<table>
<thead>
<tr>
<th>( \phi (1-R) )</th>
<th>1500°</th>
<th>1600°</th>
<th>1700°</th>
<th>1800°</th>
<th>1900°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.60</td>
<td>4.68</td>
<td>4.62</td>
<td>4.69</td>
<td>4.69</td>
</tr>
<tr>
<td>10</td>
<td>4.32</td>
<td>4.31</td>
<td>4.28</td>
<td>4.28</td>
<td>4.27</td>
</tr>
<tr>
<td>100</td>
<td>4.05</td>
<td>3.99</td>
<td>3.95</td>
<td>3.95</td>
<td>3.91</td>
</tr>
</tbody>
</table>

Calculated values of effective work function at 1500-1900°K with true work function value = \( 4.52 \times 10^{-5} T \) for different \( \phi (1-R) \).

Thermionic emission constants are determined from the Richardson-Dushman equation:

\[ J_s = AT^2 \exp \left( -\frac{e\phi}{kT} \right) \]  

where \( J_s \) = saturation current in amperes/cm²

\( A \) = fundamental constant equal to = 120.4 A/cm² deg²

\( T \) = temperature (°K) of the emitter.

\( k \) = Boltzmann constant in electron volts/deg

\( \phi \) = work function in electron volts.

A plot of log \( J_s/T^2 \) versus \( 1/T^2 \) gives a straight line. The work function \( (\phi) \) is determined by the slope of the line and "A" (Richardson constant) by its intercept (extrapolated to \( 1/T = 0 \)).

For the determination of the saturation current following methods are used.

(i) The Schottky Plot.

Here log \( J \) vs \( V^\frac{1}{2} \) is plotted which results in a straight line. The extrapolation of this line at \( V=0 \) provide the zero field saturation current.

(ii) Space-charge Break Method.

In this method the current and voltage (in space-charge region) are plotted on two-third-power paper or log log paper. The plot is a straight line. The first point which falls appreciably below this straight line gives the value of zero field emission.

A modification of the above method is illustrated in Fig 8 (77).
Fig.8. Bell Telephone Laboratories emission test.

Here a straight line is drawn passing through the origin and parallel to the initial straight part of the experimental plot (solid line). Another straight line with 20% less slope is then drawn. The interaction of the last line with the experimental plot determines the value of saturation current. This method has been very useful where the currents are not saturated.

The value of "A" determined by Richardson plot always differs with its theoretical value (= 120.4 A/cm² deg²). The recent trend (78) is to put $A = 120.4$ A/cm² deg² and then determine the value of work function.

For the evaluation of thermionic parameter of the presently investigated emitters the following treatment is used.

(i) For the saturation current, the experimental values are directly used as they are well distinct and since Schottley plot is not satisfactorily applicable in "patchy surfaces" (here porous and uneven surfaces).

(ii) Theoretical values of $A = 120.4$ A/cm² deg² are used.
(iii) A comparison between the estimated values (with $A = 120.4 \text{ ams/cm}^2 \text{ deg}^2$) and those obtained by Richardson plot will be made (see Section V).
III. APPARATUS.

III.1. DESIGN OF EXPERIMENTAL DIODE.

III.1.1. Diode Envelopes.

The pyrex glass was used in making the glass diode tubes, and in all, three diode envelopes were constructed for the investigation of thermionic studies. These are shown in (Figs. 9,10).

(1) is the first envelope for the study of the first few cathodes. Preliminary tests and experiments were conducted with this envelope.

(2) is an improved version of no. (1). The diameter of the tube is slightly smaller and six Tungsten rods were used to serve the purpose of electrical connections and of mounting the assembly. Provision was also made to screen stray electrons from reaching the anode. A special arrangement was made to mount the screen and providing a lead for a retarding potential.

Both these diode envelopes could not be used indefinitely, because each time they had to be cut and resealed for insertion and extraction of a new specimen.

(3) Shows the final demountable system using stainless steel flanges with glass to metal seals. The whole tube with a copper gasket, is bakeable at 450°C. The specimen can easily be changed by dismantling the flanges. The top flange has six stainless steel ½" lead-throughs in a tube of length 8½" and diameter 3".
Fig 9. Experimental Diodes
Fig 10  Demountable experimental diode
III.1.2. Heater.

In indirectly heated cathodes, the transfer of heat from the heater to the cathode in vacuum is by means of radiation only. The following formula (79) has been used as a guide for the approximate calculation of temperature of the heater which heats the cathode to its operating temperature

$$t_2^4 = t_1^4 / 1 + \frac{a_2}{a_1}$$

(15)

where $T_2 =$ temperature of cathode; $T_1 =$ temperature of heater; $a_1 =$ area of heater (spiral) + area of cathode; $a_2 =$ area of cathode.

The nomogram given by Kohl (81) was used for the magnitude of heater current, temperature and size of wire.

A spiral heater to raise the temperature of cathode sufficiently to produce the optimum thermionic emission is made from tungsten wire 0.3 mm diameter. A conical basket shape is preferred for efficient heating.

The number of turns of the heater were determined by trial and error. The former to wind the heater coil is shown in Fig. 11.
Method of winding heater coil.

The locknut (L) and guide nuts (G) are first removed from former. One end of the wire is then pushed along groove in the stud and down the hole in the centre of stem, until enough wire comes through to enable it to be gripped in jaws of a lathe chuck (together with the former).

The other end of the wire is then pulled taut so that it is at right angle to the system. Guide and lock nuts are then replaced. The free end of the wire is held taut while the chuck is rotated until the required number of turns have been applied. The former, lock and guide nuts are removed and coil is taken off. The lead ends of coil are then formed by hand.

Heater connecting lugs.

Two heater connecting lugs, 5 cm long, were cut out of 0.3 mm tantalum sheet and spot welded to the heater leads. These connecting lugs provide a very convenient way of clamping the heater in position (Fig. 12).
III.1.3. Radiation Shield.

