

# The Use of Platinum Metals in Modern Thermionic Emitters

By Richard A. Tuck

THORN EMI-Varian Ltd, Hayes, England

*The performance of dispenser cathodes has been considerably improved over the last quarter of a century. This review considers advances made in the materials used either for the matrix of the thermionic emitter, or to coat its surface, which have resulted in lower effective work functions. The use of iridium, osmium and ruthenium has played a significant role in this improvement.*

In a world where integrated circuits and microprocessors are regularly making new inroads into our daily lives, it is all too easy for those not in the business to assume that the thermionic valve is obsolete; nothing could be further from the truth. The majority of households still have at least one thermionic device, the television picture tube. The U.H.F. signals the television set receives are broadcast using a high power klystron amplifier, another thermionic device. These signals in turn come from a TV camera which uses thermionic pick up tubes. In just the field of communications this list can be extended to include satellite "up-link" and "down-link" electron tubes.

There is no doubt that the triode, tetrode and pentode receiving valves of twenty-five years ago, are, except for a few specialised uses, gone for good. For some uses, however, vacuum devices have remained pre-eminent. One such area is power microwave devices and it is this field that is continually making new demands of thermionic emitter materials.

The devices which are currently stretching the performance of thermionic emitters, are

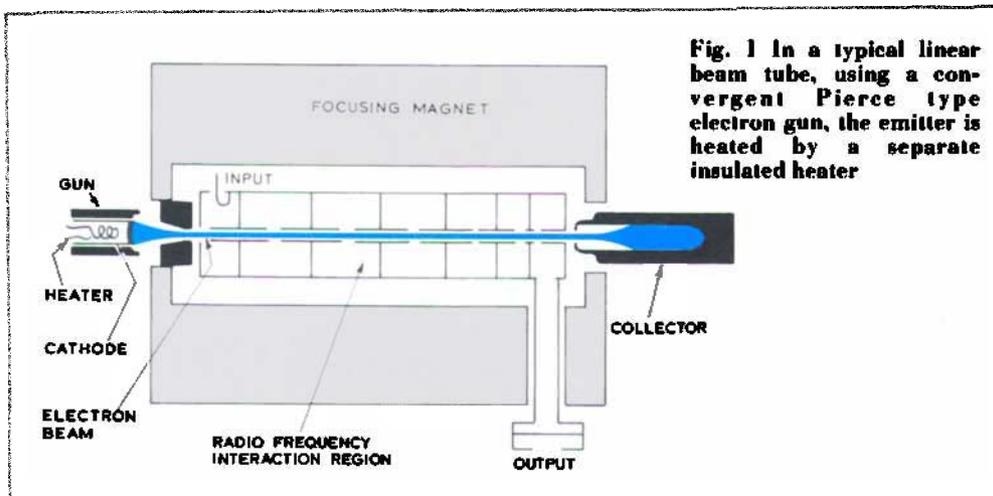
known as velocity modulated linear beam tubes, the two major variants being the klystron and travelling wave tube. In these devices, which are amplifiers, an electron beam, formed by an electron gun, passes through an interaction space and thence into a collector electrode. The interaction space is arranged so that the radio frequency signal to be amplified either slows down or speeds up the electron beam a little; after drifting for a period, the faster electrons catch up with the slower ones, resulting in a bunched beam. The time varying current then interacts with the circuit, causing further bunching, and so on along the device. At the end of the device the energy in the time varying component of the beam is coupled out, leaving the spent beam to be collected.

The physics of these devices dictates that the interaction region, and more significantly for the gun, the tunnel through it, change in proportion to the wavelength at which the device operates. Consequently, if power output is to be maintained as the frequency is increased, the current density required from the cathode in the electron gun increases also. To see why this presents a problem we must look at the mathematics of thermionic emission.

At the surface of all solids there is a potential barrier, which the electrons in that material have to overcome if they are to leave. The energy required to overcome this barrier is called the work function, and is traditionally measured in electron volts. When a solid is heated, some of the electrons acquire sufficient energy to escape into the surrounding vacuum. The magnitude of this current is given by the Richardson-Dushman equation:

$$J = 120 T^2 \exp - (11600 \phi/T)$$

where J is the current density at the emitter



**Fig. 1** In a typical linear beam tube, using a convergent Pierce type electron gun, the emitter is heated by a separate insulated heater

surface in  $A/cm^2$  and  $\phi$  the work function in electron volts,  $T$  the temperature is measured in kelvins.

Linear beam tubes use convergent Pierce type electron guns, illustrated in Figure 1, which require the emitter to be heated by a separate insulated heater; temperatures above 1500K cannot be used if the device is to have a long life.

