ELECTRON EMISSION FROM OXIDE COATED CATHODES

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ABSTRACT

The work has been mainly concerned with the irregularities which are found in the electron images of emitting oxide cathodes. An electron emission microscope has been designed to produce pictures at magnifications of up to x 120. Electron pictures from oxide cathodes have been compared with the optical picture of the cathode surface and a correlation has been found to exist between the two types of picture from the same part of a cathode. This result is in contradiction to the findings of earlier investigators. In view of this new evidence of the correlation, the causes of irregularities in the emission picture have been reconsidered and a revised list of the possible causes has been given.

In an attempt to produce a cathode which emits uniformly, a technique has been developed for coating the core of the cathode. The polished core is coated by evaporating the oxide on to it. The cathodes produced in this way had smooth surfaces and uniform emission pictures were obtained. The emission pictures did not remain uniform but altered in character during the life of the cathode. Experiments were performed to establish the reasons for the observed sequence of emission pictures.

A theoretical explanation of the emission pictures has been attempted using a semiconductor model for the oxide coating. An equation for the saturated emission current is derived for different forms of the semiconductor model and it is shown that all the models lead to an equation of the form

$$I = A_0 T^n \exp - \frac{e\phi}{kT}$$

where A, n and ϕ are constants which depend on the model used. The emission from a metal coated with a semiconductor is considered and it is shown that with a model of the contact between the metal and the semiconductor which assumes space charge barriers, an explanation of the sequence of emission patterns is possible.

CONTENTS

Part 1

THE OXIDE CATHODE

Part 2

THEORIES OF THERMIONIC EMISSION FROM OXIDE COATED CATHODES

Part 3

EMISSION MICROSCOPY ON OXIDE COATED CATHODES

Part 4

DESIGN OF THE APPARATUS

Part 5

COMPARISON OF THE EMISSION AND OPTICAL PHOTOGRAPHS OF THE SURFACE OF OXIDE CATHODES

Part 6

COATINGS DEPOSITED BY AN EVAPORATION TECHNIQUE

Part 7

EMISSION PHOTOGRAPHS FROM CATHODES WITH COATINGS DEPOSITED BY THE EVAPORATION PROCESS

page

Part 8

THE THEORY OF ELECTRON EMISSION FROM OXIDE COATED METALS

Part 9

PROBABLE MECHANISM OF THE FORMATION OF EMISSION PICTURES

GENERAL INTRODUCTION

Chapter 1

Electron emission from metals has been studied for many years and the problem has had many theoretical treatments. With the discovery of the oxide cathode a new and more copious thermionic electron emitter was made available. In order to understand the mechanism of the emission from these cathodes a great amount of experimental and theoretical effort has been expended. Much discussion has occurred and some early theories have been exploded.

Today, in spite of the enormous commercial use of these cathodes, and in spite of numerous careful investigations, there still exists a very great doubt as to what is the real mechanism of emission of the oxide cathode.

In an attempt to solve the problem of the emission mechanism, the technique of emission electron microscopy has been developed. With this technique, the electrons emitted from the heated cathode can be focussed to form an image on a fluorescent screen. In this way the emission from the surface of the cathode can be examined, and useful information on the mechanism of emission can be obtained.

In the following chapters a general description of oxide cathodes and the factors which influence their performance will be given. The theory of electron emission as it stands today is developed and the forms of emission equations applicable to oxide cathodes are derived.

The object of the research has been to investigate the causes of the non-uniform emission from oxide cathodes and to provide some explanation based on a theoretical model. Earlier investigations of this kind have led to the result that there is no correlation between the emission pattern and the optical picture from the surface of the normal cathode. It is evident, however, that if the surface of the cathode is marked by scratching or deforming the surface, then there is an obvious correlation between these large markings and the form of the emission pattern. For this reason it would appear that surface structures on the cathode may indeed be an important cause for the production of non-uniformities of emission. It therefore seemed worthwhile to make a further investigation of oxide cathodes in the emission microscope and to attempt to correlate the emission pattern with the optical picture of the cathode surface, for with the higher magnification emission microscope available and more advanced optical techniques, a more detailed study of the cathode can now be made than was possible at the time of the first investigations of this kind.

Should it prove possible to identify the causes of non-uniform emission, it is then intended that the results of the investigation should be applied with a view to manufacturing a cathode which will emit uniformly over all its surface. Such a cathode, providing it also possessed suitable emission characteristics would find application in devices such as travelling wave tubes, where the uniformity of the emission is a factor which influences the noise of the device used as an amplifier.

Part 1

THE OXIDE CATHODE

Chapter 2 The development of the oxide cathode.

The fact that various metal oxides give considerable thermionic electron emission was first noticed by Wehnelt[1] in 1904. He undertook a detailed examination of these oxides and found that the alkaline earth oxides were particularly good emitters. The oxide cathode, consisting of a core metal coated with a layer of alkaline earth oxide was a direct result of his experiments. Since its discovery the importance of the cathode as an electron source has grown and today it plays an enormous part in the field of electronics which has influenced the lives of us all.

With such great commercial possibilities it is understandable that a great deal of effort has been directed towards the improvement of the cathode. Therefore a big proportion of the research and development programme has been concerned with the investigation into the conditions which govern the emission properties of the cathodes. The technological research on the oxide cathode thus deals with such matters as the composition of the core metal, the composition of the coating material, the state of the vacuum surrounding the cathode and many other problems connected with the manufacture and operation of these cathodes. A comprehensive account of this aspect of the work which has been carried out since the discovery of the oxide cathode has already been compiled and published in the book 'The Oxide Coated Cathode' by Hermann and Wagener[2]. Adequate references to the original papers are given.

The more basic research into the mechanism of the emission process has led to much controversy. Jentzsch[3] established that the thermionic emission from an oxide cathode followed the Richardson empirical law. The early measurements of the work function of the oxide cathode by different workers varied considerably because the vacuum conditions under which the experiments were done were not good enough. With the improvement of vacuum technique more reliable values were obtained. The work of Koller[4], Rothe[5] and Becker[6] in the 1920's showed the importance of excess barium in the coating for good emission from the cathode. Koller therefore proposed that the emission was due to the free barium. The question then arose as to the manner in which the barium was present in the oxide. Rothe supposed that the emission came from pools of barium deposited on the surface of the coating. An alternative theory was advanced by Reimann and Murgoci[7], and other workers. They suggested that the barium was produced at the core metal surface and diffused through the coating to the cathode surface. Both these theories were shown to be invalid. Heinze and

Wagener[8], using the emission microscope, showed that there was no increase in the area of the emitting regions of a cathode during activation, that could account for the observed rise in the emission current. Therefore the theory of Rothe cannot account for activation. Becker was able to show that the emission current suddenly decreased when the coating was removed. If the core metal surface was the seat of emission this would not be expected.

With the presentation of the semiconductor theory by Wilson[9] a theory of thermionic emission from oxide cathodes was developed. The theory of impurity semiconduction was applied and it was postulated that the excess barium behaved in a similar manner to the impurity. Hermann and Wagener[2] consider that the work function of the cathode consists of two parts, the internal and the external work function. During activation they postulate that the internal work function is decreased due to formation of excess barium within the coating, while the external work function remains unaltered.

Soon after the above theory was postulated a completely different account of thermionic emission was put forward by de Boer[10]. He postulated that the emission occurred by thermal ionisation of atoms of barium absorbed on the surface and that the conduction of electrons through the coating occurred by an atom losing an electron to a neighbouring ion. Thus the thermionic emission, since it depends on the conduction process, will depend on the number of barium atoms absorbed in the coating.

Both the semiconductor theory and the de Boer theory can satisfactorily explain the known characteristics of emission from oxide cathodes and thus there still remains some doubt which theory is correct.

Chapter 3 Manufacture of the oxide cathode before mounting in the envelope

3.1 The core metal

Various types of core metal are used, but the choice is limited to those metals which can satisfy the following conditions. Most oxide cathodes at some time during their life are heated to temperatures of around 1100°C. It is therefore necessary for the core metal to maintain its mechanical strength at these temperatures. Also the metal must not give off gases after its final outgassing treatment. It is undesirable that any reaction may take place between the core metal and the coating that would poison the emission but on the other hand reactions enhancing the emission are sometimes advantageous. Since cathodes are often made in intricate shapes a metal capable of being machined without difficulty, is an advantage. Of the metals available platinum, molybdenum and nickel are commonly used. Of these nickel is by far the most widely used and in particular an alloy called '0' nickel has been developed specially for cathode cores. This material has, like other alloys designed specially for core metals, certain additives which reduce the barium oxide in the coating and produce an increase in the excess barium with consequent improvement in the emission. The main additives in the '0' nickel are Fe 0.12% Mg 0.05%.

In the case of indirectly heated cathodes, the core is machined to the appropriate shape and then is subjected to a cleaning process. The core is rinsed in a degreasing agent such as Trichlorethylene and then heated in a hydrogen atmosphere at 1100°C. The core metal is then ready for coating with a suitable form of emission paste.

3.2 Preparation of the emission paste

The basic ingredient of all emission pastes is a compound of an alkaline earth element which, on heating under vacuum, will decompose to form the oxide. The most commonly used compounds are the carbonates of barium, calcium and strontium. Most pastes in fact consist of a mixture of two or all three of these carbonates in various quantities.

The carbonates are usually prepared by precipitation from solution of the nitrates or hydroxides. It is, however, an important fact that these carbonates can form a series of mixed crystals which on decomposition form mixed oxides. These oxides give higher emission than a mechanical mixture of the same proportions. The investigation into this matter was the subject of a number of papers e.g. Benjamin and Rooksby[11,12].

The mixture of carbonates is usually milled to a standard particle size for the best emission results. The further treatment of the substance depends on the proposed use for the mixture.

Each method of applying the coating to the core requires its own special type of coating mixture. For this reason particular attention is paid to the properties of the coating pastes. The viscosity, particle size and drying rate of the mixture and the density and surface finish of the coating as well as the bond between the coating and the core are all important factors which can be influenced by addition of different solvents and binders to the mixture as well as by the methods of manufacture and storage of the solutions.

3.3 Application of the emission paste to the core metal

There are four main methods of applying the paste to the core metal. These are:-

(1) spraying
(2) dragging
(3) painting
(4) electrophoresis

The spraying method requires a low viscosity paste for the spray gun but at the same time the deposit on the core must remain there and thus a quick drying solution is needed. Specially designed sprays, to give uniform coatings and to avoid agglomeration of the particles in the coating, are used. The coatings are usually applied layer by layer and up to twenty or so layers are sometimes used.

The dragging method is more suitable for coating directly heated wire type cathodes. The solutions required are generally more viscous than those for spraying. The cathode is usually dragged through a succession of baths of paste with a drying process between each one.

Coating by painting is rarely used when large numbers of cathodes are required, but this method is quite convenient for coating special cathodes. In this case the drying properties, in particular the effect of surface tension forces on the final surface shape, must be suitably controlled.

Coating by electrophoresis is a very convenient method for cathodes of irregular shape. This method is capable of producing very smooth coatings when colloidal paste solutions are used. The main disadvantage is the fact that the bond between the cathode and the core is not very strong. This can of course be very serious if the cathode is subsequently to be jolted when in use. This method is thus usually restricted to special purpose cathodes.

Chapter 4 Further processing of the cathode

4.1 Mounting in the vacuum envelope

Before the oxide cathode can be used it must be fitted into an electrode system and then operated at a pressure lower than $5. 10^{-6}$mm. of Hg. In the case of indirectly heated cathodes a heater must be fitted inside the cathode core. The assembly of the cathode, heater and electrodes is usually supported on stiff wires held in a glass pinch. A glass envelope with a pumping stem is then sealed round the assembly. In order to obtain the most efficient valves the whole assembly must withstand a baking process at between 500°C and 600°C.

4.2 Decomposition of the alkaline earth carbonates to the oxide

The process of decomposing the coating takes place after the metal parts of the valve have been heated by high frequency induction heating to about 600°C and the envelope has been baked out under vacuum. The temperature of the cathode can only be raised slowly, otherwise the pressure of gases set free in the coating may cause the coating to come loose from the core and even fall off. The pressure in the valve is a good guide to the rate of decomposition and it is desirable to increase the temperature of the cathode at such a rate that the pressure does not rise above 10^{-5}mm of Hg.

There are a number of peaks in the pressure as the temperature of the cathode is raised. According to Haas and Jensen[13] peaks occur, at around 100°C due to desorption of gases and water vapour, at around 200°C due to decomposition of the binder, and the main peaks are at temperatures between 600°C and 900°C and correspond to the decomposition of the different carbonates in the coating.

In order to decompose the coating it is therefore necessary to raise the cathode temperature in excess of 900°C. A temperature of 1000°C is usually the maximum that is used during the process. In order to avoid the absorption of the gases emitted from the cathode during decomposition, by the metal and the walls of the valve, they are usually held at the baking out temperature during the decomposition.

A getter is used in most valves in order to absorb any gases which may be given off after sealing off the valve from the pump. The getter is usually evaporated on to the envelope walls at this stage of the manufacture. The cathode in the sealed off valve is then activated.

4.3 Activation of the cathode

The activation of the cathode is the name given to the phenomenon whereby the cathode at the beginning of its life gives an emission current which rapidly increases sometimes by a factor as big as 10^4. With cathodes having the normal pastes with organic binding materials and cores with reducing agents present, the activation can be carried out merely by heating to a high temperature. According to some results of Huber quoted by Hermann and Wagener[2] there is an optimum temperature in the region of 1000°C for this process.

For cathodes in which there are no possibilities for causing reactions between the oxides and other reducing agents, the activation process may alternatively be accomplished by an electrolytic process which occurs when a current is drawn from the cathode.

The final part of the activation process consists of using the emission current to bombard the electrodes in the valve to set free any residual gases still absorbed. These gases at first poison the emission but the emission recovers with further activation by drawing current and the gases are absorbed by the getter.

Themechanism of the activation has been the subject of much speculation. The explanation of the phenomenon varies according to the model of the emission mechanism that is used. There seems, however, to be general agreement amongst various authors, e.g. Reimann[14], de Boer[10] and Hermann and Wagener[2], that the activation process is essentially one of building excess barium into the oxide layer. The manner in which this excess barium exists in the coating will be discussed later in the sections dealing with the various models of the oxide cathode. From a purely chemical point of view the addition of reducing agents to the core metal and the coating will assist the formation of excess barium. The electrolytic decomposition of the coating would also assist in supplying excess barium and it is thus to be expected that the activation process will depend on the efficiency of these two processes for the production of the excess barium.

Part 2

THEORIES OF THERMIONIC EMISSION FROM OXIDE COATED CATHODES

Chapter 5 The Richardson empirical formula

The early theory of thermionic emission of electrons from metals had been based on the classical model of the metal. It was assumed that the electrons moved freely in the metal and all those electrons with sufficient energy to overcome a potential barrier at the surface, could be emitted. The theory was first presented by Richardson[1] in 1901. The emission equation took the form

$$I = Ne\sqrt{\frac{kT}{2\pi m}}\, \exp\frac{-C}{kT} \tag{1}$$

where I is the emitted current density, N the number of electrons per unit volume, k is Boltzmann's constant, T the absolute temperature, C a constant denoting the minimum energy an electron requires before it can be emitted, and e and m are respectively the charge and mass of the electron.

Although the agreement between theory and experiment was not very good it was found that the empirical formula

$$I = AT^{\frac{1}{2}} \exp\frac{-e\phi}{kT} \tag{2}$$

would represent actual emission data if suitable values of A and ϕ were chosen. These constants are characteristic of the material.

Following the derivation of the above formula by Richardson, H. A. Wilson[2] showed that an emission formula could be derived on the basis of a thermodynamical method. A similar expression for the current density was obtained.

After the discovery of the oxide cathode its emission current was measured and it was also found to obey the Richardson empirical formula with suitable choice of constants. The value of these constants could be found by measuring the slope and intercept of a graph of $\log i - \frac{1}{2}\log T$ against $\frac{1}{T}$.

The early classical theory of emission from metals was soon to be replaced by the theory based on quantum theory. Following the success of Planck's radiation laws, and also the Einstein and Debye theories of specific heats, the methods of quantum statistics were applied to the problem of electron emission from metals. Since the Bohr theory of the atom had demonstrated that the electrons in the atom could be considered to possess only certain discrete energies, it was assumed that the electrons in the metal lattice would also exist in discrete energy states, but because of the Pauli exclusion principle, electrons in similar states in the atoms in the lattice cannot possess the same energy and instead of the discrete energy levels obtained with the atom, there are instead bands of energy levels. It was further assumed that the processes of conduction and emission could be regarded as due solely to the motion of the electrons in the outermost shell of the atom.

These electrons are the ones least tightly bound to their parent atom and are termed the free electrons. In order to determine the distribution of the free electrons in the energy levels making up the band of levels available to the free electrons, the methods of quantum statistics were used. Both Bose-Einstein and Fermi-Dirac statistics have been applied but the latter were found to be the correct statistics for the case of the free electrons.

Using Fermi-Dirac statistics and assuming that only those free electrons, with velocities normal to the surface greater than a certain value, can surmount the potential barrier at the surface, the emission equation that is derived[3] has the form

$$I = AT^2 \exp -\frac{e\phi}{kT} \qquad (3)$$

where A is a constant and ϕ is a constant usually called the work function. It depends on the Fermi energy and the potential barrier at the surface of the metal.

Later theories of thermionic emission based on thermodynamic reasoning also resulted in emission equations of a similar form to equation (3) provided the results of quantum theory were used. The review article by Herring and Nichols[4] deals with the fundamentals of this thermodynamical approach to the theory and also gives adequate references.

The experimental results obtained from measurements of the saturated emission current at various temperatures are insufficientto differentiate between the $T^{\frac{1}{2}}$ and the T^2 formulas.

Although these equations may be applied to metals there is no reason to believe that the theoretical values of the constants will correspond to the values calculated from experiments on oxide cathodes.