The use of a radiation shield is essential at high operating temperatures. A .3mm tantalum strip was formed into a multilayer (spiral) cylinder, and a tantalum cup spot welded on to the top end of the cylinder. The cup has a 6 mm hole and is used to support the cathode. The radiation shield is held together by wrapping and spot welding two tantalum strips together as shown in Fig. 12. This strip provides a convenient way of mounting the whole assembly in the apparatus. Another inverted tantalum cup, with two holes for heater's legs, is spot welded, (after inserting the heater), at the bottom end of the cylinder to stop downward radiation.

In order to stop electrons emitted from the heater from reaching the Anode, a cone was spot welded at the bottom end of radiation shield in the second tube (9.b.) The use of heater connecting lugs (Fig.12) eliminates the need of cone in the final tube (Fig.10)

A recess was cut in the upper edge of radiation shield so that the edge of the cathode could be seen for temperature measurement.

III.1.4. Anode.

A pure nickel plate was used in making the circular anode (with fins attached). The fins are elongated by the sides and rolled back to grip the leads. The fins rest on supporting nuts. The design is shown in Fig. 12.
Fig 12  Components of Anode Cathode assembly. a-heater.
b-cathode cups, c-cathode, d-anode; e-cathode assembly 
t-heater lugs.
III.2. DIODE ASSEMBLY

III.2.1. Cleaning of Components

The components used in the diode assembly were cleaned in a ultrasonic bath. The procedure being as follows:

1) cleaning in inhibisol
2) thoroughly washed in running water
3) cleaning in Quadraline
4) cleaning in distilled water and then dried in air.

The anode was cleaned chemically, the composition of the solution being:

50 cc Acetic Acid
30 " Nitric Acid
10 " Hydrochloric Acid
10 " Orthophosphoric Acid

III.2.2. Mounting of Anode and Radiation shield.

The fins of the anode were wrapped around the anode leads and supported by the nuts. (The height of the anode can be adjusted by turning the nuts.)

Next the radiation shield with holding strips is mounted by resting it on two further nuts on the cathode leads. The one mm interelectrode gap is adjusted by turning these Cathode nuts, and using a standard one mm spacer. Finally the lugs of the heater are clamped between the two pair of nuts on heater leads, in such a way that there is no electric leakage between the heater and radiation shield or between adjacent turns of heater. The diode assembly is shown and illustrated in Fig 13.
Fig 13 (a) Diode assembly. (b) Illustration of diode assembly. (1-anode, 2-cathode; 3- radiation shield; 4-heater)
III.3. PREPARATION OF CATHODE

III.3.1. Fabrication

Small rectangular pieces were cut from a rectangular bar of green as-pressed Tungsten made from a single batch of hydrogen reduced Tungsten powder supplied by Murex Ltd. The Tungsten bar was pressed at 18 tons per sq.inch, giving bars having a cross section of 19.20 x 3.70 mm. The Tungsten powder had an average particle size of 3.8 microns, the green density of the compact being 10.40 g/cc. The composition of the Tungsten powder is given in Table XI.

Table XI
Composition of Tungsten Powder

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.p.m.</td>
<td>90</td>
<td>30</td>
<td>90</td>
<td>35</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td>900</td>
</tr>
</tbody>
</table>

Cut slices were shaped on emery paper to make thin circular discs 11.0 mm diameter, care being taken to remove any loose debris.

III.3.2. Preparation of Salt Solution, Impregnation and Drying

A known quantity of metal salts, previously determined to give 0.317 weight percent of Pd and 0.130 weight percent of Ni, Co or Cu was dissolved in the 10 c.c of solvent (Alcohol or Acetone). The quantity is such that it gives a monolayer of alloying metal around each particle of Tungsten. The following quantities of salts are used for the preparation of solutions.
PdCl₂ · 2H₂O = 1.5 gm.
NiCl₂ · 2H₂O = 1.5 gm.
CoCl₂ · 6H₂O = 1.5 gm.
CuCl₂ · 2H₂O = 1.07 gm.

Impregnation

A test tube containing solution is held horizontally and the porous cathodes is placed near the neck of the test tube. The solution enters through the bottom surface of the cathode and impregnates the whole cathode by capillary action. After being properly impregnated, the cathode is put into a drying furnace, the drying temperature and time being 130°C and 5 minutes respectively.

III.3.3. REDUCTION AND SINTERING

The reduction and sintering were carried out in a tube furnace consisting of recrystallised Alumina tube of 24 mm bore and 100 cm long. The furnace was heated by Silicon Carbide rods, capable of reaching a temperature of 1900°C. Temperature was controlled by an Ether Controller which gave a control cycle of ±5°C. Various atmosphere could be introduced in the furnace tube.

The tube was first flushed with Argon and then the Hydrogen at a rate of 200 cc/mm is passed through the tube and activating salts are reduced at 600°C for 30 minutes. Finally the emitters were sintered at 1000°C for 20 hours. The sintered emitters were taken out of the furnace and were tested in the experimental diode.

Porous emitters do not require sintering at 1000°C and were taken out of the furnace at the end of reduction.

The apparatus to attain the pressure of the order of $10^{-8}$ mm of Hg is shown in Fig. 14. It consists of a rotary pump, molecular sieve trap, mercury diffusion pump, two liquid nitrogen traps and the experimental tube. The molecular sieve trap (designed and constructed in the department) is used to suppress the migration of oil and water vapours into the tube from the rotary pump. This trap is regenerated by baking at $300^\circ$C at $10^{-3}$ torr.

The use of a liquid nitrogen trap prevents the back diffusion of vapours from the rotary pump, and by outgassing the mercury pump enhances the pumping speed of the system.
Fig. 14  Vacuum Apparatus
IV. EXPERIMENTAL PROCEDURE AND MEASUREMENTS.

IV. 1. Outgassing and Activation.

When the pressure falls to $3 \times 10^{-6}$ torr, the tube is baked out for at least 1½ hours at $400^0C$. The pressure falls to $1 \times 10^{-6}$ torr at the end of the bake out. For outgassing and activation of the emitter the following procedure is adopted.

(i) At the end of the bake out (i.e. $1 \times 10^{-6}$ torr) the temperature of the cathode is slowly increased to $1000^0C$ while at the same time watching and maintaining the pressure between $10^{-5} - 10^{-6}$ torr in the tube to prevent any contamination on anode (the initial sharp increase in pressure is due to outgassing of the heater).