The best pure metal thermionic emitter is tungsten which has a work function of 4.54 eV which at 1500K can provide  $1.5 \times 10^{-7} A/cm^2$ . Modern microwave tubes operate with cathode loadings of 1 to 8  $A/cm^2$ , so we can see how inadequate pure metal emitters are.

The oxide cathode has been the mainstay of the receiving tube designs for many decades. At direct current densities of 0.3 to 0.5  $A/cm^2$  or pulse loadings of a few amps per square centimetre for all but the shortest duration, problems are encountered with ohmic heating in the thick oxide layer. Modern electron guns are built to exacting mechanical tolerances which oxide cathodes, with their sprayed coatings, cannot meet.

The class of cathodes which have become more or less standard in the microwave tube industry are called dispenser cathodes. The evolution of these cathode materials from the earlier oxide is well reviewed by Beck (1). The purpose of this review is to pick up the story

from where Beck finished. During the last two decades or so since Beck's paper, the use of platinum metals, though not platinum itself, has significantly improved the performance of thermionic emitters.

## Dispenser Cathodes

### 1. The B-type or Impregnated Cathode

The starting point for the majority of modern developments is the B-type cathode; its invention is usually ascribed to Levi (2) though as with most things many earlier workers made significant contributions.

The cathode comprises a porous tungsten matrix made by sintering tungsten powder. The pore diameter is around  $5 \mu m$  and the interpore separation  $5 \mu m$  to  $10 \mu m$ . The emitter pellet, or button as it is called, is machined to size with the matrix filled with either copper or plastic. This filler is then removed.

The pores are then filled with a barium containing ternary mixed oxide, which in Levi's cathode had the composition:



the so called 5:3:2 mix. Cathodes are also manufactured with other impregnant compositions, 6:1:2 and 4:1:1 being in common use. The material is infiltrated into the matrix at 1600 to 1800°C in dry hydrogen, the excess removed either mechanically or chemically, and

the emitter mounted together with a heater into the final structure.

The current explanation of its operation is as follows. Reactions between the impregnant and the tungsten produce free barium. This migrates by Knudsen flow and surface diffusion to the surface. At the surface, and to an extent on the way to the surface, some of this reacts with oxygen to produce what we shall rather loosely call barium oxide. This forms a vertically ordered double layer with barium outermost. The dipole so produced lowers the work function from the 4.54 eV of bare tungsten to around 2.1 eV. Excess activator (Ba/BaO) evaporates from the pore ends and surface, the "BaO" layer being in dynamic equilibrium with the supply. This enables the cathode to repair itself after poisoning by residual gases or positive ions. This virtue is in another way a vice, since the evaporated Ba/BaO coats nearby electrodes, making them more likely to emit stray electrons both by secondary and thermionic emission. The cathode life time is determined by the reservoir of available barium in the matrix.

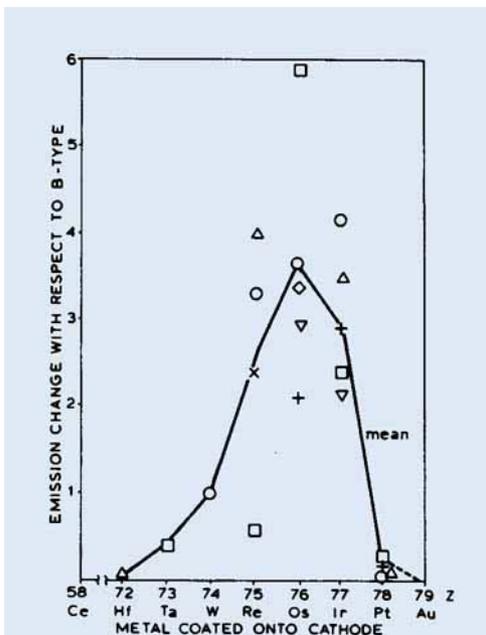
The effective work function of the B-type cathode is 2.05 to 2.10 eV, equivalent to approximately 2 A/cm<sup>2</sup> zero field emission at 1300K; this was considered to be a high current density in 1955.

For nearly two decades the B-type cathode was the microwave tube industry standard. During this period, however, the power frequency product of new devices increased steadily. This trend, together with the introduction of grid controlled guns on most new tube types, pushed cathode loading up to 7 to 10 A/cm<sup>2</sup>. To supply this current density a B-type cathode would need to be operated at temperatures well over 1500K. At such temperatures life is short both for the emitter material and the heater assembly.