It was not until the ideas of wave mechanics had been developed that a suitable approach could be made to the problem of conduction and emission of substances having periodic lattices with more than one constituent.

Chapter 6 The Wilson Theory

6.1 The theory of semiconduction

Following the wave mechanical treatment by Bloch[5], of the motion of electrons through periodic potential gradients such as would be found in a one dimensional array of atoms, the passage of electrons through a metal could be envisaged, and the high conductivity of metals could be explained. The phenomenon of semiconduction had still to be accounted for. An attempt to account for this was made by Wilson[6].

On the basis of the work of Bloch and Bethe[7], Wilson assumed a cubic lattice of atoms and set out to calculate the possible energy states which the electrons in the atoms may have. He considered the case where the electrons in the outermost shells of the atoms are not influenced by the atoms, i.e. the case of the free electrons. Under these conditions the electrons may exist in any of a continuous range of energy levels. In the case of electrons which are influenced by their parent atom i.e. tightly bound electrons, the result is more complex. It is then possible that the electrons may have energies lying in certain ranges separated by bands of forbidden levels. The bands of permissible energy levels correspond to the states which the electrons of the atoms may take up. There are S-bands, P-bands etc. corresponding to the S and P quantum states of the electrons. These bands will be separated by an energy gap, say W. For an electron to be able to transfer from the lower S-band to the higher energy P-band it must have sufficient energy to cross the gap.

In the case of a metal, where one of the bands is only partially filled, the application of a small potential can cause the electrons to move from one energy level to the other within the band, and conduction can take place.

In the particular case for example, where the outermost shell of the atom contains two electrons, the number of levels in the S-band when electron spin is taken into account, will be exactly equal to the number of electrons in the outermost shell. At the absolute zero of temperature the electrons will occupy the lowest energy levels and thus the S-band will be completely filled and the P-band empty. Since there are no empty levels in the S-band the application of a small potential cannot cause conduction provided that the potential is not large enough to transfer any electrons across the energy gap W into the P-band. With the heating of the substance some electrons may gain sufficient thermal energy to cross the gap and then conduction can occur. In this way the phenomenon of intrinsic semiconduction can be explained. If, however, the energy gap W is so large that with normal temperatures it is still not possible for the electrons to cross the gap, then the substance remains an insulator.

After the above explanation of the properties of metals, intrinsic semiconductors and insulators, Wilson continued the work and published a further paper[8] in which he proposed a theory of impurity semiconduction. He assumed that a number of atoms were introduced into the lattice and either, because the atoms were different from those of the lattice or, because they disturbed the regularity of the lattice, additional energy levels were introduced. These levels were assumed to lie in the previously forbidden range between the other bands. If these levels are occupied at absolute zero, then, since the gap between the impurity levels and the empty P-band is now less than W, electrons require less thermal energy to transfer into the P-band and thus conduction will occur at much lower temperatures. The properties of impurity semiconductors can thus be qualitatively accounted for.

6.2 Application of the theory to the oxide cathode

The oxide cathode in its simplest form need consist only of barium oxide. For purposes of theoretical calculations, the ideal case of a single crystal of BaO of infinite extent, will be assumed. Unlike the simple cubic lattice assumed in the Wilson theory, the barium oxide lattice is cubic with alternatively placed Ba^{++} and O^{--} ions. If these ions remain at rest, they form a periodic assembly and the wave mechanical treatment of the motion of the electrons leads to solutions of the Bloch type. If, however, the ions are displaced by thermal motion, dipoles can be created and the resulting effect can be described in wave mechanics by polarisation waves. The creation of dipoles influences the properties of the lattice and in particular, their effect on the conductivity has been the subject of many theoretical papers, e.g. Howarth and Sondenheimer[9]. It appears, however, that there will arise, in the same way as for the atomic assembly, a number of energy bands separated by forbidden regions. The ionic assemblies can thus be classified into metals, semiconductors and insulators according to the ideas developed by Wilson in the case of atomic assemblies.

Although a theoretical explanation of the properties of metals, semiconductors and insulators can be attempted in the above manner, the necessary experimental evidence of the existence of energy bands in ionic structures has only been established for the simplest cases. Of these, the sodium chloride crystal is the one with which most of the work has been carried out. If it can be assumed that the results of experimental work on sodium chloride can be applied to other more complicated ionic structures, then a theoretical explanation of the thermionic emission of these structures and in particular of barium oxide, can be made.

If a stoichiometrically composed lattice of barium oxide is considered, then it should give rise to a system of energy levels of a similar form to those of the sodium chloride lattice. Calculations of the band structure of sodium chloride predict, according to Slater and Shockley[10] and Fisher[11], that the levels up to and including the 3p-Cl band will be completely filled at the absolute zero of temperature, while the 3s-Na band will be empty. Thus sodium chloride in its pure regular crystalline form would be expected to behave as an insulator. The introduction of additional levels between the 3p-Cl and the 3s-Na band would, however, cause it to become a semiconductor.

Wilson assumed that the additional levels could be introduced by adding small numbers of foreign atoms to the lattice. It may be that the presence of a stoichiometric excess of either of the constituent ions of the crystal may also cause additional levels situated in the formerly forbidden regions. An excess of one kind of ion may be caused by additional atoms occupying positions in the interstices of the lattice, or on the otherhand, a vacancy at a site of one of the ions will result in an excess of the other. Experimental evidence of the formation of crystals with excess of one of the constituents is seen in the colouring of sodium chloride crystals when heated in a vapour of the sodium metal.[12] Chemical methods[13] have shown that these crystals contain an excess of the metal. Since the excess is due to the positive metal ion, in order that the crystal will remain electrically neutral, it is necessary that it should take up a sufficient number of electrons to neutralise the positive charge due to the excess of the metal. These electrons may then be considered to give rise to the additional levels lying slightly below the conduction band.

The experimental evidence lends support to the theory of the formation of additional levels in the band structure of the sodium chloride crystals but in the case of the more complex barium oxide structure where the experimental work is more difficult and interpretation of the results is complicated, there is little direct evidence to substantiate the theory. The theory is thus based only on the work on the simpler crystals and isolated results which support various aspects of the theoretical model.

The importance of the production of excess barium in the coating, during the activation of the cathode, has already

Ba^{++}	O^{--}	Ba^{++}	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}
Ba^{++}	O^{--}	Ba^{++}	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}

Fig. 1 Stoichiometric BaO

Ba^{++}	O^{--}	Ba^{++}	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}
Ba^{++}	• •	Ba^{++}	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}

Fig. 2 Vacant O ion site lattice takes up two electrons.

Ba^{++}	O^{--}	Ba^{++}	O^{--}
O^{--}	Ba^{++}		Ba^{++}
Ba^{++}	O^{--}	Ba	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}

Fig.3

Ba^{++}	O^{--}	Ba^{++}	O^{--}
O^{--}	Ba^{+}		Ba^{++}
Ba^{++}	O^{--}	Ba^{+}	O^{--}
O^{--}	Ba^{++}	O^{--}	Ba^{++}

Fig. 4

Redistribution of electrons amongst neighbouring barium ions

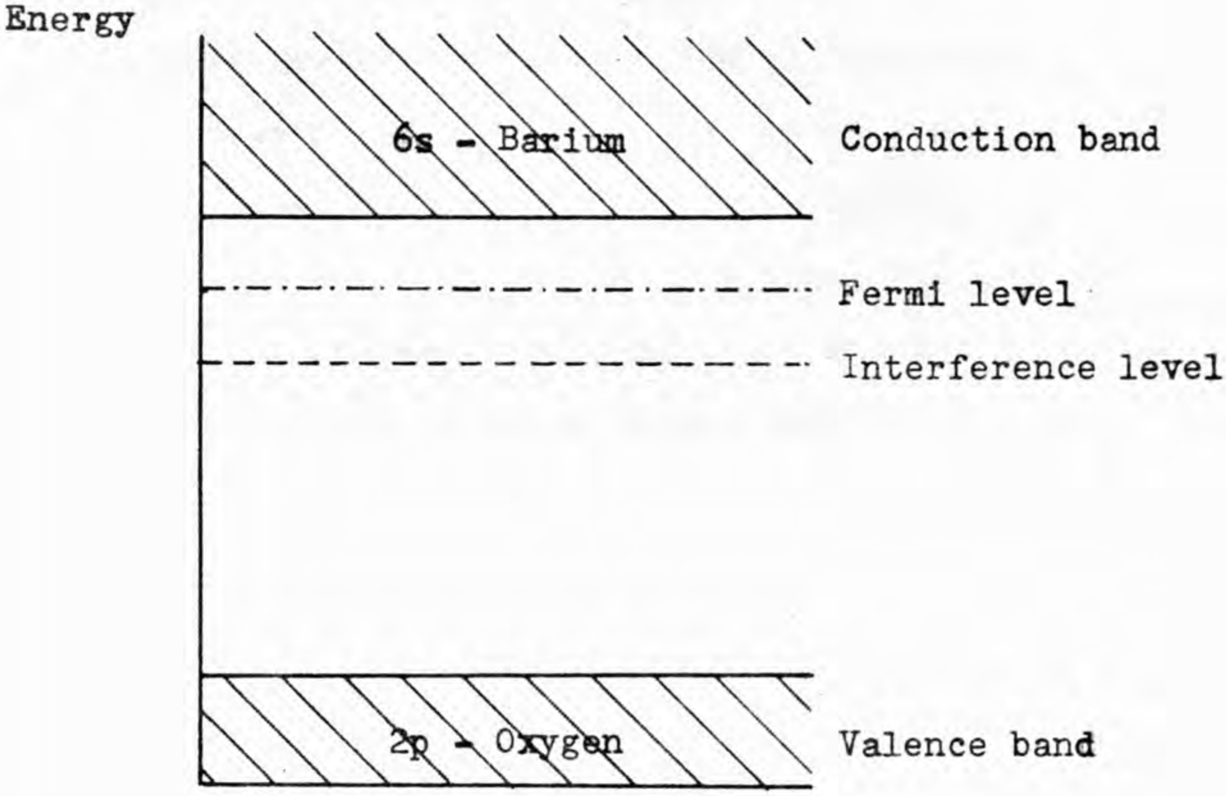


Fig. 5. Energy level diagram of Barium Oxide.

been mentioned in an earlier chapter. If it is now assumed that the oxide coating becomes a semiconductor due to the presence of excess barium, then the effect of the excess will be to introduce additional energy levels. The excess barium may either occur in the lattice due to interstitial atoms or because of vacancies at the O^{--} ion sites. On the basis of calculations carried out by Schottky[14] and Jost and Nehlep[15], Hermann and Wagener[16] have concluded that the second type of defect will be the most probable one. The additional energy levels will therefore be due to the additional electrons which the lattice with vacancies at O^{--} ion sites must take up in order to remain neutral. The electrons can associate themselves with the neighbouring ions in a variety of ways. Fig. 1 represents a plane through a stoichiometric barium oxide lattice. Fig. 2 illustrates how additional electrons must be taken into the lattice in order that it should remain neutral, and Fig. 3 and 4 show the electrons distributed amongst the neighbouring barium ions.

The electron configuration of barium being $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $5s^2$, $5p^6$, $6s^2$. and that of oxygen $1s^2$, $2s^2$, $2p^4$. it is probable that when the barium oxide lattice is formed the two 6s electrons of barium go into the 2p shell of the oxygen, and together with the four electrons already there, they form a completely filled energy band leaving the 6s levels empty at the absolute zero. The energy level diagram of the barium oxide lattice will thus appear as in fig. 5. The interference level which is the additional level occuring because of vacancies at the oxygen sites will occur as shown, just below the empty 6s band. With this model of the band structure the calculation of the emission current can be carried out.

For simplicity it will be assumed that the number of excess barium atoms remains constant, so that no ~~account of~~ diffusion or production of excess barium by chemical processes can be considered to take place. We must further assume that the cathode is fully activated since we cannot increase the number of excess barium atoms, which is according to Hermann and Wagener[16], the chief factor governing the state of activation of the cathode.

In order to obtain a theoretical expression for the emission current, it is usual to first calculate the number N_c of electrons in the conduction band at any temperature T. Various different assumptions can be made which lead to different expressions for N_c; the emission current will therefore be expressed in terms of a general value of N_c and the particular cases considered later.

If the number of excess barium atoms is small compared with the total number, Wilson[8] has shown that the electrons in the conduction band have a Maxwellian distribution of velocity. Therefore the number of electrons with velocities in the range

U to U+dU, V to V+dV and W to W+dW where U V and W are in mutually perpendicular directions, is

$$N = N_c \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} exp\left[-\frac{m}{2kT}\left(U^2+V^2+W^2\right)\right] dU dV dW. \qquad (1)$$

where k is Boltzmann's constant; in order that the results of wave mechanics will apply m should be considered to be the effective mass of the electron.

When evaluating the emission current across a boundary between the oxide and the vacuum it is usual to assume that a potential barrier exists at the surface and only those electrons with sufficient energy to cross the barrier are emitted. The nature of the potential barrier will be dealt with more fully in the chapter on metal semiconductor contacts. In the following derivation of the saturation emission current it will be assumed that the electrons in the conduction band possess only kinetic energy. It will also be assumed that only those electrons with sufficient kinetic energy to surmount the potential barrier will be emitted.

Taking the direction of U normal to the surface, the number of electrons with velocity components in the range U to U+dU is

$$N_U = N_c \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} exp\left[-\frac{m}{2kT}\left(U^2+V^2+W^2\right)\right] dU dV dW \qquad (2)$$

On integrating

$$N_u = N_c \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{2\pi kT}{m} \exp\left(-\frac{mU^2}{2kT}\right) dU \qquad (3)$$

The number of electrons emitted per unit time is then given by

$$N = N_c\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \int_{U_0}^{\infty} U \exp\left(\frac{-mU^2}{2kT}\right) dU \qquad (4)$$

Where U_0 is the minimum velocity in the U direction with which an electron can escape from the surface. If N_c applies to unit volume, then the saturated emission current density is given by

$$I = eN_c\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \frac{kT}{m} \exp -\frac{mU_0^2}{2kT} \qquad (5)$$

where e is the charge on the electron. Equation 5 may be rewitten as

$$I = N_c\, e\left(\frac{k}{2\pi m}\right)^{\frac{1}{2}} T^{\frac{1}{2}} \exp -\frac{E_p - E_c}{kT} \qquad (6)$$

where $E_p - E_c = \frac{1}{2} m U_0^2$ and represents the minimum energy necessary for an electron to escape. Since there is a finite probability that an electron with a velocity normal to the surface greater than U_0 may not escape, equation (6) is usually modified and rewritten as

$$I = N_c(1-R)e\left(\frac{k}{2\pi m}\right)^{\frac{1}{2}} T^{\frac{1}{2}} \exp -\frac{E_p - E_c}{kT} \qquad (7)$$

where R is the mean coefficient of reflection of the electrons by the barrier.

Equation (7) is the basic emission equation, and when values of N_c are calculated for particular cases and substituted in this equation, the emission equation for the particular case will be obtained.

Chapter 7 Development of the Wilson model

7.1 The case of the single impurity level

Suppose that there are N_o states which an electron may occupy in the interference level arising from the excess barium. Further, let all these states have the same energy and let all the states be occupied at the absolute zero.

If we ignore the possibility of an electron from the full 2p band reaching the empty 6s conduction band, then the sum of the number of electrons in the conduction band and those in the single interference level, will be constant and equal to N_o,

$$\text{therefore} \quad N_i + N_c = N_o \tag{8}$$

where N_i is the number of electrons in the interference level at some temperature T.

Applying Fermi statistics, the number of electrons in the interference level is given by

$$N_i = \frac{N_o}{\exp\left(\frac{E_i - E_o}{kT}\right) + 1} \tag{9}$$

where E_i is the energy of the interference level and E_o is a constant. Also the number of electrons in the conduction band is given by

$$N_c = \int_{E_c}^{\infty} \frac{C}{\exp\left(\frac{E - E_o}{kT}\right) + 1} \, dE \tag{10}$$

where C is the number of cells available to the electrons in the energy range E to E+dE. If we assume the energy of the electrons to be purely kinetic and take into account the two possibilities of electron spin, the expression for C may be written as

$$C = \frac{4\pi}{h^3}\left(2m\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \tag{11}$$

where h is Planck's constant. Then

$$N_c = \frac{4\pi}{h^3}\left(2m\right)^{\frac{3}{2}}\int_{E_c}^{\infty}\frac{E^{\frac{1}{2}}dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} \tag{12}$$

where the conduction band is assumed to extend from energy E_c to ∞

Combining equations (8), (9) and (12) we obtain

$$\frac{N_0}{\exp\left(\frac{E_i-E_0}{kT}\right)+1} + \frac{4\pi}{h^3}\left(2m\right)^{\frac{3}{2}}\int_{E_c}^{\infty}\frac{E^{\frac{1}{2}}dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} = N_0 \tag{13}$$

from which a value of E_0 may be found. An exact value cannot be calculated but by making simplifying assumptions an approximate value may be obtained. If it is assumed that $\exp\left(\frac{E-E_0}{kT}\right)$ is large compared with 1, the integral can be evaluated; changing the variable to E' where $E = E' + E_c$, we have from (12)

$$N_c = \frac{4\pi}{h^3}\left(2m\right)^{\frac{3}{2}}\int_{0}^{\infty}\frac{E'^{\frac{1}{2}}dE'}{\exp\left[\frac{E'-(E_0-E_c)}{kT}\right]} \tag{14}$$

On integrating (14)

$$N_c = 2\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}}\exp-\left(\frac{E_c-E_0}{kT}\right) \tag{15}$$

If it is assumed that $\exp\left(\frac{E_0-E_i}{kT}\right)$ is large compared with 1 and the R.H.S. of (15) is taken as the integral of the second term in (13), then the expression resulting for

E_0 is $$E_0 = \frac{E_i + E_c}{2} - \frac{kT}{2}\log\left[\frac{2(2\pi m kT)^{\frac{3}{2}}}{N_0 h^3}\right] \qquad (16)$$

Thus for T = 0 the fermi level lies halfway between the interference level and the bottom of the conduction band. If the value of E_0 is now substituted in (15), a value of N_c is obtained which is expressed in terms of the energy gap $E_c - E_i$ between the interference level and the bottom of the conduction band, and also of the number of states in the interference level.