(ii) The anode is now heated slowly to $900^0C$ for $\frac{1}{2}$ hour by radio frequency heating. Again care being taken to prevent the pressure rising to more than $5 \times 10^{-6}$ torr.

(iii) The cathode and anode are heated alternately to avoid the evaluation of the gases to condense on either surface.

(iv) When a vacuum level of $10^{-6}$ torr is reached after step (iii) the radio frequency heating is discontinued and the pressure usually improves to $10^{-7}$ torr.

(v) Finally the temperature of the emitter is raised to its operating temperature and the current is drawn.

IV. 2. Current measurement.

The circuit shown in Fig. 15 is used for the determination of the electron current. The smaller current of the order of $10^{-7} \sim 10^{-9}$ amps, was measured by means of the potential drop across 1k resistor ($i = \frac{V}{r}$) which is
Fig 15 Electrical circuit for current measurement.
then measured by a high impedance microvoltmeter (Rikadenki), the lowest voltage measurable being 1 microvolt. The larger currents (10^{-6} amps) were measured directly by a microammeter. The anode voltage is measured by a voltmeter across anode and cathode. A check was made for leakage round the diode by disconnecting the heater supply. As there was no indication of current on the meter, it was assumed that leakage current was negligible.

IV. 3. Temperature measurement.

The temperatures of the emitters were measured by two optical pyrometers (total radiation and disappearing filament) focussed on the edge of the emitter. The observed temperature is always less than the actual temperature and hence corrections were made for the spectral emissivity and absorption of the glass wall.

Variations in temperature of indirectly heated cathodes is very slow owing to their large heat capacity.
V. RESULTS

V.1. Solid Tungsten (W) Emitter

Initial experiments were performed with solid Tungsten to obtain standard reference thermionic curves and to check if any background effects on emission were present. All other results refer to identical activation procedures for each emitter (as described in the previous section) and all the emitters were fabricated from the same batch of Tungsten.

V.1.1. Thermionic Curves (I - V)

Thermionic curves (I vs V) for bulk Tungsten at 6 operating temperatures are shown in Fig 16. It can be seen that the nature of the curves are similar to the thermionic curves of standard Tungsten reported in Literature.

V.1.2. Thermionic Constants of Tungsten

Values of work function ($\phi_R$) and Richardson constant ($A_R$) have been determined from the slope and intercept at $1/T = 0$ of the Richardson plot $\log (I/T)^2$ vs $1/T$ (Fig 24.). These can be compared with the estimated values of the constants from equation (1) with $A = 120$ amps/deg$^2$.cm$^2$. (Table XII) The value of work function ($\phi_R$) from the present results is 4.5 ev while $A_R = 62$.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1350</th>
<th>1400</th>
<th>1450</th>
<th>1500</th>
<th>1550</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work function (ev)</td>
<td>4.57</td>
<td>4.54</td>
<td>4.58</td>
<td>4.60</td>
<td>4.58</td>
<td>4.59</td>
</tr>
</tbody>
</table>

$A = 120$, amps/cm$^2$.deg$^2$.

$A_R = 62$ amps/cm$^2$.deg$^2$.

Work function  | 4.50 ev
Fig 16 I-V Characteristics of solid Tungsten
V.1.3. Decay Characteristics

No decay has been detected from the solid Tungsten emitter at 1600°K for 2 hours.

V.2. Porous Tungsten Emitter

Fig 17 shows the thermionic curves of a porous emitter. The nature of the curves at low temperature (1350-1450°K) are similar to that of solid Tungsten (Fig 16). At high temperature (1600°K) it has an additional hump between 600-800 volts, and the current has not saturated at 1550-1600°K.

V.2.1. Evaluation of work function (φ) and total emitting area (S) for porous Tungsten.

The values of 'φ' and 'S' obtained from the Richardson plot (Fig 24) are given in Table XIII. The intercept at \( \frac{1}{T} = 0 \) gives a value which is the product of Richardson constant (\( \phi R \)) and the total emitting area (S). S has been estimated by dividing the intercept value by the standard value for Tungsten (\( \phi R = 60 \)) as determined experimentally in Section V.1.2. The estimated values of work function based on the conventional value of \( A = 120 \text{amps/cm}^2\cdot\text{deg}^2 \) combined with \( S = 10 \) are also given in the Table.
Fig.17 I-V Characteristics of Porous (Presintered) Tungsten
TABLE XIII The values of work function and total emitting area of Porous Tungsten emitter

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Work function</th>
<th>Emitting Area S</th>
<th>Richardson Constant A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350-1600 K</td>
<td>4.53</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>1350</td>
<td>4.60</td>
<td>&quot;</td>
<td>120</td>
</tr>
<tr>
<td>1400</td>
<td>4.58</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1450</td>
<td>4.61</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1500</td>
<td>4.51</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1550</td>
<td>4.60</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1600</td>
<td>4.62</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

V.2.2. Decay characteristics

The porous Tungsten emitter was kept at 1600°K for 2 hours but no decay of emission observed.
V.3. **Alloy Emitters** (W-Pd, W-Ni, W-Co, W-Cu)

V.3.1. **Thermionic curves for fully sintered alloys**
(90% theoretical density)

Thermionic curves of W-Pd and W-Ni alloys are shown in Figs. 18, 19. The nature of these curves are seen to be similar to that of solid tungsten (Fig. 16).

V.3.1.1. **Thermionic curves for presintered alloys**
(55% theoretical density)

Thermionic curves of the porous W-Pd; W-Ni, W-Co; W-Cu are shown in Figs 20, 21, 22, 23, respectively. The dashed curves represent the emission before the start of decay while the solid line curves give the values of stable emission current after 3½ hour decay in emission. The W-Cu emitter curves are stable for this period and do not show any effect of decay in emission.

The emission curves before decay show a tendency for saturation only at higher anode voltages (800-1000v). The curves after decay show three stages of saturation in the region of 300-500V, 600-700V and 800-1000V. The saturation regions are more distinct at higher temperature (1330-1350°K) than at lower temperatures (1250-1300°K). Vertical lines have been drawn between the curves to emphasize changes in the saturated regions. The saturation regions of the solid curves are more distinct and start at lower anode voltages (i.e. at 300V; 600V and 800V) than those for the dashed curves.