## 2. The M-type Cathode

The first improvement to the B-type cathode is attributable to Zalm and van Stratum (3). They noticed that for alkali metals on crystal surfaces it was the face with the highest bare work function which had the lowest value after adsorption. By analogy they agreed that by

Mean Change in Electron Emission of B-type Cathodes when Coated with Various Metals		
Coating on cathode	Mean emission change	References
Titanium	<0.1	24
Nickel	2.0	18
Copper	0.6	19
Zirconium	$\sim 10^{-5}$	16
Molybdenum	1.0	8
Ruthenium	2.8	3,20
Tantalum	0.4	20
Tungsten	1.0	Reference surface
Rhenium	2.7	15,17,18,20
Osmium	3.7	3,14,17,20,23
Iridium	2.7	14,17,18,20,23
Platinum	0.1	17,20
Gold	$\sim 10^{-5}$	22,24



**Figure 2** The change in electron emission of B-type cathodes when coated with elements from the bottom of the periodic table, by various workers:

- △ Maloney (18, 19)
- Nekrasov and Druzhinin (20)
- Housten (17)
- ▽ EMI-Varian
- + Bhide and Wray (14)
- ◇ Zalm and van Stratum (3)
- × Branscombe and Weaver (15)

increasing the work function of a matrix surface, the cathode would have a lower final work function.

It is at this point that the platinum group metals enter the story. The metals which satisfied the high work function and other criteria were osmium, iridium, ruthenium and rhenium; platinum, palladium and gold were rejected because they formed intermetallic compounds with barium. The work function of B-type cathodes coated with osmium, ruthenium, iridium or rhenium are approximately 0.1 eV less than the uncoated samples; this represents a threefold increase in emission at the same temperature.

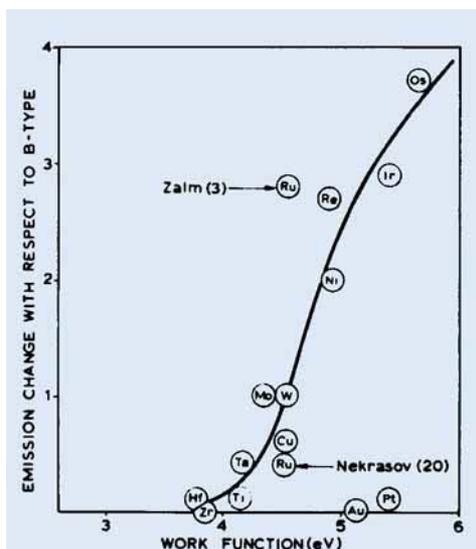
Various techniques for coating cathodes have

been used, including vacuum evaporation, chemical vapour deposition, chemical deposition and, the most widely used, sputtering. The films are normally 0.2 to 1  $\mu\text{m}$  thick.

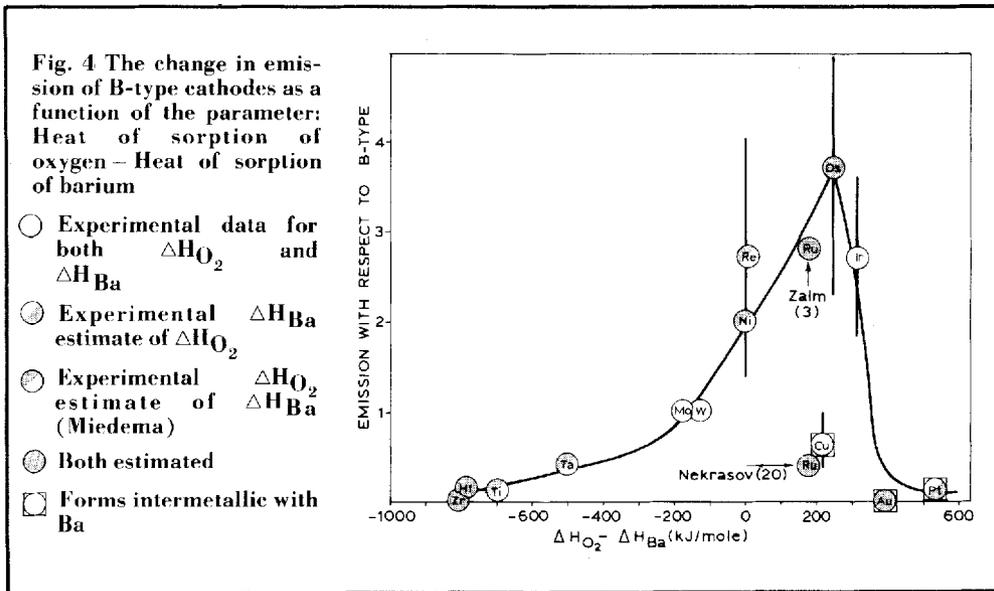
Since Zalm's paper many other workers have duplicated his work, though the results have varied considerably from author to author.