Thus $$N_c = (2N_0)^{\frac{1}{2}}\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{4}} \exp -\left(\frac{E_c - E_i}{2kT}\right) \qquad (17)$$

Finally on substituting this value of N_c in equation (7), the expression for the emission current density for this model of the semiconductor becomes

$$I = N_0^{\frac{1}{2}}(1-R)\, e\sqrt{2}\left(\frac{2\pi m k^5}{h^6}\right)^{\frac{1}{4}} T^{\frac{5}{4}} \exp\left[-\left(\frac{2E_p - E_c - E_i}{2kT}\right)\right] \qquad (18)$$

i.e.

$$I = A N_0^{\frac{1}{2}} T^{\frac{5}{4}} \exp -\left(\frac{2E_p - E_c - E_i}{2kT}\right) \qquad (19)$$

where A is a constant given by

$$A = \sqrt{2}\left(\frac{2\pi m k^5}{h^6}\right)^{\frac{1}{4}}(1-R)e \qquad (20)$$

A similar equation has been given by Fowler[17] and Schottky[18].

7.2 The case of a narrow band of impurity levels

In the previous case the energy states arising from the excess barium atoms were assumed to lie altogether in one sharply defined energy level. According to Mott and Gurney[19], if the number of excess atoms is sufficiently high, the electrons in the interference levels will interact and instead of a single level, the states will occupy a narrow band of energy levels. It will be assumed that the possible states of the electron lie in a narrow band of levels with energies in the range E_i to $E_i+\Delta E_i$. The calculation of the number of electrons in the conduction band for this model was first carried out by Busch[20].

Let $n_0(E)dE$ be the number of states in the interference levels in the energy range E to $E+dE$. Applying Fermi statistics, the number of electrons having energies in the range E to $E+dE$ is then

$$\frac{n_0(E)\,dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} \tag{21}$$

and on integrating over the energy range E_i to $E_i+\Delta E_i$ the number of electrons in the interference band is given by

$$N_i = \int_{E_i}^{E_i+\Delta E_i} \frac{n_0(E)\,dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} \tag{22}$$

Assuming as before that the states in the interference band are all completely filled at the absolute zero, and that no electrons from the valence band reach the conduction band at temperature T, then corresponding to equation (13), we may write for this case

$$\int_{E_i}^{E_i+\Delta E_i} \frac{n_0(E)\,dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} + \frac{4\pi}{h^3}(2m)^{\frac{3}{2}}\int_{E_c}^{\infty}\frac{E^{\frac{1}{2}}\,dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} = \int_{E_i}^{E_i+\Delta E_i} n_0(E)\,dE \qquad (23)$$

i.e.

$$\int_{E_i}^{E_i+\Delta E_i} \frac{n_0(E)\,dE}{1+\exp\left(\frac{E_0-E}{kT}\right)} = \frac{4\pi}{h^3}(2m)^{\frac{3}{2}}\int_{E_c}^{\infty}\frac{E^{\frac{1}{2}}\,dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} \qquad (24)$$

If it is assumed that the energy states are distributed linearly among the available levels in the band, then for $n_0(E)$ one can write

$$n_0(E) = \frac{N_0}{\Delta E_i} \qquad (25)$$

where, as before, N_0 is the number of states in the interference levels. The L.H.S. of (24) can now be integrated if it is assumed that $\exp\left(\frac{E_0-E}{kT}\right) \gg 1$ over the range of integration. In order to integrate the R.H.S. it is assumed, as before, that $\exp\left(\frac{E-E_0}{kT}\right) \gg 1$

With these assumptions we obtain

$$E_0 = \frac{E_c+E_i}{2} - \frac{kT}{2}\log 2\left(\frac{2\pi mkT}{h^3}\right)^{\frac{3}{2}}\frac{\Delta E_i}{N_0 kT}\left[\exp\left(\frac{\Delta E_i}{kT}\right)-1\right]^{-1} \qquad (26)$$

Using this value of E_0 in the expression for N_c (see equation 15), and substituting in (7) the value of N_c which is obtained, the emission current density for the semiconductor model described in this section is

$$I = (1-R)\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{4}}\left\{\frac{N_0 k T}{2\Delta E_i}\left[\exp\left(\frac{\Delta E_i}{kT}\right)-1\right]\right\}^{\frac{1}{2}} e\left(\frac{k}{2\pi m}\right)^{\frac{1}{2}} T^{\frac{1}{2}} \exp\left[-\left(\frac{2E_p - E_c - E_i}{2kT}\right)\right] \tag{27}$$

Assuming $\exp\frac{\Delta E_i}{kT} \gg 1$ this expression reduces to

$$I = \left(\frac{N_0 k T}{2\Delta E_i}\right)^{\frac{1}{2}} A T^{\frac{5}{4}} \exp\left[-\left(\frac{2E_p - E_c - E_i - \Delta E_i}{2kT}\right)\right] \tag{28}$$

where A has the value given in (20).

7.3 The Nijboer model

Previously it has been assumed that there were vacancies at the oxygen sites only; it may be that there are also some vacancies at barium sites. Provided that there were more oxygen vacancies than barium, there would still result a stoichiometric excess of barium. The additional electrons which the lattice must take up in order to remain electrically neutral will, as before, be associated with the barium ions around the vacant oxygen sites, but since the number of vacant oxygen sites is no longer proportional to the amount of excess barium, there are obviously a greater number of available energy states which the electrons may occupy. It will therefore be assumed that besides the N_0 states in the interference levels due to the excess barium, there are an additional N_a states due to the further possibilities of trapping the electrons. It will also be assumed that the states are in a single interference level with energy E_i.

If N_i signifies the number of electrons in the interference level at temperature T, and N_c the number in the conduction band, then corresponding to equation (8)

$$N_i + N_c = N_0 \tag{29}$$

where N_0 is the number of states arising due to the excess barium atoms and is also the total number of electrons in the interference level and the conduction band, for only this number of states will be occupied at the absolute zero. Applying Fermi statistics to the electrons in the interference level we have, since the total number of states available to the electrons is N_0+N_a

$$N_i = \frac{N_0 + N_a}{\exp\left(\frac{E_i - E_0}{kT}\right) + 1} \tag{30}$$

where as before, E_0 and E_i represent the energy of the Fermi level and interference level respectively.

Equation (15) is still valid for N_c thus from (29) by substitution

$$\frac{N_0 + N_a}{\exp\left(\frac{E_i - E_0}{kT}\right) + 1} + 2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \exp\left[-\left(\frac{E_c - E_0}{kT}\right)\right] = N_0 \tag{31}$$

Equation (31) must be solved in order to obtain the fermi energy E_0. The method to be used here was first given by Watanabe, Takagi and Katsura[21].

Rewriting (31), we have,

$$\frac{N_0 + N_a}{\frac{y}{x} + 1} + Bx = N_0 \tag{32}$$

where
$$B = 2\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}} \tag{33}$$

$$x = exp\left[-\left(\frac{E_c - E_o}{kT}\right)\right] \tag{34}$$

$$\text{and} \quad y = exp\left[\frac{E_i - E_c}{kT}\right] \tag{35}$$

On solving the equation (32) which is quadratic in x we obtain

$$x = \left(\frac{By + N_a}{2B}\right)\left[\left\{1 + \frac{4N_o y B}{(N_a + By)^2}\right\}^{\frac{1}{2}} - 1\right] \tag{36}$$

where we have taken the positive square root.

If now we consider the value of x when $(N_a + By)^2 \ll 4N_o y B$ then

$$x = \left(\frac{N_o y}{B}\right)^{\frac{1}{2}} \tag{37}$$

$$\text{i.e.} \quad exp\left(\frac{E_o - E_c}{kT}\right) = \left(\frac{N_o}{2}\right)^{\frac{1}{2}}\left(\frac{2\pi m k T}{h^2}\right)^{-\frac{3}{4}} exp\left(\frac{E_i - E_c}{2kT}\right) \tag{38}$$

$$\text{hence} \quad E_o = \frac{E_i + E_c}{2} - \frac{kT}{2}\log\frac{2(2\pi m k T)^{\frac{3}{2}}}{h^3 N_o} \tag{39}$$

Equation (39) for E_o is identical to equation (16) and thus the appropriate form of the emission equation is that given by (19). Therefore the assumption that $(N_a + By)^2 \ll 4N_o y B$ must be equivalent to assuming the model of the semiconductor used in section 7.1.

We will now consider the case where $(N_a + By)^2 \gg 4N_o y B$. From (36), taking only the first two terms of the binomial expansion of the square root, we have

$$x = \frac{N_o y}{N_a + By} \tag{40}$$

In addition to the foregoing condition, if we assume $N_a \gg By$ then (40) reduces to

$$x = \frac{N_0 y}{N_a} \tag{41}$$

and on substituting the appropriate values we obtain

$$exp\left[-\left(\frac{E_c - E_0}{kT}\right)\right] = \frac{N_0}{N_a} exp\left[\frac{E_i - E_c}{kT}\right] \tag{42}$$

therefore

$$E_0 = E_i + kT \log \frac{N_0}{N_a} \tag{43}$$

Using this expression for E_0 we obtain for the number of electrons in the conduction band, by means of equation (15)

$$N_c = \frac{N_0}{N_a} 2\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} exp\left[-\left(\frac{E_c - E_i}{kT}\right)\right] \tag{44}$$

The emission current density corresponding to this value of N_c is then

$$I = \frac{N_0}{N_a}(1-R)e\left(\frac{4\pi m k^2}{h^3}\right)T^2 exp\left[-\left(\frac{E_p - E_i}{kT}\right)\right] \tag{45}$$

The expression for N_c was first derived by Nijboer[22] using an argument based on thermodynamics.

According to the law stipulated by Schottky[18], there will be at any temperature, an equilibrium between the number of defects caused by vacancies at lattice sites and those caused by interstitial atoms. It would therefore be expected that the number of states N_a which were assumed to be present in the semiconductor, would in fact be dependent on the temperature. However, Nijboer takes N_a as a constant below a certain temperature. He assumes that at the temperatures at which the cathode would normally be activated, the equilibrium condition favours the formation of vacancies. On cooling the cathode to the normal running temperature, one passes through a temperature below which the equilibrium can no longer be maintained because the diffusion of the vacancies becomes impaired at the lower temperatures. The vacancies thus become 'frozen in' and their number remains virtually constant. Hence N_a can be considered a constant.

Returning to equation (40), if we now assume that $N_a \ll By$ we obtain instead of (41)

$$x = \frac{N_0}{B} \qquad (46)$$

On substituting the appropriate values we obtain a value of E_0 such that

$$E_0 = E_c + kT \log \frac{N_0}{2\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}} \qquad (47)$$

Hence the emission current density for this case is given by

$$I = eN_0(1-R)\left(\frac{k}{2\pi m}\right)^{\frac{1}{2}} \exp.\left[-\left(\frac{E_p - E_c}{kT}\right)\right] \qquad (48)$$

7.4 Summary of the semiconductor theory

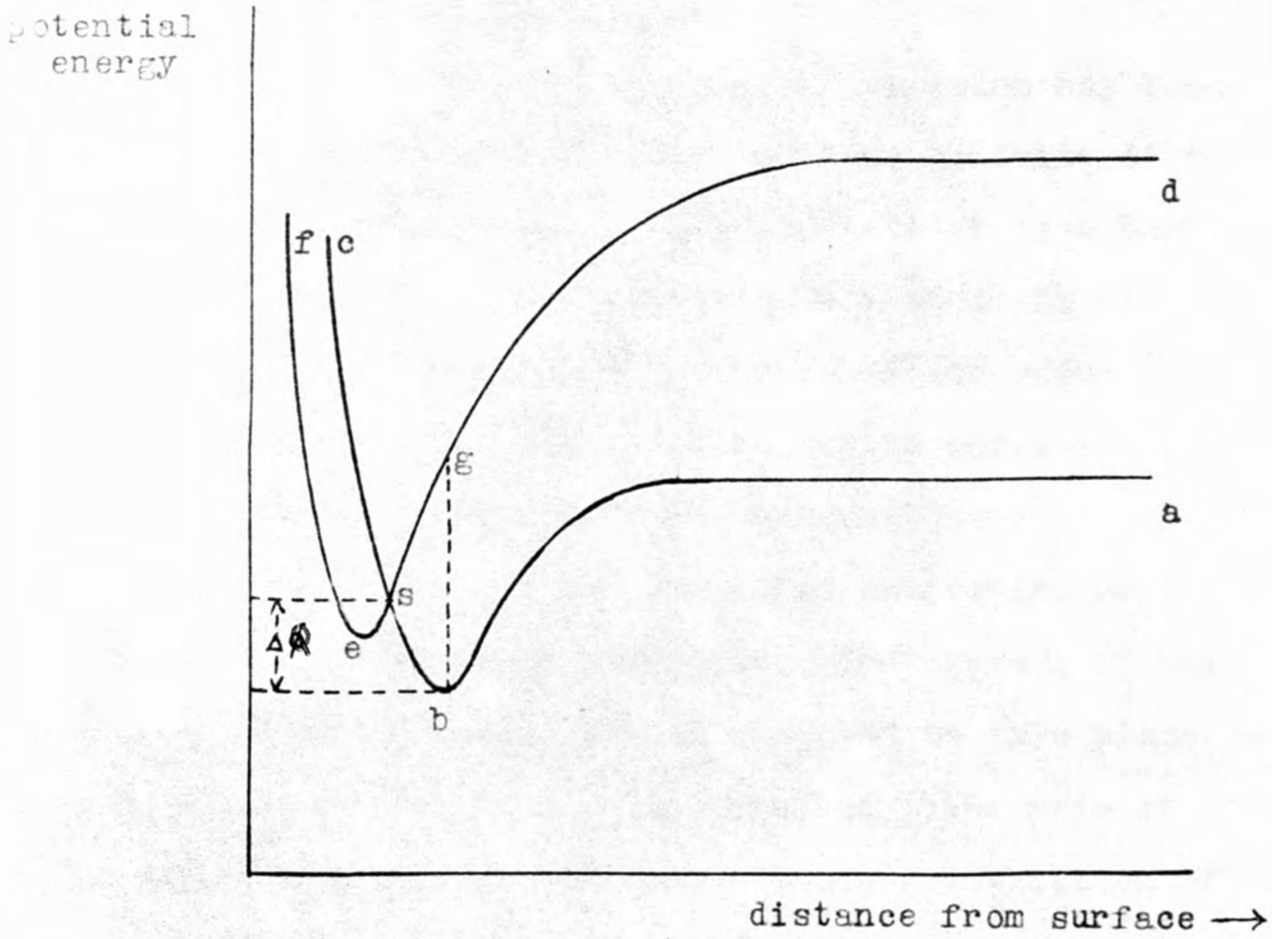
In the previous sections we have derived the emission equation for various models of a semiconductor. Each of the resulting emission equations (19), (28), (45) and (48) can be expressed in terms of a general emission equation of the form

$$I = A_0 T^n \exp -\frac{e\phi}{kT} \qquad (49)$$

where A_0, n and ϕ are constants. This equation resembles the empirical Richardson formula but the work function ϕ in (49) is dependent on the model of the semiconductor which is used.

Since the value of A_0 depends on the value N_0, the number of states in the interference level, then if N_0 were increased, the emission current would increase. The emission equation can therefore account for the rise in emission current with increased activation of the coating. In the particular case of equation (28), the emission equation for the model with a band of interference levels, the work function depends on the width of the band. It has been pointed out by Mott and Gurney[19] that the width of the band will increase with increase of the number of excess barium atoms. Since an increase in the width of the band will lead to a decrease in the work function, an even greater activation effect will be predicted by equation (28).

It would thus appear that the semiconductor model of the oxide cathode can account for the observed variations in the saturated emission current from oxide cathodes arising from changes of temperature and concentration of excess barium.



Curve abc - adsorption of an atom

Curve def - adsorption of an ion

Fig. 6. Potential energy curves for the adsorption of an atom and an ion

Chapter 8 The de Boer theory

A completely different mechanism of emission has been proposed by de Boer[23]. He assumes that the activity of the cathode is due to the presence of a quantity of free barium in the oxide layer. In order to activate a cathode it is necessary to produce this free barium by either reducing some of the barium oxide, causing an electrolytic current to flow, or introducing the barium from some external source. He quotes evidence to support the view that activation may be carried out by any of these processes. The process of emission from the activated cathode is then supposed to take place as the result of two effects working together. The primary cause of the emission is assumed to be the thermal ionisation of adsorbed barium atoms.

In Fig. 6 are shown the potential energy of both a barium atom and a barium ion at different distances from the surface of the oxide. Curve abc represents the potential curve of the atom and def that of the ion. The difference in energy between the curves at a and d corresponds to the ionisation energy of a free non-adsorbed atom. An atom would be considered to be adsorbed on the surface if it were situated at the point b on the curve. If sufficient thermal energy were now imparted to the surface and the atom, so that the atom on account of its thermal vibration could move along the curve to the position s, then there is a certain probability that the atom will transfer to the other curve. In order to do this, the atom must give off an electron and become an ion. The number of atoms which reach the point s will be proportional to $n_0 \exp -\frac{\Delta Q}{kT}$ where ΔQ is the potential difference between b and s, and n_o is the number of atoms absorbed per unit area.

The number of electrons emitted will therefore be

$$n = n_0 A \exp -\frac{\Delta Q}{kT} \qquad (50)$$

where A is a constant.