It can be seen that the magnitude of decay in emission ($\phi_i$) is proportional to the operating temperature and decreases with decreasing temperatures. The $\phi_i$ at a given
Fig. 18 I-V Characteristics of fully sintered Tungsten—Palladium.

- 1300°K
- 13.30 "
- 13.50 "

Fig. 19 I-V Characteristics of fully sintered Tungsten—Nickel.
Fig. 20 I-V Characteristics of Porous (Presintered) Tungsten-Palladium
Fig. 21. I-V Characteristics of Porous (Presintered) Tungsten-Nickel.
Fig 22 1-V Characteristics of Porous (Presintered) Tungsten-Cobalt
Fig. 23. I-V Characteristics of Porous (Presintered) Tungsten-Copper
temperature for different emitters varies from
\( A_i = 85; 52 \) and 35 for Pd, Ni and Co respectively.

V.3.2. Evaluation of the Work Function (\( \phi \)) for alloy Emitters.

The work functions at various temperatures have been evaluated from the Richardson equation (1) by putting \( A = 120 \) amps/deg\(^2\)cm\(^2\) using \( S = 1 \) for sintered and \( S = 10 \) for porous emitters. (see Table XIV) The work functions values for W-Pd, W-Ni, W-Co and W-Cu are 4.30, 4.35, 4.00 and 4.25 ev. respectively. Also shown are the value of Richardson work function obtained graphically from Fig. 24.
### TABLE XIV
The work function values of various alloy emitters

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>W - Pd</th>
<th></th>
<th>W - Ni</th>
<th></th>
<th>W - Co</th>
<th></th>
<th>W - Cu</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sintered</td>
<td>Porous</td>
<td>Sintered</td>
<td>Porous</td>
<td>Porous</td>
<td>Porous</td>
<td>Porous</td>
<td>Porous</td>
</tr>
<tr>
<td>1175</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td>1230</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>1250</td>
<td></td>
<td>4.28</td>
<td></td>
<td>4.32</td>
<td>4.00</td>
<td>4.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>4.27</td>
<td>4.28</td>
<td>4.33</td>
<td>4.33</td>
<td>4.10</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1330</td>
<td>4.29</td>
<td>4.30</td>
<td>4.34</td>
<td>4.35</td>
<td>3.99</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350</td>
<td>4.29</td>
<td>4.30</td>
<td>4.34</td>
<td>4.35</td>
<td>3.99</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Work Function</td>
<td>4.30</td>
<td>4.35</td>
<td>4.00</td>
<td>4.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Work Function from Fig. 24.</td>
<td>4.12</td>
<td>4.16</td>
<td>3.48</td>
<td>4.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3. Decay in Emission.

The decay in emission current of the emitters at the highest operating temperature 1350°C and for an anode voltage of 1000V has been followed for 3½ hours. The decay curves (I vs t) of porous W-Pd, W-Ni and W-Co emitters are shown in Fig. 25. No decay has been detected for sintered W-Pd, W-Ni and porous W-Cu emitters.

In the beginning of the decay curves the fall in emission current is rapid while at the end it becomes very small. (For W-Ni and W-Co no decay takes place for the first 10-20 minutes). The total decay i for each W-Pd, W-Ni and W-Cu emitter has been 85, 52 and 35 respectively which are 30%, 27% and 11% of the total emission.

Decay in emission at 300, 400 and 500 voltages has also been recorded for W-Pd alloys. The curves are shown in Fig. 26. The decay in emission was found to be negligible.

3.3.1. Rate exponent (52)

A plot of log \( \frac{N}{t} \) against log t is shown in Fig. 27. The rate exponent (a measure of decay rate) for W-Pd and W-Ni and W-Co is 0.56; 0.50 and 0.40 respectively.
Fig. 25. Decay Characteristics of Emission current.
Fig. 26. Decay Characteristics of Emission Current. ($V_A = 300, 400, 500$.)
Fig 27 Rate exponent of Decay for various alloys
V. 3.4. **Density Measurement.**

The density of the porous emitters after drawing emission for 3½ hours have been determined by the following formula:

\[
D = \frac{W \times H_g}{W + W_1 - W_2}
\]  
(16)

where

- \( D \) - is the density of specimen (emitters)
- \( W \) - is the weight of the specimen in air.
- \( W_1 \) - is the weight of the basket in mercury.
- \( W_2 \) - is the combined weight of specimen and basket in mercury.
- \( D_{Hg} \) - is the density of mercury.

and shown in Table XV. No change in density of sintered alloy and pure tungsten was observed.

**TABLE XV.**

Densities of alloys after 3½ hours emission.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Density g/c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W - \text{Pd} )</td>
<td>11.80</td>
</tr>
<tr>
<td>( W - \text{Ni} )</td>
<td>11.60</td>
</tr>
<tr>
<td>( W - \text{Co} )</td>
<td>10.65</td>
</tr>
</tbody>
</table>
V. 3.5. **Surface studies.**

Stereoscan photographs of W-Pd, W-Co and W-Cu are shown in Figs. 28, 29a, 29b, 29c.

Fig. 28 shows W-Pd sintered to a density of 17.9 g/cc. (90% of tungsten) for 20 hours in hydrogen atmosphere.

The surface is only slightly rough and the apparent surface area is approximately equivalent to that of solid surface.

Figs. 29a, 29b, 29c, are the photographs of porous W-Pd, W-Co, W-Cu. These structures are very porous (Density - 55% of tungsten) and the geometrical surface area is at least three to four times more than that of a plane surface.
Fig. 28. Stereoscan photograph of Sintered W-Pd alloy (x 5700)

Fig. 29. Stereoscan photograph of
(a) Porous W-Pd alloy (x 5500)
(b) " W-Co " (x 1100)
(c) " W-Cu " (x 5000)
VI. DISCUSSION

Thermionic emission results of the investigated alloys reveal two effects - (1) a Porosity effect and (2) a reduction in work function.

VI. 1. Porosity Effect

The effect of porosity shows itself in both the nature of the thermionic curves and in decay curves, the following reasoning is used to interpret the results.