### How the Coating Works

After Zalm's paper many metals were coated onto dispenser cathodes to try their effect; the Table and Figure 2 summarise the results. These are taken from a paper by Skinner, Tuck and Dobson (4); Figure 3 is from the same work, and shows the mean emission change as a function of coating work function. The data would fall on a smooth curve were it not for platinum and gold, which are serious anomalies. The authors present an alternative model based on the difference between the heat of sorption of oxygen and barium on the surface, Figure 4 shows their data. Their reasoning is that to form a stable vertically ordered dipole layer with oxygen closest to the surface, one needs an



**Fig. 3** The change in emission from B-type cathodes as a function of coating work function shows the anomalous positions of gold and platinum



oxygen/substrate bond. If this bond is too strong, as in tungsten say, an adverse dipole is formed between oxygen and the substrate, reducing the beneficial effects of the “BaO” dipole. Osmium, iridium, ruthenium and rhenium fulfil this condition. However, with platinum and gold the bond is too weak for a stable layer.

A molecular orbital approach to the bonding is used by Green (5), drawing on theories of heterogeneous catalysis. He presents a theoretical covalent bonding model of gas phase BaO and then discusses how this might bond to a transition metal surface. He argues that the bonding is via unoccupied d-orbitals at the surface. Using the arguments of heterogeneous catalysis, metals are divided into categories depending on the orientation and number of unoccupied d-orbitals. Tungsten falls into one group: osmium, iridium, ruthenium and rhenium into another, while platinum, the anomaly, falls into a third. The second group, containing osmium, is believed to have unoccupied orbitals which fit with the BaO orbitals. Green’s model and that of Skinner and her colleagues have large areas of compatibility.

Several groups are currently using surface analytical techniques to investigate the nature

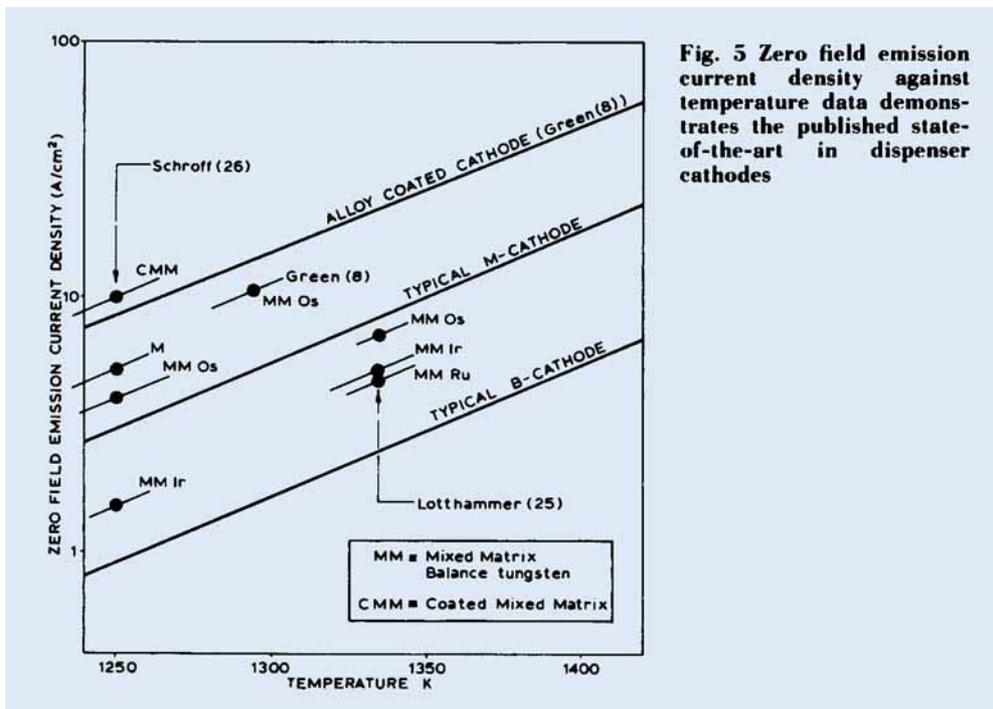
of dispenser cathode surfaces, with considerable success. However, the heterogeneous nature of the surfaces involved will mean that a really definitive solution will take some time.