In order that the emission will not decrease as the number of adsorbed atoms is decreased due to thermal ionisation, there must be a second mechanism by which the adsorbed ions may recapture an electron from within the oxide layer. It is assumed that there exists internally absorbed atoms and that these atoms are continually losing their valence electrons to an adsorbed ion nearby and then regaining an electron from another atom. In this way the electrons may be transported through the oxide coating.

The emission will therefore depend both on the number of adsorbed atoms on the surface, which will depend on the roughness of the surface, and also on the rate at which electrons recombine with the adsorbed ions. The latter effect will be governed by the ease with which the electrons can be transported through the coating. This will in turn depend on the number of internally adsorbed atoms and thus on the state of activation of the cathode.

Chapter 9 The Loosjes and Vink model

Loosjes and Vink[24] have proposed a model of the oxide which has two mechanisms of conduction of electrons through the coating. At low temperatures, i.e. less than 800°K they propose that the conduction takes place through the grains of the coating according to the ideas of the semiconducting model. At higher temperatures the pores between the grains become filled with an electron gas which provides an easy path for conduction of electrons. At temperatures in the range 800°K to 1000°K the two mechanism act in parallel. With this model the experimentally obtained dependence of the conductivity of the coating on the temperature can be accounted for. A plot of $\log\sigma$ against $1/T$ shows three distinct regions. In the range T less than 800°K, the plot is linear and corresponds to the semiconducting model. Between 800°K and 1000°K, the plot is curved and corresponds to the two mechanisms working in parallel. Above 1000°K the plot again becomes linear and corresponds to the two mechanisms in parallel, but the pore conduction mechanism is now influenced by space charge effects which result in the further region of linear relationship.

Experiments to support the theory are reported and full references given.

Part 3

EMISSION MICROSCOPY ON OXIDE COATED CATHODES

Chapter 10 Emission patterns from oxide cathodes

10.1 Review of the literature

The discovery of the oxide cathode in 1903 was important in that it provided a convenient method of obtaining a source of electrons. It was therefore an obvious choice of electron source for those workers interested in the problem of electron microscopes. For this reason, there are a number of accounts of work carried out for the purpose of development of electron lenses, in which there appear electron emission patterns of oxide cathodes. The workers at the Forshungs Institute A.E.G. in Berlin were particularly interested in the development and assessment of these lenses.

One of the first of these reports on the lenses was by Johannson[1]; he developed the immersion objective and gave illustrations of emission patterns from oxide cathodes which were obtained with the lens. Further development of this lens was undertaken by Johannson[2] himself as well as Mahl[3], Mecklenberg[4] and Heidenreich[5]. In all these reports, pictures of oxide cathodes are shown. Knecht[6] used the oxide cathode as an object which he examined with both an electrostatic lens and a magnetic lens.

Using the same region of the specimen, he was unable to distinguish any differences in the pictures obtained with the two types of lens. Bruche[7] and Mecklenberg[4] used oxide cathode specimens in order to determine the resolving power of their microscopes. Fox and Bailey[8] used an electron microscope to measure intensities of emission from different types of oxide.

In all the pictures displayed, various irregularities of the emission were apparent and some of the workers were therefore interested in the reasons for the variations of emission. Bruche and Johannson[9] studied the change of emission patterns of oxide cathodes as the temperature was varied. Bruche[10] using very thinly coated oxide cathodes and cathodes activated by evaporating barium on to their surfaces, observed grain boundaries and patchwork patterns due to the metal core. Richter[11] studied changes in the intensity of the pictures during the life of the object.

Of particular interest to some workers were the variations of intensity in the emission patterns which occured at irregularities in the surface of the cathode. Some workers compared the electron pictures with the pictures of the cathode obtained by optical microscopy. Knecht[6] and others found a correlation between the larger structures on the cathode surface and the emission pattern. The correlation was only clearly observable for the major structures and did not account for the detail observed in the emission pattern from an oxide cathode. This pattern consists of a large number of brightly emitting regions separated by non-emitting regions. The reasons for the appearance of these emission centres, i.e. the brightly emitting regions, were investigated by Heinze and Wagener[12].

10.2 Emission centres on oxide cathodes

The possible causes of emission centres can be divided into two main classes. They may be caused either by irregularities in the coating which depend on the structure of the coating, or they may depend on chemical composition of the coating. Heinze and Wagener[12] showed that the formation of emission centres was not dependent on either the proportions of BaO, SrO or CaO in the coating or the presence of impurities such as carbon from the binder used in the paste. Furthermore, they showed that the effect of various gases or impurities which may arrive on the cathode surface from the walls of the envelope, could not be responsible for the formation of emission centres.

In the second of the papers on the causes of emission centres Heinze and Wagener[13] dealt with the possible causes due to structure of the cathode. They used an apparatus with which it was possible, by magnetic focusing, to obtain emission pictures from commerical type, cylindrical, indirectly heated oxide cathodes. Without demounting the specimen, it was possible to obtain optical pictures from corresponding parts of the cathode. They concluded that there was no correlation between the surface structures and the emission centres.

On the basis of the simple emission equation

$$I = AT^2 \exp -\frac{e\phi}{kT} \tag{1}$$

they argued that local variations of the work function ϕ would lead to local variations in the emission. They proposed that the main reason for the formation of emission centres was that various crystallites in the coating present surfaces to the microscope which, on account of the random distribution of the crystals in the coating, would have varying crystallographic orientation. If the work function of the surface varied with the crystallographic orientation, then variations in intensity of emission from point to point in the cathode surface would occur and emission centres would thus be explained. They also concluded that the reduction of the work function by electric fields acting on the surface, could be a cause of emission centres. Due to surface structures, variations in field strength at the cathode surface would occur and this could lead to variations in the intensity of emission and the formation of emission centres.

Other investigators, e.g. Benjamin, Huck and Jenkins[14] found a dependence of the distribution of emission centres on the size of the crystallites in the coating. These investigators also proposed that surface structures might produce irregularities in the emission pattern due to the formation of space charge in hollows and also to increased emission because of the effect of fields at the surface.

Although the previous investigations at first sight appear to be decisive in their conclusions for the causes of emission centres, it is the opinion of the author that further experiments could be carried out in order to clarify the reasons why surface structures can cause emission centres, yet according to Heinze and Wagener, the emission centres cannot be correlated with the surface structures. In the following chapters an account will be given of the experimental work carried out in the present investigation into the causes of emission centres.

Part 4

DESIGN OF THE APPARATUS

Chapter 11 The emission microscope

11.1 General specification

When examining oxide coated cathodes it is desirable that all observations should be made on properly activated specimens. In order to successfully operate an oxide cathode a vacuum of at least 5×10^{-6} mm of Hg is necessary. It was therefore of great importance to design the emission microscope so that a vacuum of this quality could be maintained inside the chamber under operating conditions.

Since it was hoped to correlate surface structures with the emission pattern, it was thought desirable to construct the microscope so that any part of the specimen could be selected for examination and if necessary, the whole area of the cathode photographed in sections.

It was also desirable to have control of the magnification of the lens and to be able to vary this whilst examining the specimen.

The system needed to be demountable so that components could be cleaned when necessary and specimens could easily be mounted.

11.2 The microscope lens

There were two types of lens which could have been used, i.e. a magnetic device or an electrostatic device. Observation under the optical microscope had shown that a typical oxide cathode had surface structures that were visible with magnifications of the order of 100. Heidenreich[1] had used an electrostatic lens which was capable of magnifications of that order and had produced some very clear emission pictures with it. The electrostatic lens has an advantage over the magnetic lens in its simplicity of construction and also in its rather less stringent requirements in the type of power supply necessary. It was therefore decided to use the electrostatic lens.

The lens which was used, followed closely the pattern of that used by Heidenreich; his lens was an improved version of the immersion lens first studied by Johannson[2 & 3]. The lens consists of three electrodes, the anode, grid and cathode. The cathode is the plane surface of the specimen which in our case was an oxide cathode. The grid and anode are two discs placed parallel to the cathode surface. They each have a small hole in them and the line through the centre of the holes should be normal to the plane of the discs. Johannson showed that the power of the lens depended critically on the separation of the cathode and grid, and also on the ratio of the voltages applied between the grid and cathode, and the anode and cathode. The lens was therefore designed so that the grid cathode spacing and the voltages on the electrodes could be varied during operation of the microscope. The grid and anode were made as one unit which could be moved in a direction normal to the plane of the specimen. Fig. 7 is a diagram of the grid anode section of the lens. The anode can be screwed along the axis of the lens so that the separation of the anode and the grid can be preset. Adjustments are provided for aligning the hole in the grid with that in the anode. The insulators supporting the grid can withstand voltages up to 25 kV.

The bulk of the anode was made of copper but the actual disc was made of molybdenum. The grid disc was also made of molybdenum. According to Johannson[2] the aberrations of the lens are less severe if a suitably shaped grid disc is used. For this purpose the hole in the grid protrudes towards the cathode and is shaped as shown in Fig. 8. The size of the hole was usually between 1 mm. and 2 mm. being slightly larger than that in the anode.

11.3 Design of the rotary vacuum seals

In order to carry out the adjustment of the cathode to grid spacing and enable one to move the specimen so that all parts could be examined and still maintain a high vacuum in the microscope chamber, it was necessary to introduce five rotary movements into the vacuum. Since it was desirable that the

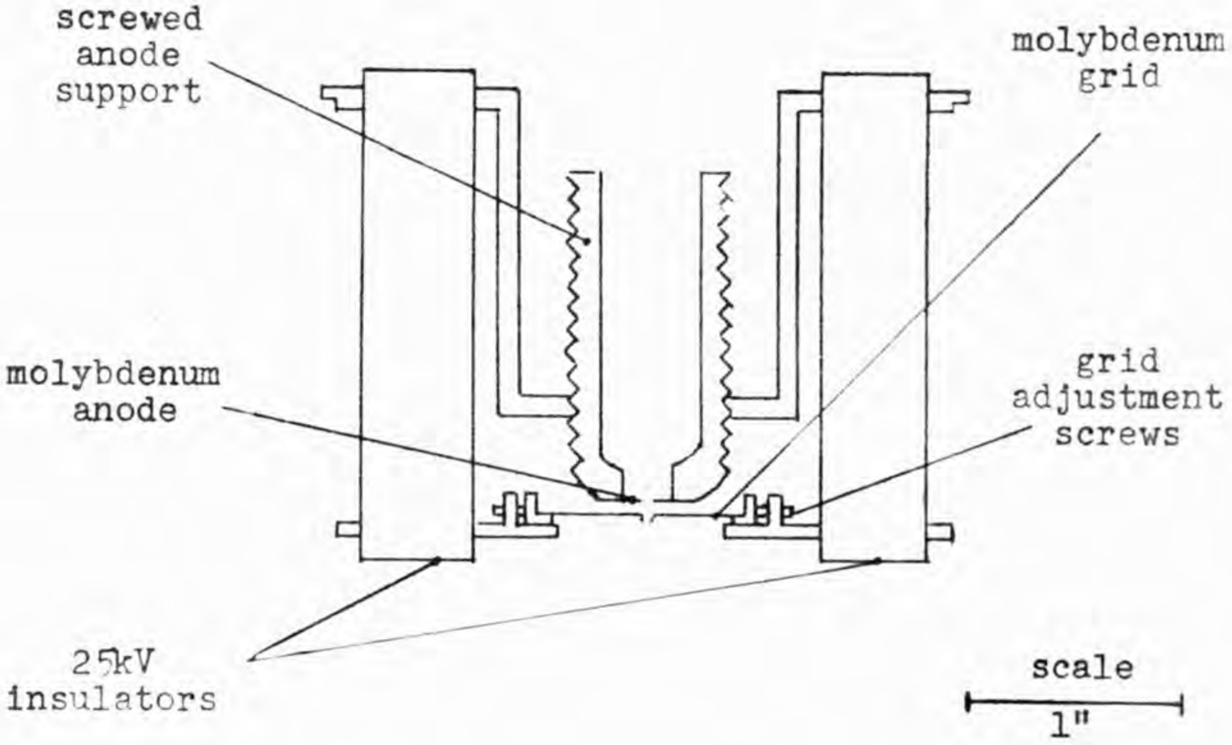


Fig. 7 Grid and anode section of the electrostatic lens

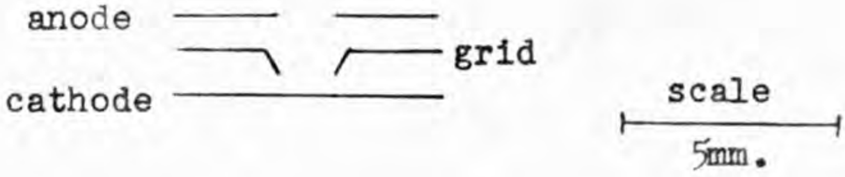


Fig. 8 The electrode system

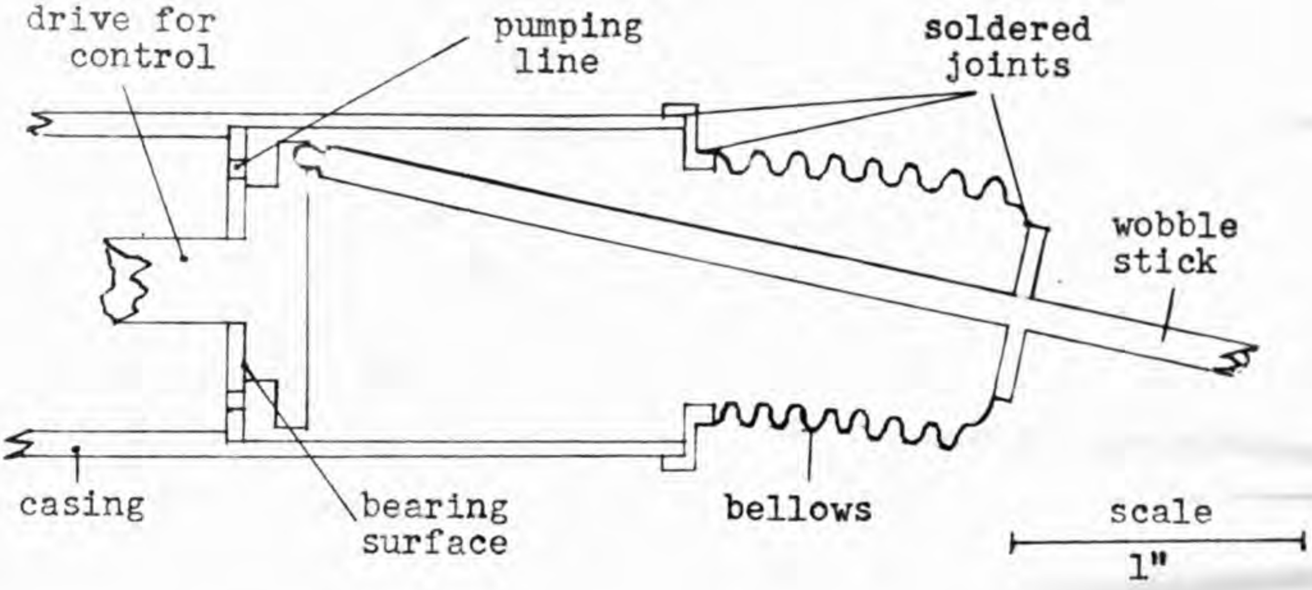


Fig. 9 Rotary vacuum seal for goniometer controls

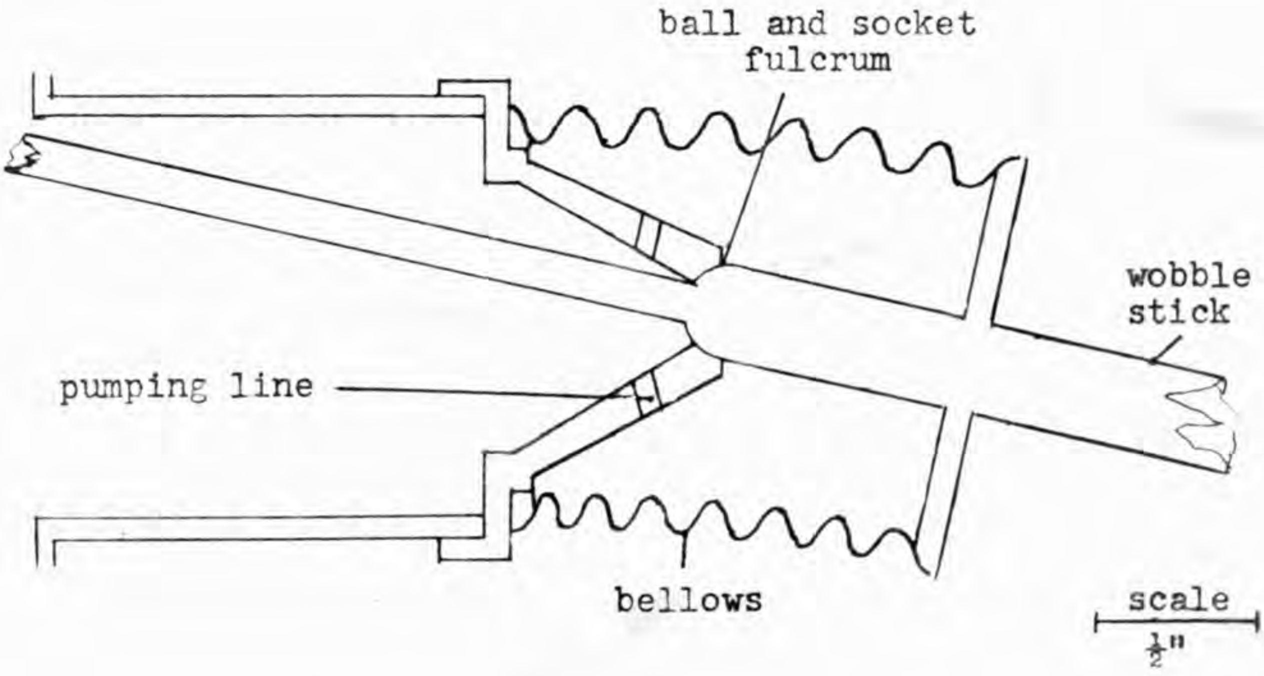


Fig. 10 Vacuum seal for drive for lens raising mechanism

chamber could be baked to help in reaching the high vacuum conditions, the normal Wilson seal was not satisfactory. A seal using bellows was designed. Fig. 9 is a diagram of one such seal. By describing a circle with the free end of the lever which passes through the centre of the bellows a rotary motion can be imparted to the shaft inside the vacuum. The compressed side of the bellow acts as the fulcrum for the lever so that as the lever is moved, the fulcrum moves round the perimeter of the bellows The adjustment of the length of the lever inside the vacuum is critical and the seal works most easily if this length is adjusted so that when the chamber is evacuated, the compressed side of the bellows is just at its maximum compression. For the four controls governing the position and orientation of the specimen relative to the grid, seals made with phosphor bronze bellows to the above design were found to be completely satisfactory. They could be heated to 150°C. It is also to be noted that they have the further advantage over the Wilson seal that there is no break in the wall between the vacuum and the atmosphere.