VI.1.1. Emission Characteristic

Since porous emitters are characterized by a surface which consists of protuberances and cavities (Fig 29), it may be expected that the total emission current will be heterogeneous in its structure being composed of electrons coming from different regions of the cavities. At low anode voltages only the electrons from the surface nearest to anode will be collected showing a typical space charge region followed by a trend towards saturation. At higher voltages additional electrons, originating from deeper regions of the cavities will be attracted. Finally, the highest anode voltages will collect the remaining electrons from the deepest region of the cavities. This model accounts for the three stepped saturation regions of Figs 20, 21, 22 (solid curves). Volatages of 0-500V seem to correspond to emission from the surface of emitter nearest to anode; potentials of 600-700 V correspond to emission from the next layer while a potential of 800-1000V is sufficient to produce the final emission step.

Thermionic curves before decay (dashed line) do not have such distinct regions of saturation. This could be due to the fact that initial surface is so rough that all the steps tend to merge.
Sintering, due to the presence of activator produces a more definite structure (Fig 28) and hence distinct regions of saturations appear. Some redistribution of the activator can also be considered, but is difficult to estimate.

The start of saturation steps take place at lower anode voltages after decay has taken place, which may be attributed to sintering. Sintering of deeper regions will stop emission from such regions and hence a lower anode voltage will be sufficient to start the saturation of emission from these regions. (The portion of the curves marked by vertical lines, drawn between the curves, indicate the trend of saturation due to sintering. Figs 20, 21, 22)

VI.1.2. Decay Characteristics

Different percentage of decay in emission may qualitatively be related with the activation power of activator (Table XVI).

**Table XVI** Percentage of emission decay and activation power of activators

<table>
<thead>
<tr>
<th>Activation</th>
<th>Activation % (52)</th>
<th>Decay in emission %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>$40.7 \times 10^2$</td>
<td>30</td>
</tr>
<tr>
<td>Ni</td>
<td>$35.9 \times 10^2$</td>
<td>27</td>
</tr>
<tr>
<td>Co</td>
<td>$4.74 \times 10^2$</td>
<td>11</td>
</tr>
</tbody>
</table>
Since Pd and Ni are strong activators, they can result in a larger decrease in emission due to reduction in emitting surface area than Co and Cu, the activation power of the latter being smaller.

The rates of decay in emission (Fig 27) are found to be approximately equal to the rate exponent (sintering rate) of the activators (See Table XVII). The similarity of the rates justify the

**TABLE XVII** Emission decay rate and rate exponent of activator.

<table>
<thead>
<tr>
<th>Activator</th>
<th>Rate exponent (51,52)</th>
<th>Rate of decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0.54</td>
<td>0.56</td>
</tr>
<tr>
<td>Ni</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>0.40</td>
</tr>
</tbody>
</table>

above attempt to relate the magnitude of decay with the activation power of activators.

The magnitude of emission decay is found to be greater than the corresponding change in density due to sintering (See Table XVIII).
The difference may be explained on the basis of the different shrinkage parameters used. In emission it is the "emitting surface", while in density it is the volume parameter. A little change occurring at the surface (e.g. necking or closing of the opening of cavities) may decrease the emission appreciably while the change in bulk material (volume) may not be so correspondingly high.

No decay in emission has been observed for periods of 30 minutes at lower anode voltages (300, 400, 500 V; Fig 26.) Sintering obviously does take place, but owing to the lower applied electrical field, it is assumed that emission changes occurring in the deeper region of the cavity, are not detected. Nevertheless, the effect of an electrical field does not seem to have been studied so the effect of this variable is unknown.

Solid (W) and sintered alloy does not show multiple saturation regions, since these specimens have negligible porosity. The absence of decay in emission from solid (W), sintered alloy emitters, and Porous W support the idea that changes of porosity (owing to activator) are responsible for decay.

### TABLE XVII

<table>
<thead>
<tr>
<th>Activator</th>
<th>Density %</th>
<th>Decay in emission %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>Ni</td>
<td>16</td>
<td>27</td>
</tr>
<tr>
<td>Co</td>
<td>8</td>
<td>11</td>
</tr>
</tbody>
</table>
VI.2. Theories accounting for a reduction in work function

Covered surfaces generally have their work function ($\phi$) reduced when an activator is present on the substrate surface. This effect has been discussed in the Literature Survey (Sec. II).

A reduction in "$\phi$" in the case of film type emitter (Cs, Th, Ba) is usually explained by the Levine's "dipole moment" model or Gyftopolous' "Electronegativity" model of thermionic emission as described in Sec. II. According to Levine the reduction in work function is caused by changes in the dipole barrier. In the Gyftopolous model the reduction in work function, is attributed to the changes in electronegativity produced by the adsorbate atom.

These two theories were developed specially for cesiated surfaces, and can be applied to some extent, to other system such as thoriated and bariated surfaces. However, its application to alloy emitters seems to be very difficult owing to the different structure of the alloy surfaces.

Investigation of the thermionic parameter of alloy emitter is still in its early stages and hence no suitable theory exists in the literature which can explain the results satisfactorily. Gurov (81) has attempted to find a relation between the $\Delta \phi$ and the difference of ionic charges of the alloy component.

The relation is

$$\Delta \phi = \frac{Z_c}{n_A(E_F)} \quad \ldots \ldots \ (17)$$

where $Z_c$ = ionic charge
$E_F$ = Fermi Level energy
$n_A$ = density of states

only a few results of W - Hf and W - Ta are explained by this equation. But when applied to W-Mo or W-Ti alloys it
cannot account for the large reduction in work function of these alloys. B.Ch. Dyubuya (36, 82) has attempted to explain his results first by relating the work function changes with the lattice parameter and then by assuming the adsorption of the component of lower melting point on the alloy surface. Such lattice parameter consideration cannot explain thermionic results in W-Mo, W-Ta, W-Nb. The adsorption phenomena itself cannot account for many other results of different alloy system. Specially when the concentration of the alloy component changes.

Owing to the lack of information available on alloy emitters, no current theory can be thought of as satisfactory and complete. Most attempts to explain the results are very primitive and are only valid for a given alloy system under a given environment.