### 3. Alloy Based Cathodes

During the last five years, the use of alloys both as coatings and matrices, has considerably improved dispenser cathode performance.

The first use of alloys dates back to the beginning of the M-type cathode. There was concern about the volatile and toxic  $OsO_4$  being formed on pure osmium films. The solution adopted throughout the U.S.A. was to replace pure osmium with an osmium-20 per cent ruthenium alloy, which was claimed to reduce oxidation (6). The author’s company has used pure osmium for many years without hazard, so the problem may be more imagined than real. The performance of cathodes coated with either seems identical.

The use of alloys to actually improve performance was pioneered by Falce at Varian Associates (7) and Green, Skinner and Tuck at THORN EMI-Varian Ltd (8). Falce produced mixed matrix cathodes using iridium-tungsten alloys. In a mixed matrix cathode, the tungsten matrix of the B-cathode is replaced by one of



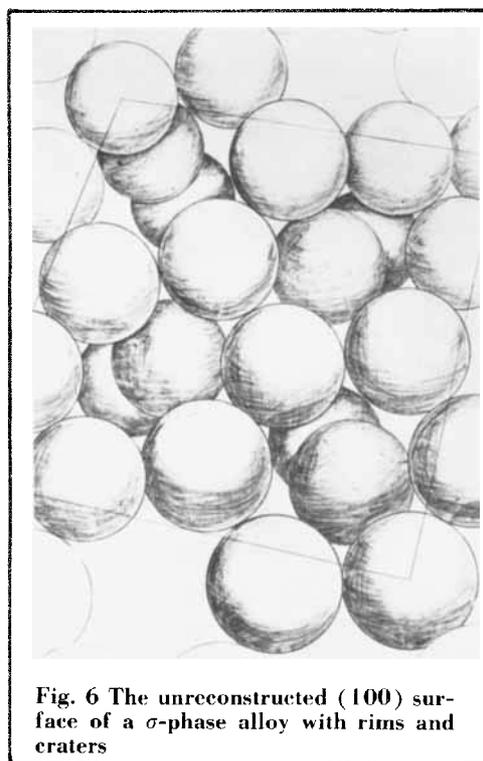
sintered mixed powders, which is impregnated in the usual way. Matrices with 20 per cent iridium were found to be optimum, though the maximum is rather broad, 40 per cent iridium alloys producing very similar results.

Work at THORN EMI-Varian Ltd (8) on the osmium-tungsten system, correlated improved emission with the formation of the tetragonal  $\sigma$  phase. B-type cathodes coated with this intermetallic showed reductions in work function of up to 0.2 eV, a further factor of three in emission, compared to the M-type cathode.

Subsequently, other groups duplicated and expanded upon the work, trying other combinations of metals. Figure 5 shows the published state-of-the-art. Schroff (9) has produced a coated mixed matrix cathode, combining perhaps the best of both worlds.

### Why Are the Alloys Better?

Currently there is no definitive answer to this question; theory and experiment are much less advanced than for pure metal coatings, which



are still by no means fully understood.

There are, however, some ideas. The inter-metallic compounds which seem beneficial are likely to have atomically rough surfaces, with either "ridges and valleys" or "craters and rims", Figure 6 shows the probable (100) surface of a  $\sigma$ -phase alloy which is of the craters and rims variety.

A rather elegant experiment by Pankey and Thomas (10) supports this reasoning. They activated recrystallised iridium ribbons with BaO and measured the final work functions of the crystallites with an emission microscope. Using a microbeam X-ray diffraction system they then determined the orientation of the crystallites. The activated crystallites with the lowest work functions were from the atomically rough (210) faces.

The reasoning of Smoluchowski (11), recently experimentally supported by Gardiner, Kramer and Bauer (12), says that such rough crystal faces would have low work functions. The benefits of alloys are thus further evidence against the high substrate work function

explanation for the effects of osmium, iridium and ruthenium.

The reason for the superior performance of atomically rough surfaces is not known. The author has suggested (13) that the topography of the surface may control the coverage of "BaO" at a more nearly optimum value. A definitive answer to this question may be a long way away, awaiting adsorbate experiments on single crystals.

## The Future

At the Tri-Service Cathode Workshop Conference, held at Fort Monmouth, New Jersey, in Spring 1982, the consensus was that while the best samples of alloy based cathodes were quite adequate for current state-of-the-art electron guns, the variations from sample to sample were not.

Work is now underway at a number of centres to improve the reproduceability, though none of it has yet been published. What we can be sure of, is, that platinum metals will continue to play a significant role in this work.

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