The lens raising and lowering mechanism could not be successfully operated through a seal of the type described above. This mechanism required a much greater torque to move it, and resulted in too great a strain on the bellows and consequent rupture of the walls of the bellow. This difficulty was

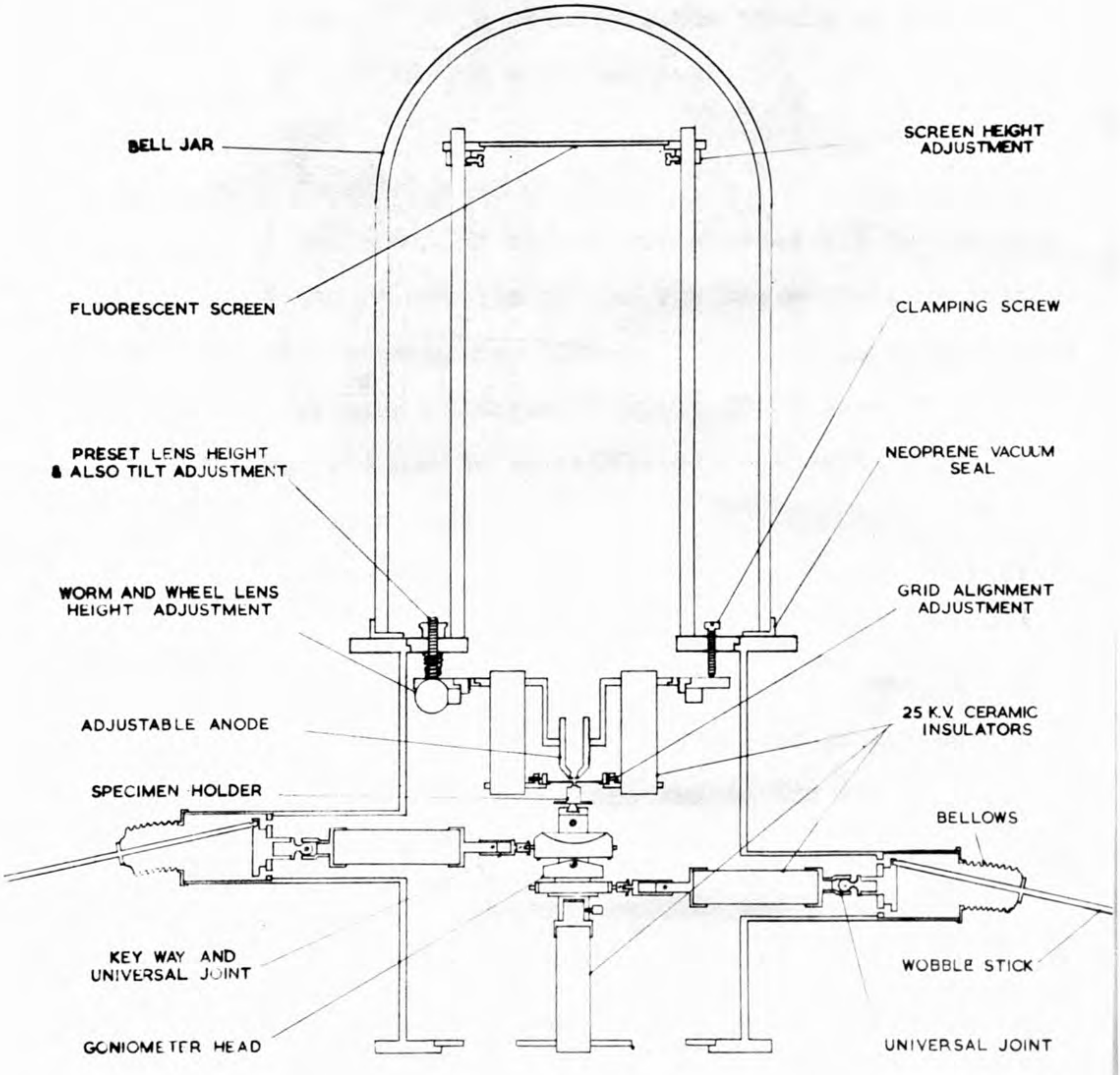


Fig. 11 Diagram of the emission microscope

overcome by using a much larger stainless steel bellow and designing a proper fulcrum for the lever so that the walls of the bellow no longer had to withstand the strain of the motion. Fig. 10 is a diagram of the modified seal.

11.4 The microscope chamber

The basic shape of the microscope chamber was determined by the size of the components of the various mechanisms inside the chamber. For convenience, the anode was at earth potential and since accelerating voltages of about 20 kV were to be used, the cathode and grid had to be insulated from earth for voltages of this magnitude.

Fig. 11 is a diagram of the complete microscope chamber. As can be seen, the specimen is mounted on a goniometer head which requires the four rotary motions for adjustment of the cathode. In order to give freedom of movement to the head, the control screws on the head are connected to the rotary seals by extendable connections. Each connection incorporates two universal joints, a sliding keyed section and a ceramic insulator. The connections are also designed so that they can easily be removed for cleaning. Since the goniometer head is mounted on a ceramic insulator the whole head is insulated from the earthed body of the chamber for voltages of 25 kV.

The mechanism for raising and lowering the grid section of the lens was a conventional worm and pinion device. The pinion was screwed to a section which was in turn attached to the ring supporting the lens section. Rotation of the worm caused the lens to be moved vertically without rotation of the lens section. The whole mechanism was supported on three screws suspended from an annular ring section which was a push fit in the top of the metal section of the casing. The coarse adjustment of the grid to cathode spacing and the alignment of the axis of the lens with the geometrical axis of the cylindrical chamber walls can be carried out by presetting the three screws. A further set of three screws enabled the mechanism to be held firmly in position. To set up the mechanism after mounting a specimen, it was only necessary to engage the lever of the bellow seal in a slot in the disc attached to the worm and then to press the whole mechanism into place. The lens section was then lowered into position. The fluorescent screen was then stood in position above the lens and the system closed with a glass bell jar.

The pressure in the system was measured with a standard Edwards IG 2HT ionisation gauge and control unit. The gauge was fitted with a $\frac{1}{2}$" diameter glass to metal seal and the metal portion was soldered into a flange in the side of the chamber at the level of the specimen.

The electrical supplies for the microscope were led into the chamber through two ceramic insulators soldered into the

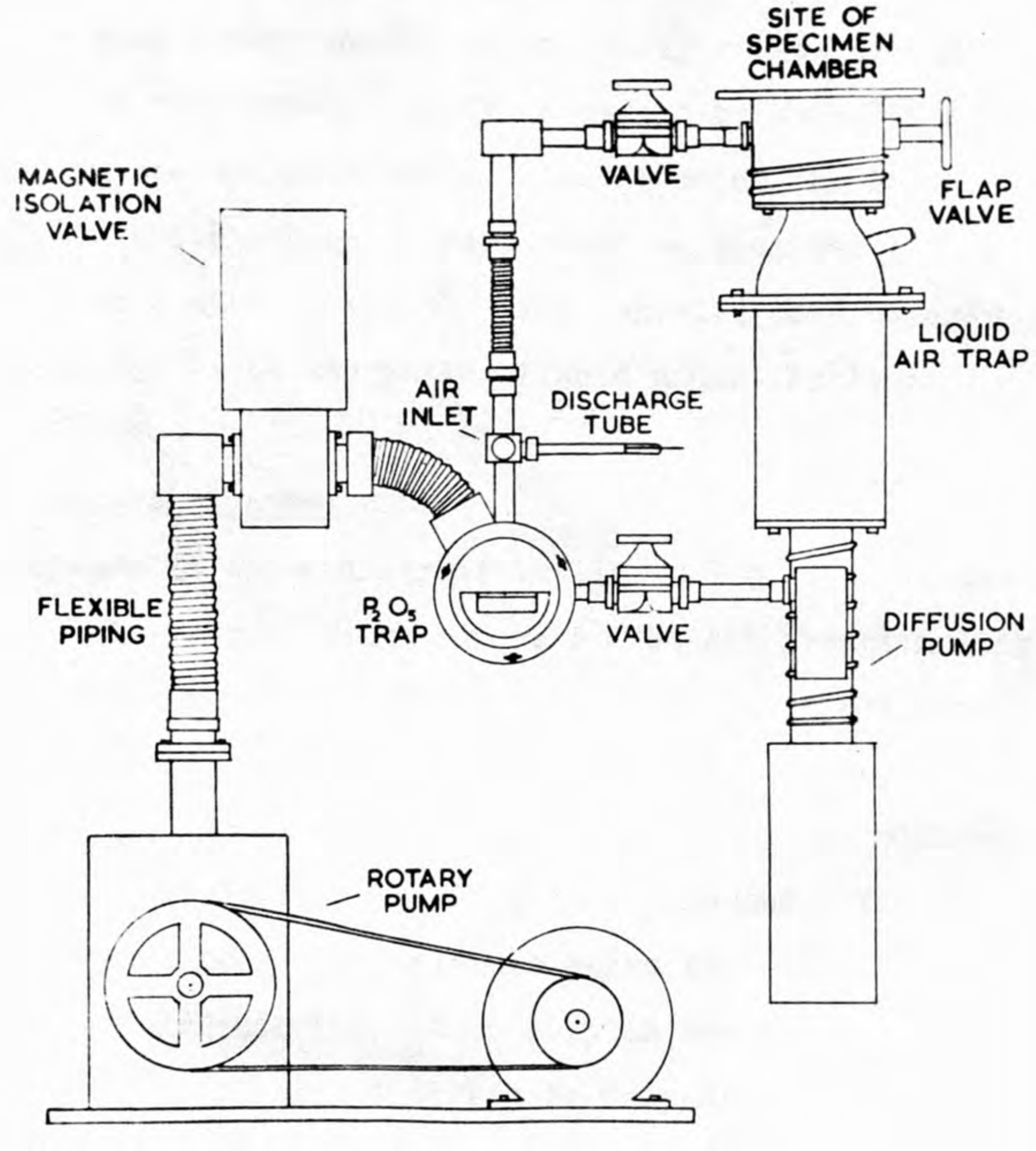


FIG. 12 DIAGRAM OF VACUUM SYSTEM

side of the chamber.

The metal section of the chamber could be heated to 150°C, this proved very useful in the early stages of pumping. The cathode to grid spacing could be varied by up to 2 mm. while under vacuum; the specimen could be moved under the lens and the normal to the specimen surface could be inclined to the vertical up to a maximum of 15°. This enabled particularly uneven specimens to be correctly aligned under the lens.

11.5 The pumping system

The system is shown diagramatically in Fig. 12. It was a fully valved system with an Edward's F203 oil fractionating pump backed by a two stage 2S 50 rotary pump. The ultimate pressure which could be obtained with this system was, according to the manufacturers, 5×10^{-7}mm of Hg, providing that the finest grade Apiezon "C" pump oil isused. The system was fitted with a magnetic isolation valve to isolate the system and let air into the rotary pump in the event of an electrical power failure. A device to prevent the apparatus restarting after such a failure was also fitted. The liquid air trap was found to be useful when the apparatus was first assembled for it acted as a condensation pump. However, after many weeks of use it was found that the ultimate pressure was the same with or without the trap, but when it was used without the trap for about a month, the apparatus became contaminated

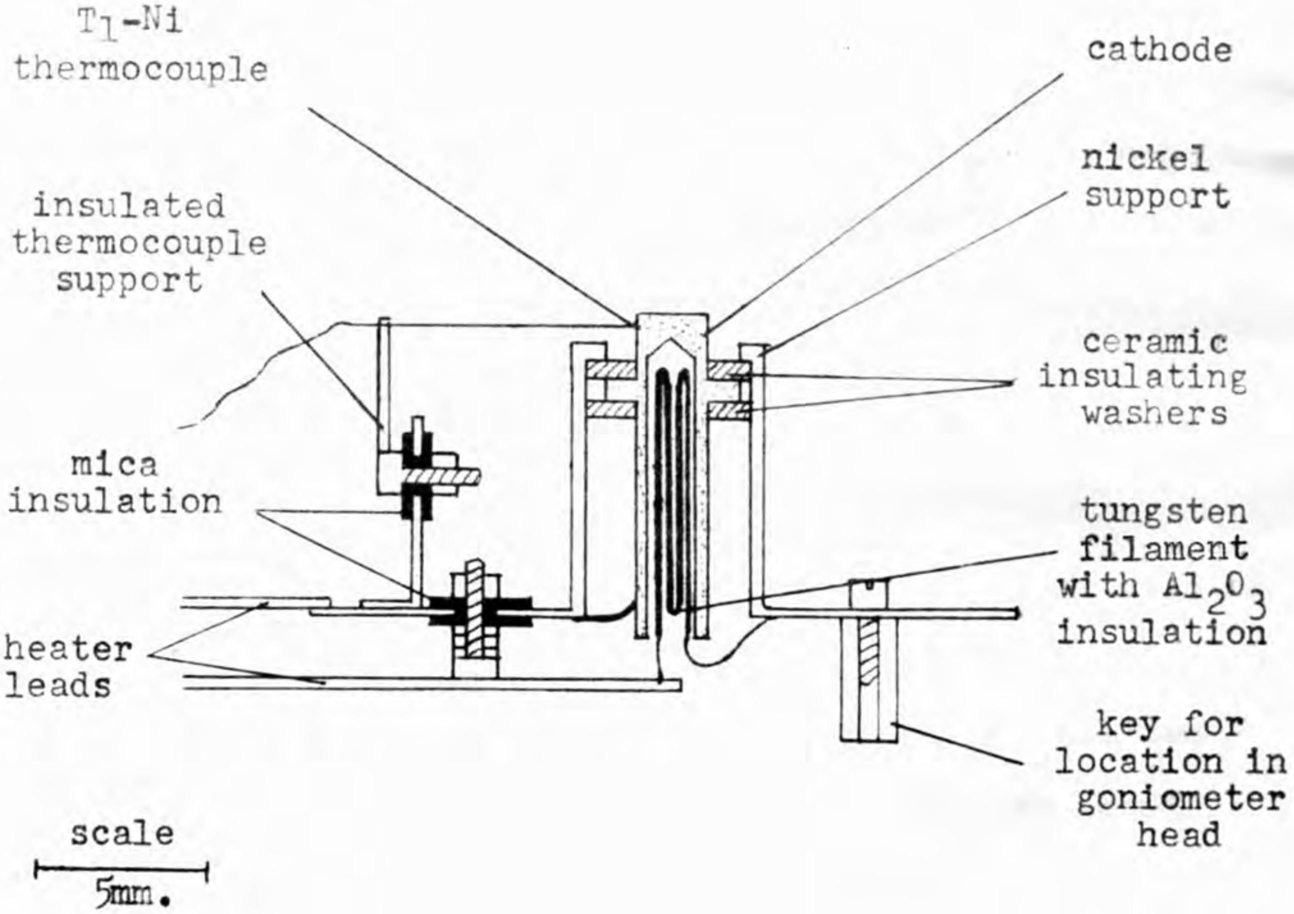


Fig. 13 The specimen holder

with an oil film which caused poor emission from the cathodes although the ultimate pressure was unaffected. The loss of emission was rectified as soon as the apparatus was cleaned with ether and degassed again. The liquid air trap must therefore be considered as essential if well activated cathodes are to be obtained consistently over long periods.

With the microscope being pumped but not in use, pressures in the range 8 x 10^{-7}mm to 2 x 10^{-6}mm of Hg are usually recorded on the gauge and when the microscope is fully operational the pressure rises slightly but remains below 3 x 10^{-6}mm of Hg.

11.6 The design of the specimen holder

The goniometer head imposed a restriction on the size of the specimen holder. It was desirable that the surface of the specimen should contain the centre of curvature of the two rotary movements on the head. If this were so, the surface could be correctly orientated under the lens without inducing a lateral movement. Since the centre of curvature was 12 mm in front of the top of the head, the specimen had to be mounted with its surface in the plane 12 mm from the head and parallel to the grid.

The specimen also had to be heated to 1100°C and facility for measuring the cathode temperature was needed.

A number of specimen holders were tried but the most suitable form was constructed as shown in Fig. 13. The main support was a nickel holder shaped like a top hat. A hole was bored in the crown and the tip of the cathode protrudes. The cathode was supported in the holder by two washers, which were turned from 'Alsil'. This is a special form of soapstone which can be machined easily but on firing at temperatures up to 1200°C becomes hard and possesses good thermal and electrical insulating properties and is suitable for use in high vacuum. These washers insulate the cathode from the holder. The cathode is indirectly heated by a tungsten filament insulated from the cathode by a coating of alumina. The nickel holder also acts as a radiation shield. The holder is fitted to the goniometer head by sliding the small key into the groove in the head. The key had to be kept to as small a size as possible to minimise heat conduction to the head. Pieces of mica were also laid in the groove to decrease heat conduction. The specimen could be heated to 1150°C with a voltage of 15 volts applied to the filament.