VI.3. New Hypothesis

An alternative approach has been introduced in Sec. II. This approach consists of an empirical correlation of properties of matter with electron in the outermost shell and an attempt is made here to extend this to the field of thermionic emission.

VI.3.1. The relation between thermionic emission and localised electron configurations

The delocalised electrons are largely responsible for the thermionic emission and thus their energy and concentration determine the work function.

The underlying idea behind this approach is to correlate the energy and concentration of the delocalised electrons with the number of electrons in the outermost atomic shell. The following assumptions are made for the development of this correlation.
(1) It is assumed that the energy and concentration of delocalised electrons are proportional to the energy and statistical concentration of the localised electrons in stable configurations.

(2) Since there are known correlations between the energy and statistical weight of stable configuration (in terms of other properties of matter), and the number of electrons in the outermost shell, (Sec.II) a similar correlation can be thought of for thermonic properties.

(3) In order to quantify the electronic configuration, the spectroscopically determined promotion energies have been used in the same way as utilised by Brewer (Section II).

(4) It is assumed that the changes in work function of covered surfaces depends upon the electronic configuration (and hence promotion energies) of the adsorbate as well as of substrate atoms.

Various examples of this correlation are shown in Fig 30. (Figs A1, A2, A3 Appendix) Fig 30 is a typical example of the type of correlation that has been obtained.

It can be seen that the work function increases with the number of electrons \( n \) in "d" shell. An increase of "n" increases the statistical weight of stable configuration of "localised electrons" (see Sec. II.5.3.), consequently reducing the concentration of delocalised electrons, which results in higher values of work function.

The values of the work function of the transition elements of 3rd and 5th group are in agreement with this scheme. The corresponding work function values of 5th group are higher owing to higher principle quantum number which result in more stable configurations. (Sec.II.5.3.)
Fig. 30. The Variation of Work function with number of electrons in the outermost d shell
Elements with $d^5$ and $d^6$ configurations (Mn, Fe and Re, Os) have similar values of work functions because these have approximately the equal statistical weights of these two stable configurations. (64). The lower value for Cobalt ($d^{n=7}$) may be explained by assuming that during the interchange between $d^5$ and $d^{10}$ stable configurations, some electrons may be temporarily free. Alternatively the tendency to form $d^5$ may be higher, thus leaving a larger number of electrons as nonlocalised which would give a lower work function.

The quantization scheme of associating Promotion energies to $d^n$ configurations is shown in Fig 31. The Promotion energy* of $d^{n-2}$ sp state of atoms increases with the number of electrons in the outer shell of atom. It also increases with the principal quantum number. (i.e. the Promotion energy of 5th group is greater than those of 3rd group).

Since the empirical correlation developed here between $\phi$ and $d^n$, has a similar trend to the variation of promotion energies and $d^n$, this provides further justification for using promotion energies as a suitable parameter for electron configuration.

The variation of work function against Promotion energy is plotted in Fig 32. It can be seen that the work function increases with increase in promotion energy.

* The promotion energies used here are the energies to promote the $d^n$ state to $d^{n-2}$ sp. The minimum values are used as electron emission can take place with the minimum energy to perturb them.
Fig. 31 Variation of the Promotion energy of $d_{n-2}^{n-2}sp$ state with number of d electrons in $d_{n}^{n}s_{n}$ state.
Fig. 32. The Variation of Work function with Promotion Energy
VI.3.2 Work function changes of adsorbate - substrate system

It is assumed that changes in work function of adsorbate - substrate systems occur due to perturbation of electronic configuration of the system. It may be assumed that the tendency of either kind of atom is such as to increase its own statistical weight of localised electrons, by attracting electrons from the other kind of atom. This process results also in a collectivized state of delocalized electrons, the population and energy of which determines the magnitude of work function changes.

The magnitude of the perturbation will therefore depend upon the relative perturbing power of substrate and adsorbate, which is determined by the principal quantum number (N) and number of electrons (n) in outershell, if the difference between the perturbing power is small, the work function changes will be low. However, the combination of strong and weak perturbing power will produce large work function changes owing to the high probability of perturbation.

a) Due to Adsorbate  Fig 33a (Fig A4, A6, Appendix) illustrate the work function changes with \(d^n\) for the various adsorbate. The work function change decreases with increasing "n", which is consistent with this model.

b) Due to Substrate

The work function changes for various substrate covered with the same adsorbate are shown in Fig 33 b (Fig A6 Appendix)

Strong perturber (large n values) produces high work function changes.
Fig 33 Variation in $\Delta \phi$ with number of electrons in the
d-shell of (a) adsorbate (b) substrate.

Fig 34 Variation of $\Delta \phi$ as a function of Promotion energy
at d electronic configuration.
VI.3.3. Work function changes and Promotion energies.

Since Promotion energies are associated with the number of electrons in outershell, a correlation can also be sought between $\Delta \phi$ and Promotion energies and is shown in Fig 34 (Fig A5, A7 Appendix) Correlation of high values of $\Delta \phi$ are associated with low Promotion energies and they support the assumption that smaller $n$ values ($d^n$) are more perturbable (Sec VI.3.2.)

VI.3.4. Explanation of work function changes in the alloys under investigation using the new correlation

The changes in work function of the alloys investigated in this research can be satisfactorily explained with this model.

Tungsten ($5d^4$) is strong perturber owing to its high principal quantum number ($N$) and $n = 4$, which gives the highest percentage ($94\%$) of statistical weight of the most energetic localised electron configuration ($d^5$).

The additives, Co, Ni, Cu and Pd ($3d^7$, $3d^8$, $3d^{10}$, $4d^{10}$) have a tendency to increase the statistical weight of $d^5$ and/or $d^{10}$ configurations. The relative proportion of these two configurations determine the remaining delocalized electrons.

Cobalt ($3d^7$) seems to have higher statistical weight of $d^5$ than that of $d^{10}$ (owing to $n = 7$) theremaining electrons either form $d^{10}$ configuration or remain unlocalised.
Nickel (3d$^8$) has a high ratio of d$^5$ and d$^{10}$ configuration due to higher n values (=8), hence less number of delocalised electrons are available for emission.