The temperature of the cathode was measured with a thermocouple; the usual method of pyrometer measurements could not conveniently be used since the cathode could not be seen from outside the chamber. In order to minimise the number of connections a thermocouple was formed between a T_1 alloy of nickel and chromium and the metal of the core of the cathode. The T_1 wire was spot welded to the core just below the level of the oxide coating. A preliminary experiment with a cathode having a standard T_1-T_2 thermocouple spot welded to its surface, enabled the T_1- core metal thermocouple to be compared with the standard one. The core was also connected electrically to the support and one side of the heater. The other heater connection was rigidly supported on the main nickel support but electrically insulated from it with mica washers. A similar arrangement was used to support the T_1 thermocouple wire. The T_1 wire, the heater lead and the lead common to the thermocouple the heater and the specimen were then brought to a glass pinch to form a plug. The heater leads were made strong enough to rigidly support the pinch. All connections were made by spot welding.

11.7 The electrical supplies for the microscope

Johannson showed that only the ratio of the voltages between the electrodes was important in governing the focus of the image. It is therefore convenient to supply the lens from a resistance chain and tap off suitable voltages for each electrode. The output of a simple E.H.T. unit is connected across the ends of the resistance chain. Any fluctuation in the voltage between the ends of the resistance chain will not affect the ratio of the voltages applied to the grid and thus the stabilisation of the E.H.T. is not essential. This is the great

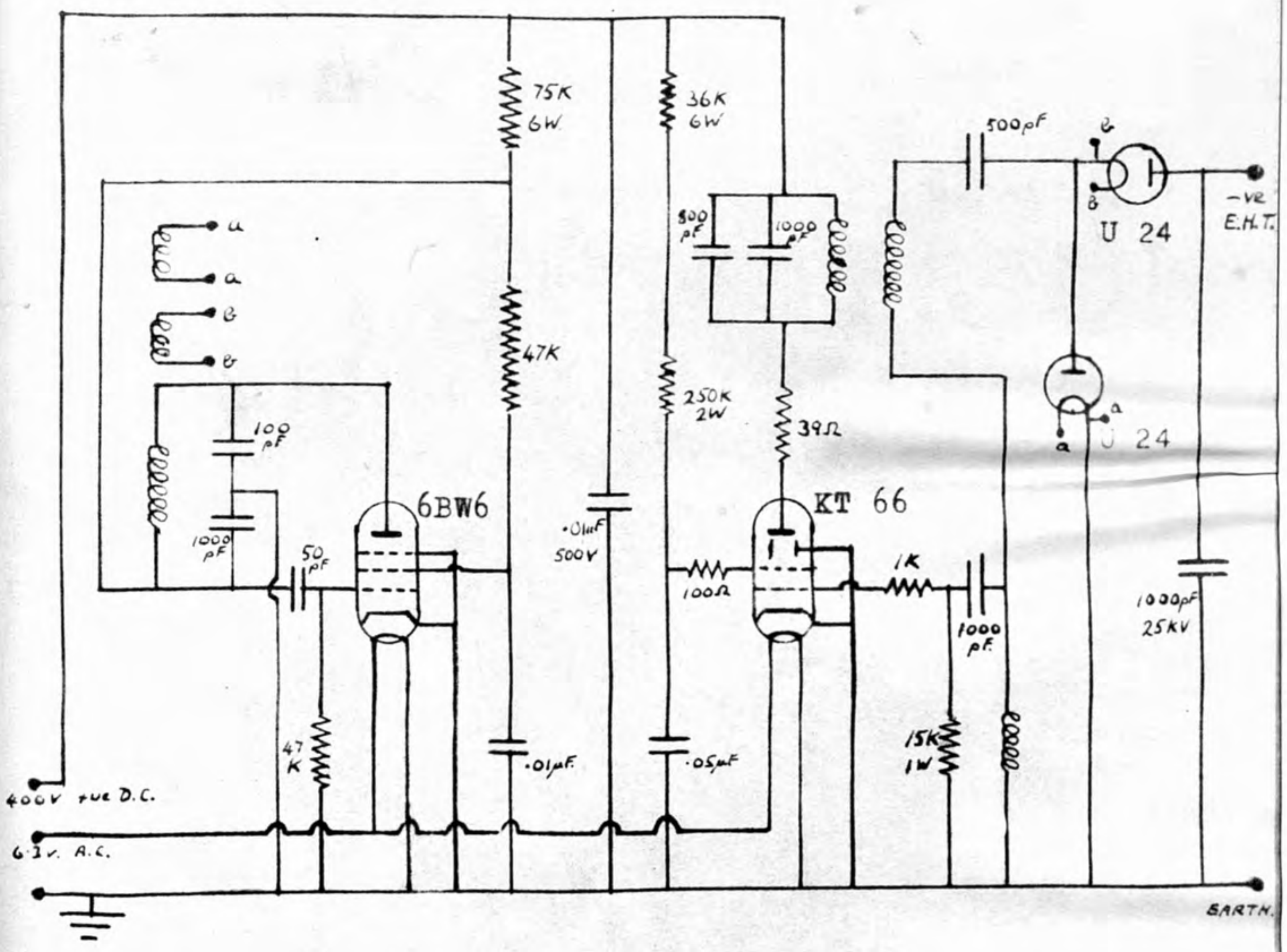


Fig. 14. Circuit diagram of E.H.T. unit

advantage of the electrostatic lens compared with the magnetic lens.

The E.H.T. unit was a simple radio frequency oscillator with amplifying and voltage doubling circuits. The unit required a 400v d.c. and a 6.3v a.c. supply. These were obtained from a stabilised power unit. The output of the whole unit was 23 kV at 250 microamp. with the positive earthed. The circuit diagram of the unit is shown in Fig. 14.

The resistance chain was made from twenty-five 20 megohm high stability 1 watt resistors connected in series. A switching device was made up into a unit whose resistance could be varied to take any value between 0 and 20 megohm. This unit could be placed at any position in the chain. Voltages could then be applied to the lens so that any ratio of the voltages on the electrodes could be selected.

The power supply for the filament was obtained from a transformer whose secondary was insulated from the primary for voltages of 25 kV. The primary of the transformer was supplied from a mains variac. The filament current and voltage could be read on two meters insulated from earth for 25 kV. The filament could stand a maximum of 16v a.c. at about 0.5amp.

The temperature of the cathode was recorded by connecting the output of the thermocouple to a microameter and series resistance. It was necessary to insulate all this equipment for voltages of 25 kV.

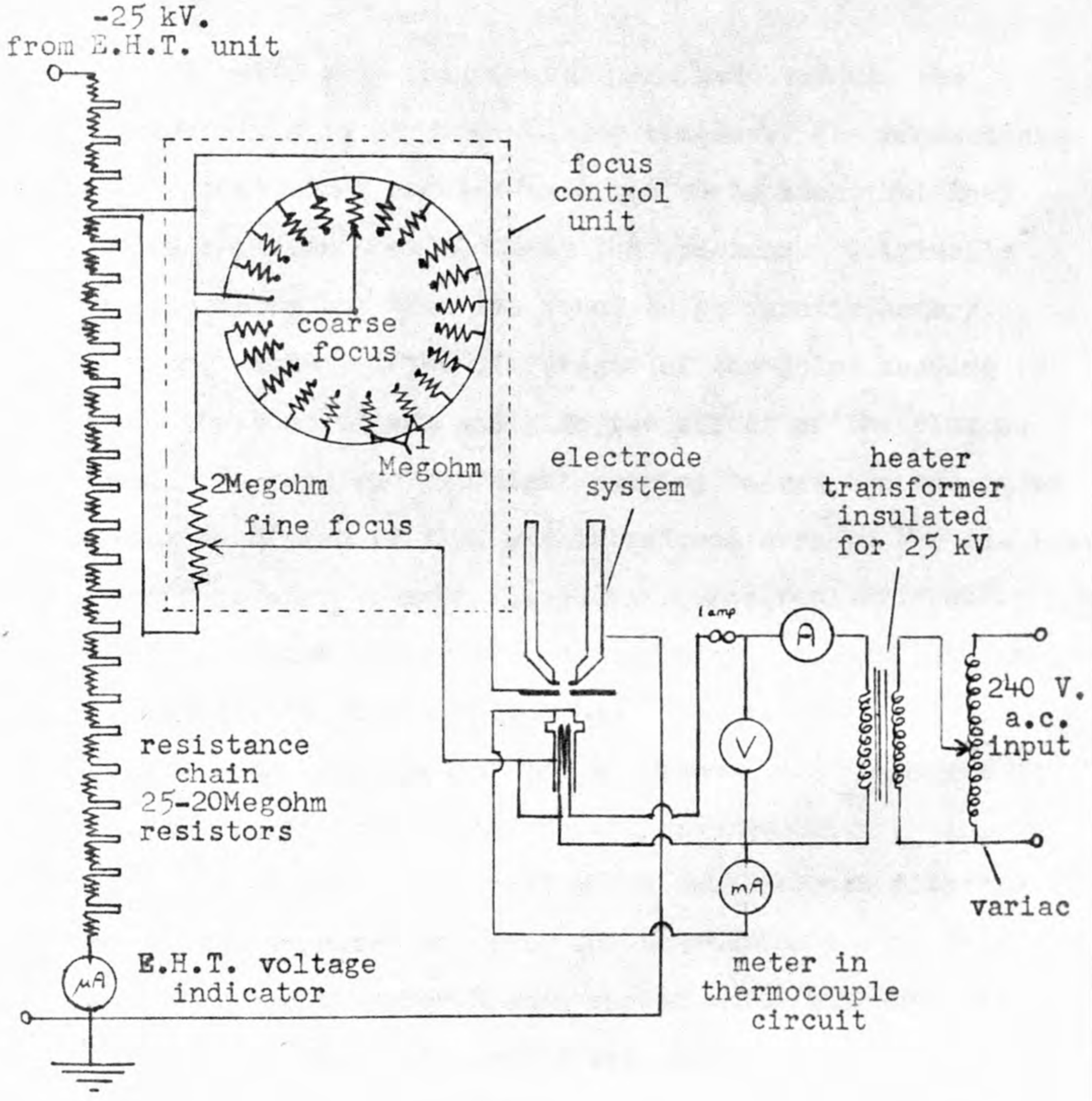


Fig. 15 Electrical circuits for the emission microscope

The circuit diagram of the electrical equipment is shown in Fig. 15.

The connections to the chamber were made through the ceramic insulators in the side of the chamber. The connections to the specimen holder and the grid had to be such that they could be easily made when mounting the specimen. Originally they were soldered but this was found to be unsatisfactory, both from the point of view of fatigue of the joint leading to failure of the connection, and also the effect of the flux on the vacuum. It required all night pumping to get the vacuum to the working condition if flux was introduced even in the smallest quantities necessary to make the joints. The real difficulty was only experienced in the latter stages of the work when it became necessary to mount the specimens in the shortest possible time to avoid contamination of the specimen. To facilitate mounting, the three connections to the specimen were permanently connected to a socket which could thenbe fitted on the plug on the specimen holder. The connection to the grid was made through a phosphor bronze spring which automatically made contact when the lens section was lowered into position. The anode, being always connected to the chamber by its support, was automatically earthed. With these connections the specimen could be mounted and evacuation commenced within three minutes of the start of the operation.

11.8 The photographic equipment

The image was formed on the fluorescent screen which gave a green light suitable for visual observation. Photographs of the image were at first obtained on 0800 Kodak $\frac{1}{4}$ plates using an f:4.5 lens with a focal length of 5". This system was satisfactory for the intense images obtained from conventional oxide cathodes but was not capable of photographing some of the transient phenomena seen at low intensity on thin film cathodes. In order to photograph these a different system was used. This improved system was an f:2 lens with a 1" focal length and the picture was recorded on kodak R55 35 mm roll film. The exposure times were much shorter with this system.

The image on the fluorescent screen was usually obtained at a magnification of x120. which was reduced to x30 on the film negative. Using fine grain developer the smallest detail that one could hope to resolve in the negative would be of the order of 1 micron at the specimen. It is unlikely that the electron lens will itself resolve detail as small as this because it suffers from astigmatism. Vibration and picture flutter reduce the resolving power of the instrument so that the printed emission pictures show detail corresponding to points on the specimen separated by 4 microns.

Plate 1 is a photograph of the complete apparatus.

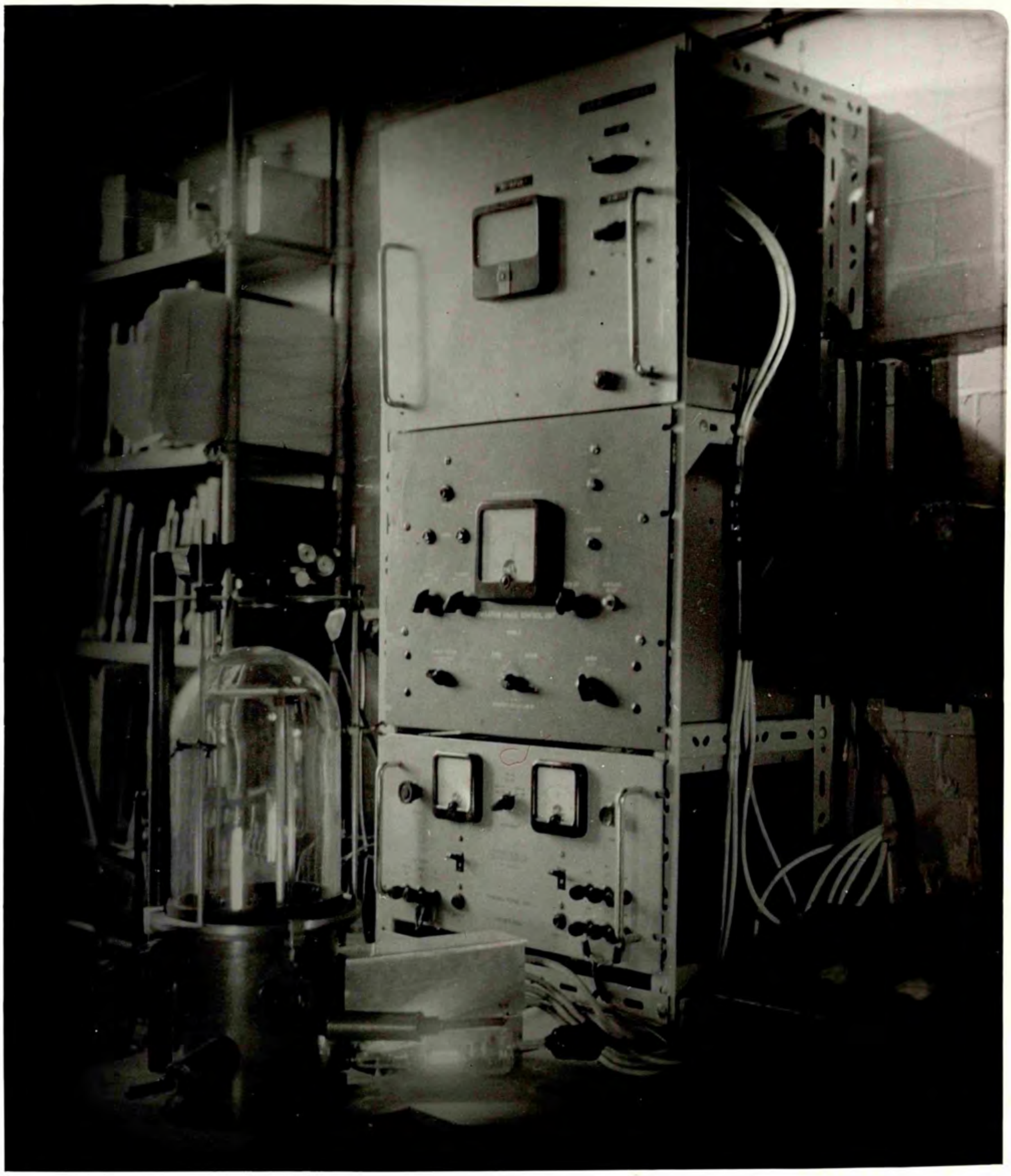


Plate 1 The apparatus

Part 5

COMPARISON OF EMISSION AND OPTICAL PHOTOGRAPHS OF THE SURFACE OF OXIDE CATHODES

Chapter 12 The methods for obtaining emission and optical photographs

12.1 Preparation of the specimen

The specimens were made with cores of 'O' nickel. The cores were machined to shape and then together with the nickel support they were subjected to a cleaning treatment. The most effective method is to heat the metal in an atmosphere of hydrogen at 1100°C. The complete specimen mounting was then assembled and all the necessary electrical connections were made with the spot welder.

The emission paste, which was a triple carbonate mixture with organic binder, was applied by hand as this was the most convenient method of preparing single specimens. A small spot of paste was applied to the cathode core and allowed to dry. Since the cathode surface was too big an area to image all at once with the emission microscope it was necessary to have some means of identifying various portions of the cathode. For this purpose it was found possible to emboss a pattern on the cathode surface. An electron microscope grid gave a convenient pattern.

When one of these grids was laid on the cathode surface and lightly pressed down on to it with a flat piece of glass and then carefully removed it was possible to leave the impression of the grid on the cathode so that the cathode surface was conveniently divided into a number of squares. Fortunately, the centre of the electron microscope grid is distinguished by the fact that each of the four squares lying round the centre of the grid, has the corner nearest the centre of the grid rounded. Thus the centre of the grid made an impression on the cathode which could be identified and used as a reference.

A specimen marked in this way was then mounted in the microscope and processed.

12.2 Processing of the specimen

The microscope chamber was evacuated to a pressure of about 5×10^{-6}mm of Hg. The heater was then turned on and the temperature of the cathode gradually raised. Care in outgassing the specimen was needed in order to prevent the coating from being blown off the core. As the temperature was raised the pressure in the chamber tended to increase due to the release first of all, of water vapour, then possibly to the release of absorbed gases in the specimen holder and most of all due to the decomposition of the carbonates with the subsequent emission of carbon dioxide. The temperature was increased at such a rate that the pressure remained below 10^{-5}mm of Hg. The temperature was increased up to 1100°C and kept there until the pressure fell again to 5×10^{-6}mm. of Hg. This outgassing procedure usually took between five and ten minutes.

Activation of the cathode had already begun due solely to the heating process, but it was found that a further increase in the emission current could be obtained by drawing current from the cathode. A voltage of 100 d.c. was applied between the grid and the cathode and the current observed on a milliammeter. The cathode temperature was usually reduced to about 900°C for this process. The activation of the cathode continued for some time and the pressure had usually fallen to around 2×10^{-6}mm of Hg before the emission current had reached its maximum.

12.3 The emission picture

With the cathode fully activated the drawing of current was discontinued and the apparatus connected in the correct manner to obtain the emission picture. The anode to cathode voltage was selected by tapping the resistance chain at a suitable point. Voltages of about 20 kV were usually used. The separation of the cathode and grid and the voltage applied to the cathode were then adjusted until a focused picture of the required magnification was obtained on the fluorescent screen. With the grid about 500v negative with respect to the cathode, a grid cathode separation of about 2 mm gave a focused picture.

With a magnification of about x100 and type 'new' 100 Athene electron microscope grids as the pattern, one square on the cathode could conveniently be imaged on the screen. The image could then be adjusted to best focus with the grid voltage control unit and if necessary, adjustments to the orientation and position of the specimen could be made to align the particular square to the best advantage. The image was then photographed.

12.4 The optical picture of the cathode

The study of the surface of an oxide cathode under the optical microscope presents a difficult task. The usual techniques of optical microscopy were tried. The picture taken in reflection with normally incident light has insufficient resolution to be of any use. Phase contrast microscopy does not give useful results. A slightly more detailed picture can be obtained by the darkfield illumination method but it still leaves much to be desired. An oblique illumination method gives better contrast but the picture obtained is not a true representation of the cathode surface.

The following method of viewing the cathode provided useful information. The cathode was first heavily silvered, i.e. coated with a layer about 1000A thick, and then viewed in reflection with normally incident light. An analyser behind the objective lens was found to give slightly better contrast.

This appeared to be the best method of obtaining a picture directly from the cathode.

12.5 The replica technique for the optical picture

An alternative to the previous method of obtaining an optical picture of the cathode surface is to make a replica of the cathode and from this negative replica, to make another replica from a transparent substance. This replica can then be observed by transmitted light and a considerably more detailed picture of the surface can be obtained.

Cellulose acetate softened with acetone is a suitable substance with which to make the first of the replicas of the surface. The material can be obtained in sheet form and a small piece stuck on a piece of glass is all that is required. A drop of acetone is used to soften a small area of the sheet and when the surplus acetone has evaporated the softened part of the sheet is carefully laid over the coating on a specimen. The substance sets again within a few minutes and after that the glass with the sheet in which the coating is now embedded can be removed. The coating has now to be stripped from the mould. For this purpose a solution of polyvinyl alcohol in water is made up. A few grams of the powder are added to water and the mixture brought to the boil. A clear solution is formed which can be used, when cool, to strip the cathode coating from the mould and also to make the positive replica. A large drop of the solution is placed over the mould and allowed to dry. When dry it forms a very strong film which can be pulled off bringing with it parts of the coating. More films are laid down and stripped until the mould is completely free from coating and then finally a film is stripped off and used as the replica. This replica is then mounted on a glass slip and used as the specimen for transmission optical microscopy. The pictures obtained from this kind of replica are similar in character to those obtained by the direct examination of the specimen.

The replica can be further exploited. If the replica is now shadowed with silver and a layer of nitrocellulose,dissolved in amyl acetate, is then poured on to the mould so that the silver is sandwiched between the replica and the nitrocellulose, very clear optical pictures can be obtained by transmitted light. This technique shows up the larger surface irregularities very well. However, since a shadowing technique is employed, some of the smaller detail is lost and the method can not be employed when comparisons between surface structures and emission pictures are made.

Chapter 13 Comparison of the two kinds of photographs

13.1 The experimental method

The oxide cathode when processed, gives off large

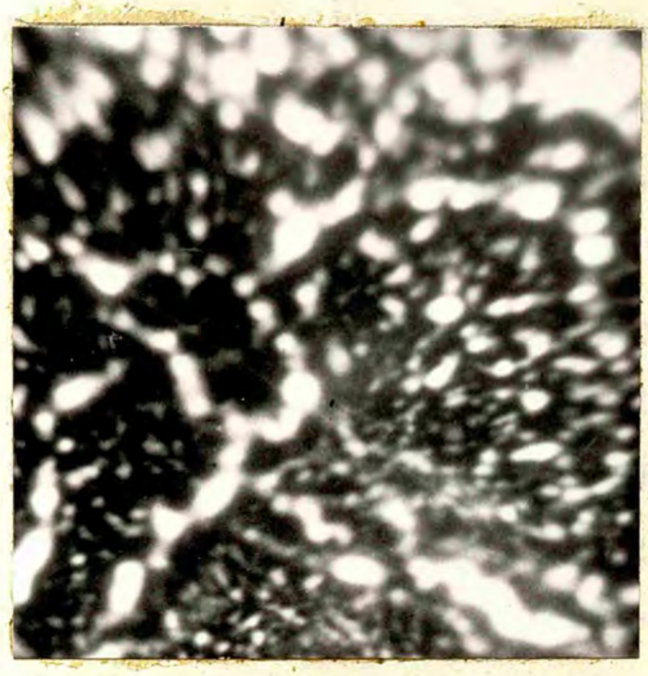


Plate 2 Emission picture
before exposure x400

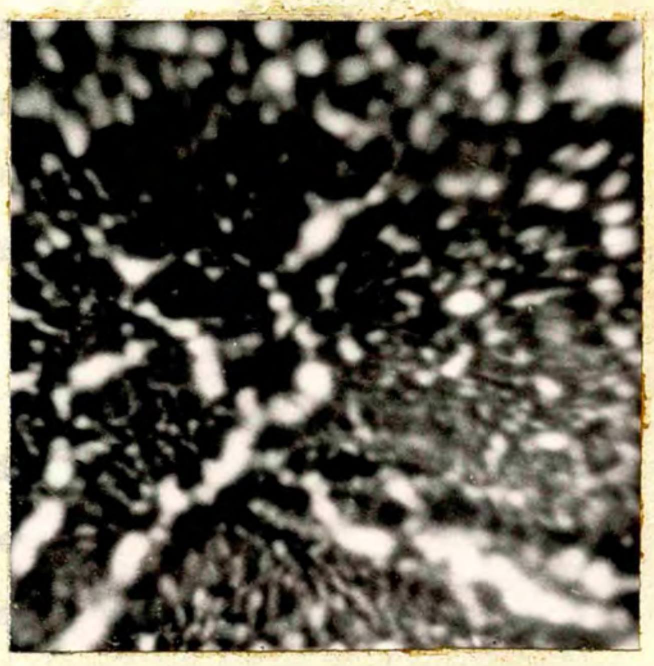


Plate 3 Emission picture
after exposure x400

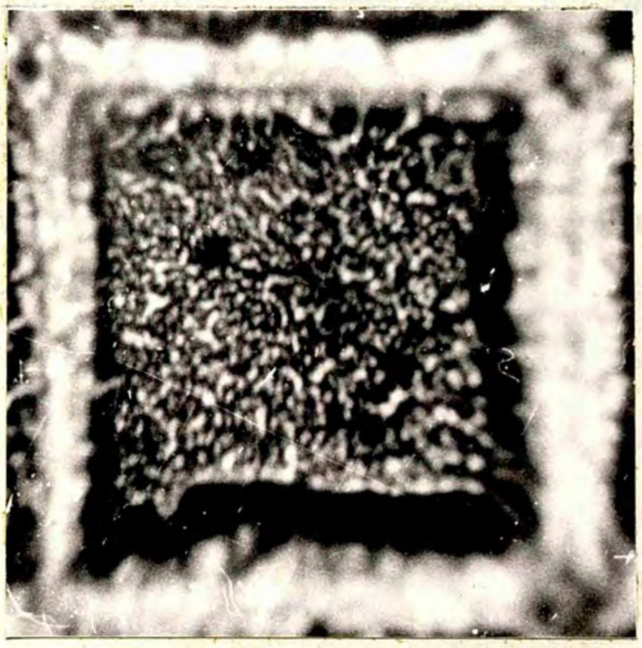


Plate 4 Emission picture
x250

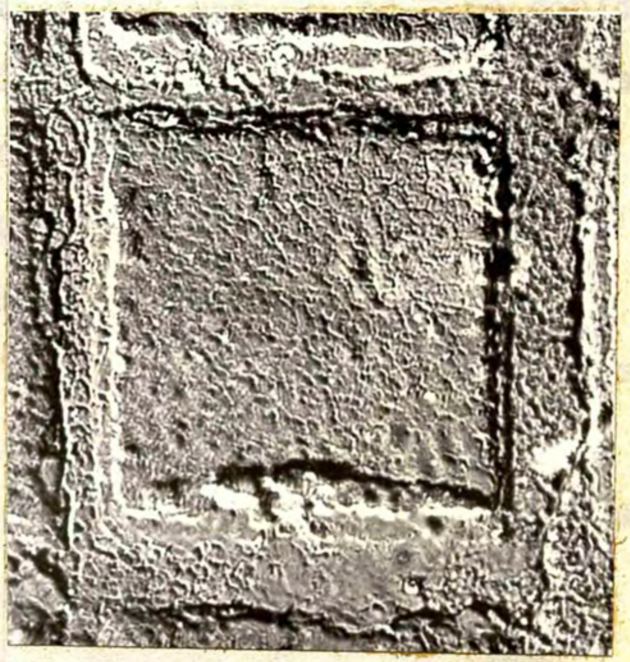


Plate 5 Optical picture from
silvered replica x250

quantities of carbon dioxide and the coating would therefore be expected to have undergone some shrinkage or at least have become more porous. It is therefore unlikely that the surface of the cathode will remain the same during processing. If one wishes to compare the cathode surface with the emission picture one is therefore obliged to obtain the optical picture after processing of the cathode. It is well known, however, that an oxide cathode is susceptible to attack if left exposed to the atmosphere after having been processed, see for example Haas and Jensen[1]. It therefore appears that only an optical picture taken without removing the cathode from the vacuum, would provide a true record of the cathode surface as it existed at the time when the emission pictures were obtained. Heinze and Wagener[2] therefore arranged that the optical picture could be taken with the cathode still in the vacuum. Their pictures were taken at magnifications of the order of x10 so that they would not have experienced much difficulty in arranging the optical system. However, it is impracticable to attempt to obtain detailed optical pictures at magnification of x100 with the specimen still in the vacuum.

A further consideration of the situation shows that it is not necessary to attempt to photograph the cathode in vacuum. Plate 2 is an emission picture of a cathode which has been prepared and processed according to the methods described previously. The cathode gave a sufficiently intense emission picture on the screen when heated to 700°C. After the picture had been taken the cathode was cooled to room temperature and left open to the atmosphere for half an hour. The chamber was then re-evacuated and the cathode again heated. The emission picture was then obtained again. It was found that the temperature of the cathode had to be raised to 800°C to get a picture equally intense as the previous one. Plate 3 is the photograph of the emission picture obtained after exposure of the cathode to the atmosphere. The two pictures are of the same area of the cathode. An examination shows that the larger emission centres seen in plate 3 appear in similar position in plate 2. We can therefore conclude, that although the exposure to the atmosphere affects the magnitude of the emission, the main emission centres of the emission picture taken before exposure to the atmosphere appear at the same places on the cathode after the exposure, for periods of exposure of less than half an hour. This is in agreement with the results of Heinze and Wagener[2]. Therefore for periods of exposure of less than half an hour, the property of the cathode that is responsible for the formation of emission centres is not affected to any extent that would cause any major change in the distribution of emission centres. Therefore if surface structures on the cathode are responsible for the formation of emission centres, then these structures cannot have been affected by the exposure, and thus an optical picture of an exposed cathode should be identical to that of an unexposed cathode. Therefore, if a correlation is found to exist between the emission centres and the optical picture of the exposed cathode, the basic assumption that surface structures are responsible for the formation of emission centres is experimentally confirmed and the method of the experiment is justified.

13.2 Correlation of emission and optical pictures

Using a cathode on which the pattern of a microscope grid had been embossed, it was apparent that the depth of focus of the emission micrsocope lens was such that not all the cathode surface was in focus at the same time. Plate 4 is the emission picture of one square of a cathode. It can be seen that the centre sqaure is in focus, while the border, which corresponds to the part of the cathode depressed by the grid bars, is out of focus. It can therefore be concluded that the depth of focus of the microscope lens is less than the thickness of a microscope grid, i.e. 10^{-2}mm. since that will be the depth by which the border is depressed below the central square. In order to avoid defocused regions in the emission picture it is necessary to prepare cathodes so that no surface structures are present, other than the grid bars, which are greater in height than 10^{-2}mm. The method used for coating the cathodes appears to give a satisfactory surface within the squares. One can see evidence of a different type of imperfection in the emission picture of plate 4. Round the edge of the central focused