Copper (3d$^{10}$4s$^1$) and Palladium (4d$^{10}$5s$^0$) have the highest percentage (98%) of d$^{10}$ configuration (followed by an unfilled s configuration).

Tungsten, being a stronger perturber, will attract the electrons from the additives to increase its (W) statistical weight of d$^5$ configuration, while the additives will try to increase their statistical weight of d$^5$ and d$^{10}$ configurations.

The high work function changes (i.e. 0.4 ev), in W-Co emitters is explainable because Cobalt (d$^7$) is easy to be perturbed. In the case of W-Ni emitters the $\Delta \phi$ is smaller (0.2 ev) than for W-Co consistent with the fact that Nickel has 8 electrons in d shell, and hence has a higher tendency to form its own d$^{10}$ configuration. In the case of the d$^{10}$s$^1$ and d$^{10}$s$^0$ configurations of Cu and Pd, the tendency exists that some of the d$^{10}$ configuration may be destroyed by the strong attraction from Tungsten (The unfilled s configuration, owing to their tendency to form the s$^2$ configuration may also disturb the d$^{10}$ configuration), which will result in greater number of collectivized electrons. This account for the higher work function changes ($\Delta \phi = 0.25$ 0.30 ev) in these alloys than in W-Ni ($\Delta \phi = 0.20$ ev).

Fig 35 illustrates the work function changes and the electron configuration of the alloys under investigation, Cu and Pd has been placed before Ni, because of their less stable d$^{10}$ configuration followed by unfilled s configuration.
Fig 35 Variation in work function changes with the electronic configuration of d shell of Co, Cu, Pd and Ni atoms.

Fig 36 Variation in work function changes $\Delta \phi$ with the Promotion energy of $d^{n-2}$sp electronic configuration.
In Fig 36 $\Delta \phi$ is plotted against the appropriate Promotion energies. The same trend is observed with the exception of nickel. The anomalous behaviour of Ni, with respect to its reduction of the work function, has also been reported for cesiated Nickel (62). Alternatively, it may be assumed that $\Delta \phi$ for W-Ni arises predominantly from the number of the collectivized electrons rather than from their energy.

The work function changes of the present alloys are plotted along with the $\Delta \phi$ of other alloys (i.e. La, Th, U, Ti, Hf) reported in the literature, in Fig 37. (The order of the metals are chosen with the consideration of N and n) La(5d$^1$), Th(6d$^2$), U(6d$^4$) and Ti(3d$^2$) yield higher $\Delta \phi$ because of the lower number of electrons in d shell. It can be seen that the general trend and magnitude of $\Delta \phi$ are explainable on the basis of the proposed electronic configuration correlation.

In Fig 38 the variation in work function changes with Promotion energies associated to the electronic configuration of Cu, Co, Pd and Ni atoms (Present work) are compared with those of La, Th, U, Ti, and Hf. The curve shows the general trend of variation in $\Delta \phi$ with Promotion energies. Variation in work function changes for La, Th, U, Ti are higher because of the lower values of promotion energies, associated to lower number of electron in d shell, than those of present alloys. Thus the work function changes are explainable with the number of electrons in the outer shell as well as with the Promotion energies associated to them.
Fig 37 Variation in work function changes with electronic configuration of present emitters compared with those of other emitters i.e., La, Th, U, Ti, Hf.
Fig 38 Variation in work function changes with Promotion energies of present emitters is compared with those of La, Ti, Hf.
(i) Alloy emitters prepared by activation sintering show a reduction in work function of 0.25 ev (Pd-W); 0.20 ev (Ni-W); 0.40 ev (Co-W) and 0.30 ev (Cu-W) in the temperature region of 1175-1350°K.

(ii) This reduction can be correlated with perturbation of d shells between atoms on the emitting surface.

(iii) Porosity increases the emission and produces stepped emission curves.

(iv) This effect can be related to multiple emission sites which are variously affected by subsequent sintering.

(v) Proposed d and s perturbation correlations are consistent with most of the results available in the literature for bare and covered surfaces as well as the results of present work, and it may be possible to predict the behaviour of other emitters yet to be developed.

VII. GENERAL CONCLUSIONS.
VIII. FURTHER WORK. - 119 -

The present work can be extended in the following directions:

(1) It may be expected that higher percentage composition of additives will not further decrease the work function, but instead will increase owing to emission predominantly from the thicker layers of adsorbates. This should be checked by a study of emitters with controlled addition of a given alloying element.

(2) Additives such as Fe, Ru, Rh would fill gaps in our present knowledge of alloy emitters.

(3) Replacement of base material by materials such as Mo, Ta etc., would yield further changes in work function and which could be checked with the proposed correlation.

(4) Ternary alloy emitters could be developed for further changes in "ϕ" due to perturbation among the electrons of outer shells. This would also provide additional information for the proposed correlation.

(5) A more systematic study of effect of porosity on the emission.

(6) A more detailed study of the effect of different powder size and microstructure.

(7) The effect of different techniques of preparation (straight alloying; pressing of powders etc.,) can be used for the emission properties of the alloy used in the present study.
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Further applications of the s-p-d correlations discussed in section VI are illustrated in Figs A1, A2, A3, A4, A5, A6, A7.

In Figs A1(a,b) the work function is plotted against the number of electrons in s and sp shell and their principal quantum number N. (The principal quantum number reflects the strength of the electron configuration; for s and sp elements the energy of the configuration decreases with the increase of N. (See Section II.5.3.)) It can be seen that:

(i) The work function increases with the increase of the number of electrons in the s or sp shell, which confirms the assumption made in section VI.3. This is consistent with the fact that an increase in the number of s and sp electrons, increases the statistical weight of the energetic stable configuration \( (s^2, s^2p^2, sp^3 \text{ and } s^2p^6) \) of localised electrons, and decreases the concentration of delocalised electrons, thus resulting in higher work function values.

(ii) The work function increases with the decrease of principal quantum number, since the energy s and sp electronic configurations increases with decrease of N.

The promotion energies (as used in 'd' type configuration; section VI.3.3.) of most of the s and sp elements do not seem to be available (except for Ba, Sr, Ca and Mg), therefore the corresponding Binding energies wherever available have been used. The Binding energy is related to the Promotion energy through the heat of atomization as follows (68):
Fig A1. Variation in Work function with (a) number of s,sp electrons
(b) principal quantum number 'N'
Binding energy = Promotion energy + Heat of atomization

The electronic configuration of the remaining elements \( \text{(Be, Li, Si, Al, Ga, Sb, Ge, Sn, Pb, As, Bi)} \) has been left unquantititized owing to the lack of necessary data.

Fig A2(a) is a plot of work function and Promotion energies of the electronic configuration, while Fig A2(b) relates the work function with the binding energies of the configuration. It can be seen that work function increases with both increase of promotion energy and binding energy.

Fig A3(a) shows the variation of work function with the principal quantum number \( N \) of the 'd' type configuration (For \( \phi \) Vs \( d^n \) see VI.3.1.)

A decrease of work function with decrease in \( N \) is consistent with a decrease in energy values as \( N \) decreases (Section II.5.3.) The abnormally lower values for Nb and Ag may be related to the presence of an unfilled "f" shell and one s electron, which make the electrons more loosely bound and hence increases the population of unlocalised electrons. Hf is an exception.

The variation of work function of \( Nd^n \) type element with Promotion energies are shown in Fig A3 (b). It can be seen that the work function increases with the increase of promotion energy. The plot of less stable configuration \( Nd^{10} \) (Section II.5.3.) is shown separately. The lower values of work function for high promotion energies may be due to the larger population of unlocalised electrons in the perturbed state of \( d^{10} \) configuration. The values for Rhodium seem to be anomalous.
Fig A2. The variation of work function as function of (a) Promotion energy (b) Binding energy.
FigA3 Variation in work function with (a) the Principal quantum number $N$ of $d^n$ shell and (b) the Promotion energy of $Na^N$ electron configuration.
Work function changes and electronic configuration of adsorbates and substrates

a) Due to adsorbates

Fig. A4 illustrates the work function changes ($\Delta \phi$) with electronic configurations of various type of adsorbates on a common substrate of W. It can be seen that the decrease in $\Delta \phi$ is related with the number of electrons in the outermost shell of the adsorbate atom (See Section VI.3.1). For a given "$N" the change in $\Delta \phi$ is proportional to $s^n$.

In the case of $s^1$ electrons, the tendency is such as to form their own $s^2$ stable configuration, consequently these states are less perturbable, and hence yield smaller $\Delta \phi$.

This is the case for all $Ns^1$ adsorbates (i.e. Cs, K, Na*).

In larger magnitude of $\Delta \phi$ obtained for higher values of "N" of s type element is due to the smaller energy associated with higher "N" values.

Fig. A5(a, b, ) shows the variation of $\Delta \phi$ with Promotion energies and Binding energies respectively of the adsorbates shown in Fig. A4. (Thorium and Uranium are not included as their Promotion energy or Binding energy were not available). It can be seen that the lower values of the Promotion energy (associated with less stable electron configuration of Ba and La through unfilled $f^0$ shells) give large work function changes.

(b) Due to substrates

Figures A6(a, b, ) are the plots of $\Delta \phi$ of a limited number of adsorbates against the $Nd^n$ of different substrates. Here $Nd^n$ reflects the perturbing power of the substrate to attract the electrons from the given adsorbate atom. It increases with N and n for "d" type elements.

The order of the substrate's electron configuration in
Fig A4 Variation in work function changes $\Delta \phi$ with the electronic configuration of various adsorbates. (W is common substrate)
Fig A5 Changes in work function with (a) Promotion energy,
(b) Binding energy of various adsorbates. (W-common substrate)
Figs A6(a,b) was chosen as follows:

(i) The energy of $5d^4$ is taken to be $>5d^3$ because of higher values of "n".

(II) The energy of $5d^3$ is taken to be $>-4d^4$ because of elements with an unfulled f shell have a higher tendency to make their own stable configuration; Mutual perturbation of adsorbate-substrate may increase the collectivized electrons for greater work function changes.

(iii) Both $5d^4$ and $5d^3$ are less than $4d^5$ since the $d^5$ is the most stable configuration with a high statistical weight $\binom{63}{63}$. (Also the probability of attracting other electrons to increase its statistical weight is low).

(iv) The same argument can be used for the relative energies of $-4d^2 > 5d^2$.

In Fig A6(b) Re is placed in the last since it has the most stable $d^5$ configuration (Section II.5.3.) which does not have further tendency to increase the population of these configurations by attracting electrons from the adsorbates. On the other hand Mo ($d^5$) is relatively strong perturber owing to its unfulled f shell and one s electron. The other configurations follow a normal course.

It can be seen from Fig. A6(a) that $\Delta\phi$ is high for substrates of high perturbing power. Therefore the different magnitudes of $\Delta\phi$ for different adsorbates seem to be related with the number of electrons in the outer shell of the adsorbate which determines the population and energy of the nonlocalised electrons. Borides ($25_2^2p^1$) yield more $\Delta\phi$ owing to the less energetic $p^1$ electrons as compared to $25_2^2p^2$ of carbon and $25_2^2p^3$ of Nitrogen.
Fig A6. Variation in $\Delta \phi$ with the electronic configuration of various adsorbates.
(a) Me-B$_2$C$_2$N$_2$  (b) Me-Cs,Th
Fig A6(b) (with metal adsorbates) has the similar trend of 
$\Delta \phi$ changes with various base metal as in Fig A6 (a) 
Small differences may be related to the inaccurate values of 
$\Delta \phi$ reported in the literature.

Fig A7 shows the variation in work function changes with 
the energies associated to the outer shell of atoms. 
The difference of energies (i.e. Binding energy of 
substrate atom - energy of atomic level of adsorbates) is 
used as the parameter (only those substrate are shown 
whose energies have been available). It can be seen that 
the variation in work function changes decreases with the 
decrease of energy difference. A general curve 
(dashed curve) is drawn to show the general trend of 
work function changes with the difference of energies 
associated to the electronic configuration of the system.
Fig A7. Variation in work function changes with the difference in energies of various substrates and adsorbates.