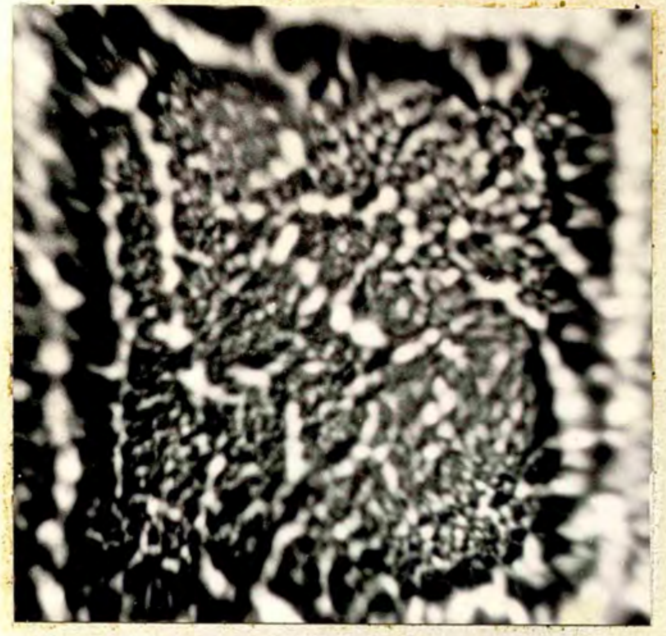


Plate 6 Emission picture

Plate 7 Optical picture of silvered cathode

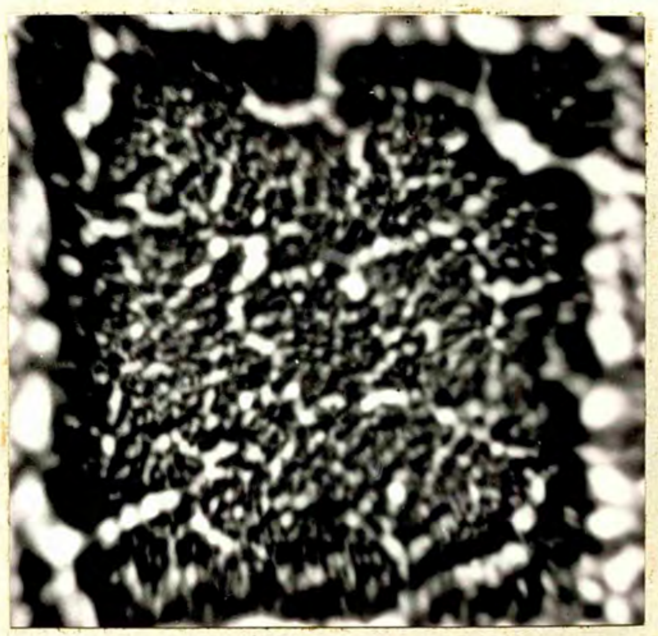


Plate 8 Emission picture

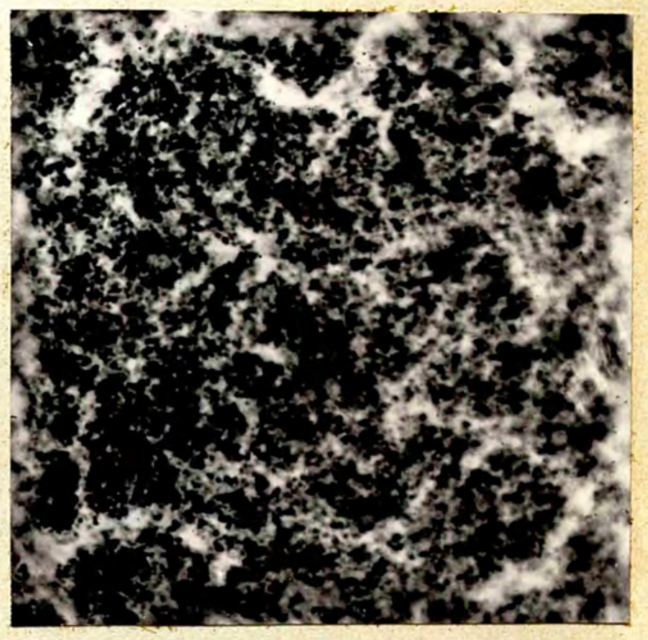


Plate 9 Optical picture of silvered cathode

Magnification of the pictures is x 325

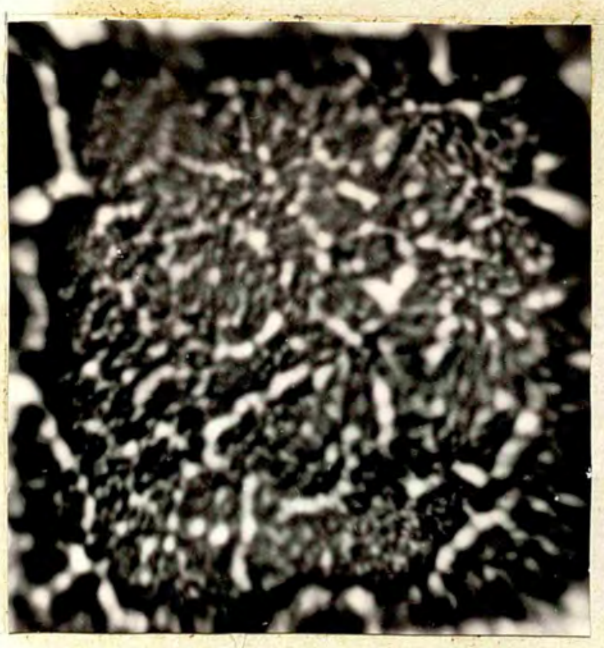


Plate 10 Emission picture

Plate 11 Optical picture of silvered cathode

Plate 12 Emission picture

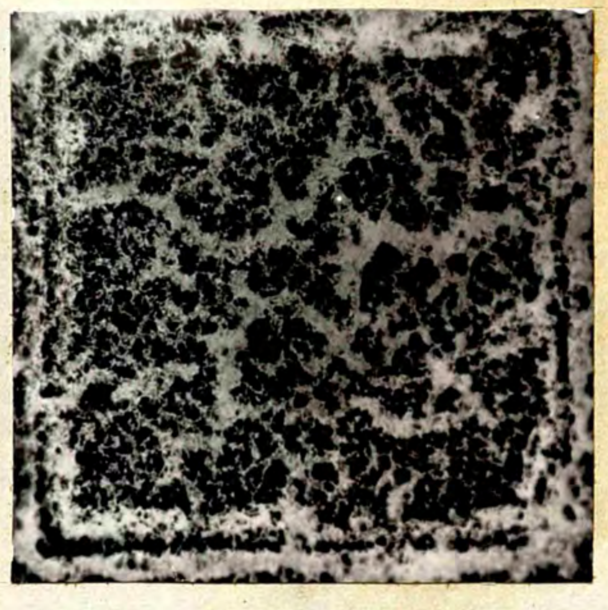


Plate 13 Optical picture of replica of cathode

Magnification of the pictures is x 325

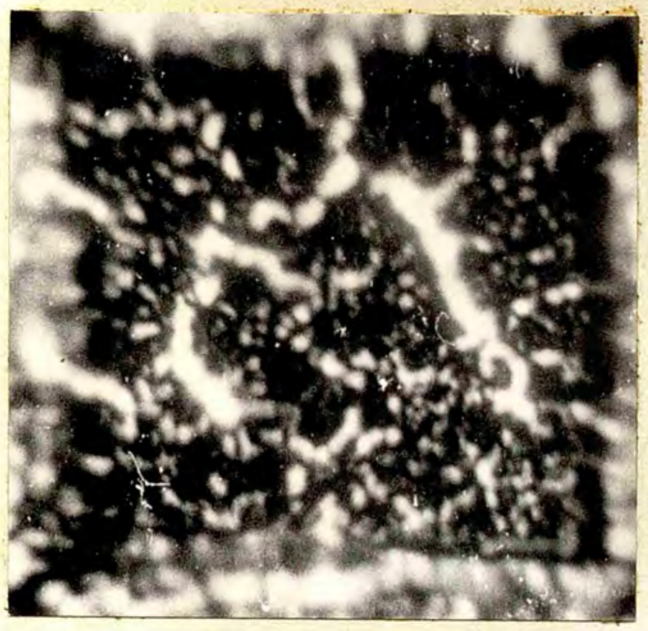


Plate 14 Emission picture

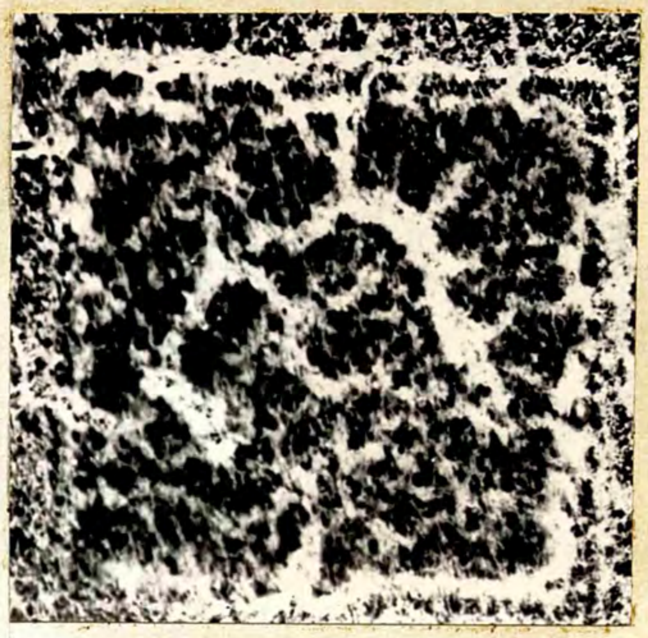


Plate 15 Optical picture of replica of cathode

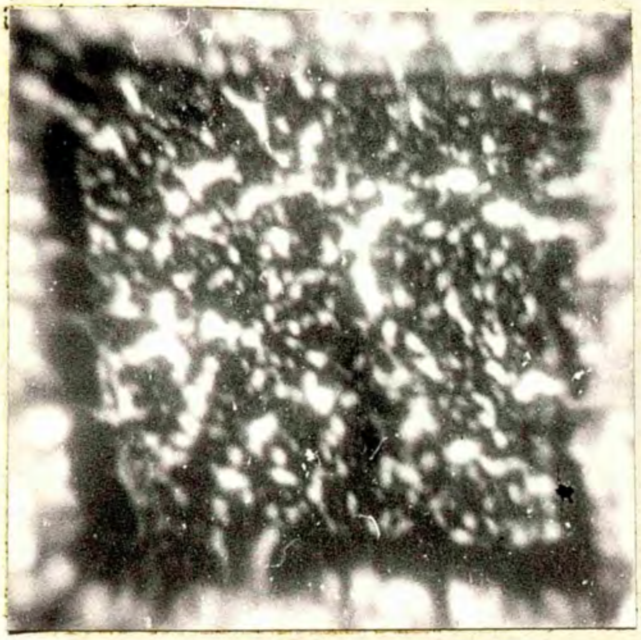


Plate 16 Emission picture

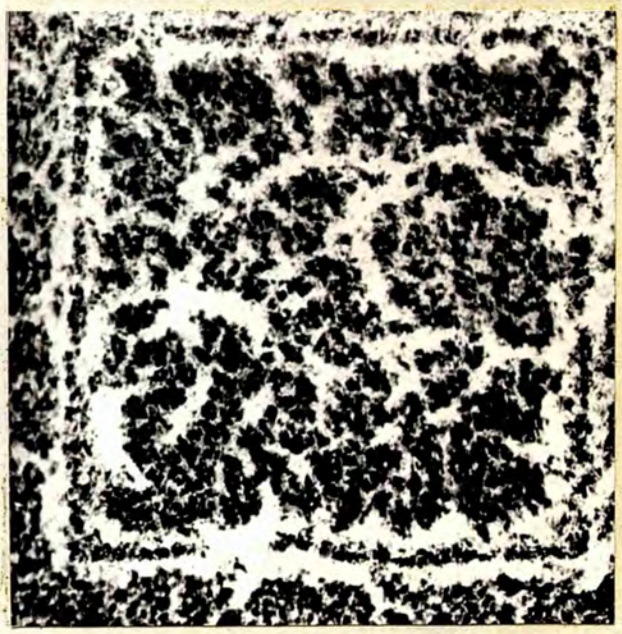


Plate 17 Optical picture of replica of cathode

Magnification of the pictures is x 325

square there is a dark non-emitting region. This region alters in shape according to the position of the cathode under the lens. Plate 5 is the optical picture of the cathode which was obtained from a silver shadowed replica of the cathode. From a comparison of plates 4 and 5 it is evident that the non-emitting region can be correlated with the large surface feature seen in plate 5. This feature is much larger than the fine detail covering the rest of the cathode surface and also much larger than any of the emission centres seen in plate 4. It is possible that when the microscope grid was removed from the cathode a part of the cathode surface was dislodged. It therefore appears that the method of coating is capable of producing cathodes with suitably smooth surfaces providing care is taken to avoid defects such as that shown in plate 5.

The fact that a correlation did exist between the bright emission centres and surface structures on the cathode was first established using a heavily silvered cathode for the optical specimen. Plates 6, 8 and 10 are the emission pictures from three different squares of a cathode. Plates 7, 9 and 11 are the pictures obtained in the optical microscope from the silvered cathode. Plates 7, 9 and 11 are obtained from the same squares as plates 6, 8 and 10 respectively. Although these are the best optical pictures which could be obtained directly from the cathode, they lack detail. However, a careful

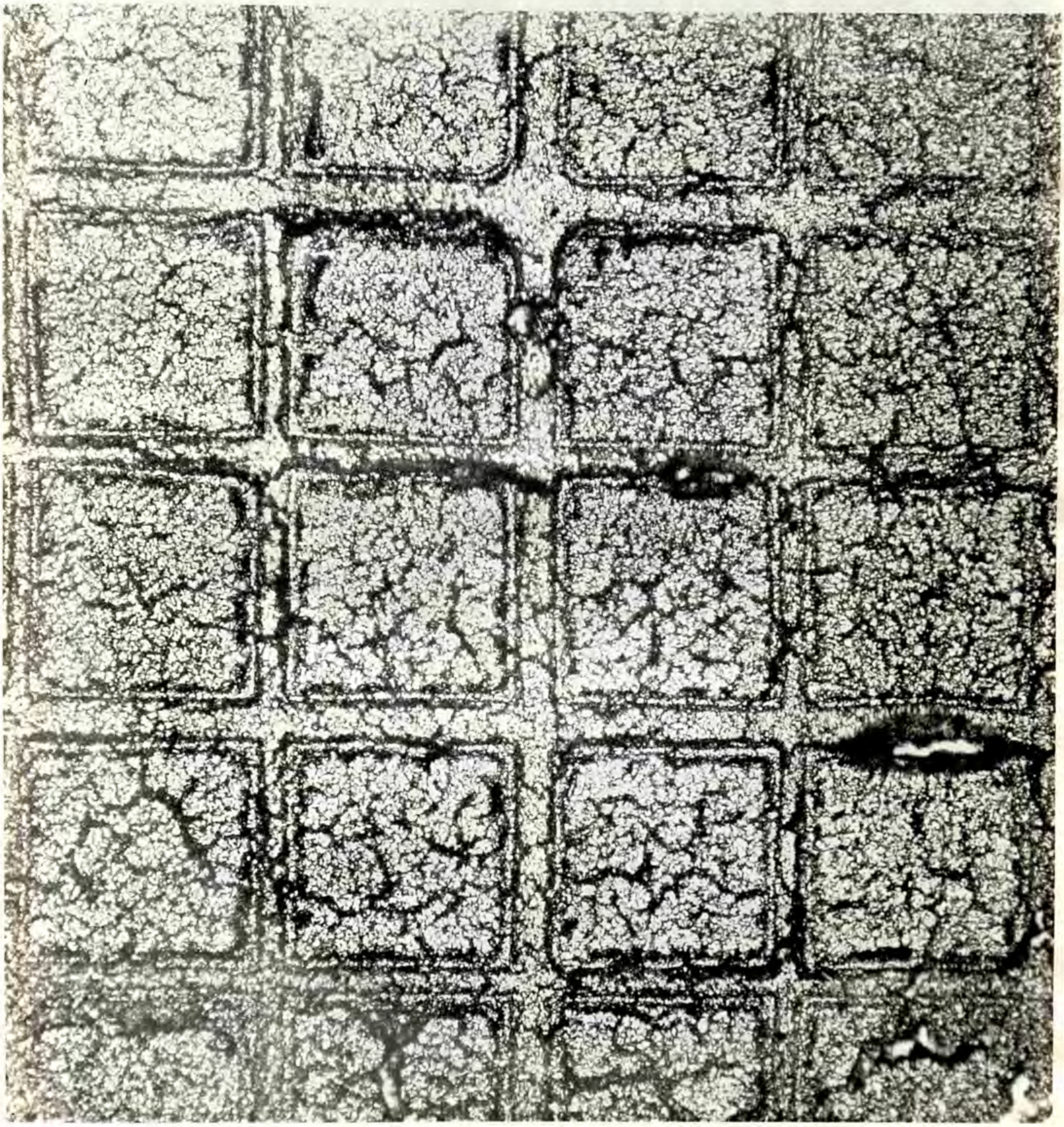


Plate 18

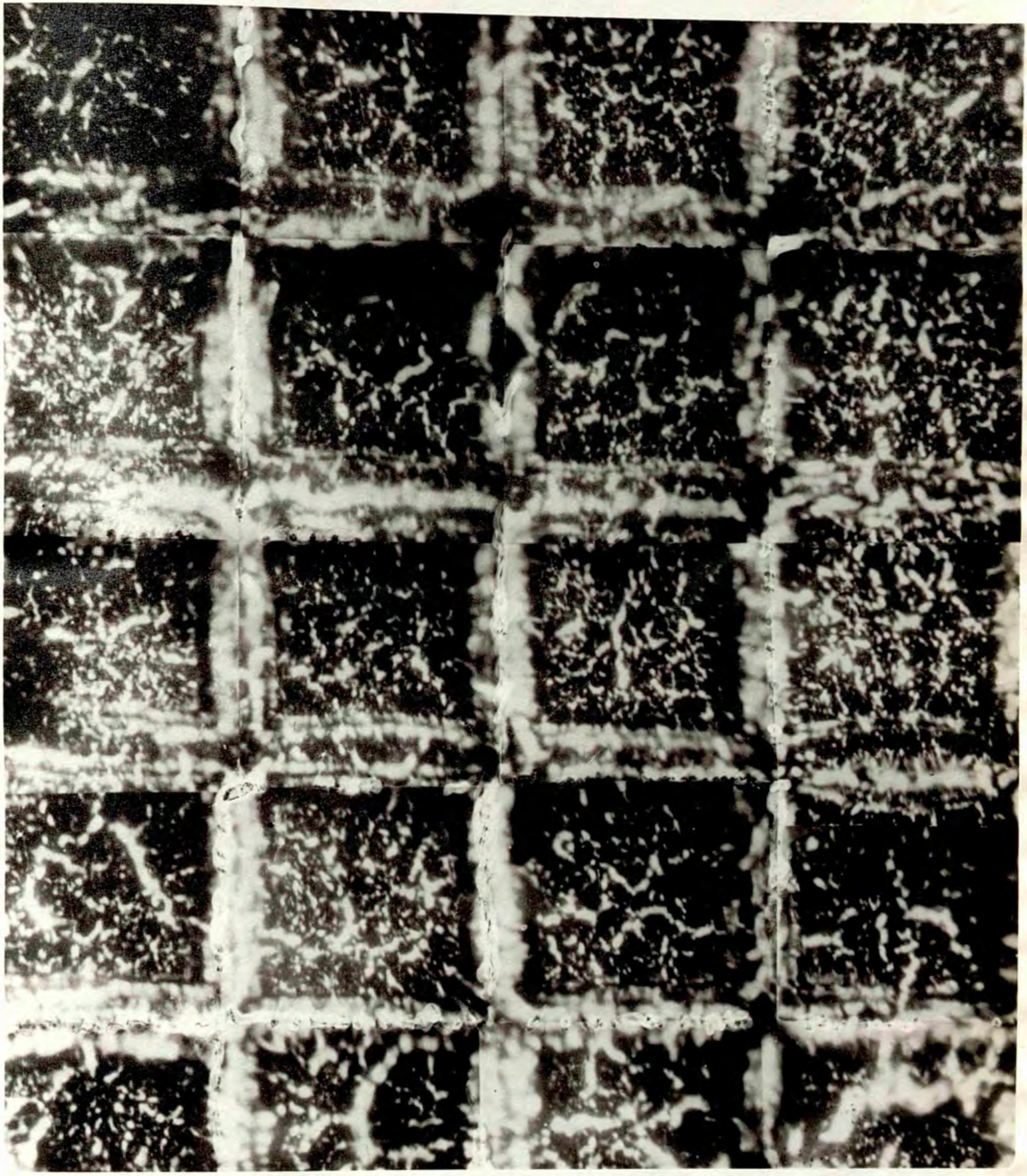


Plate 19

inspection shows that some of the larger emission centres occur on the cathode at places where surface structure is apparent in the optical picture. It should be pointed out that the optical pictures are reversed in intensity so that the surface structures appear as bright marks. This has been done to make the correlation more obvious.

When the replica technique had been perfected, a further set of corresponding emission and optical pictures was obtained. Plates 12, 14 and 16 are the emission pictures from three squares of another specimen. Plates 13, 15 and 17 are the corresponding optical pictures. These pictures were obtained from a replica of the cathode. The replica was viewed in transmission in the optical microscope. The optical pictures have again been printed as negatives. A comparison of the two sets of pictures shows that a correlation exists between the larger emission centres and surface structures on oxide cathodes. With the much more detailed optical picture obtained from the replica, the correlation can easily be seen. Plate 18 is an emission picture reproduced from a large scale emission picture formed by joining together the individual emission pictures obtained from each square. Plate 19 is the corresponding optical picture printed as a positive. The emission picture is not completely free from distortion. This fact may be the reason why only the larger emission centres can definitely be correlated with surface structures while some of the smaller ones cannot be.

The nature of the surface features is obviously of interest. After the examination of the silvered cathode under the optical microscope it was found that the specimen began to flake so that by the following day large cracks had appeared in the coating and were visible to the naked eye. A further examination of the cathode under the microscope showed that these cracks appeared similar to the structure seen on the cathode at the time of the first investigation. In some cases the cracks were found to be extensions of the surface structures. Therefore the surface structures seen in the optical pictures are in fact cracks in the coating.

It must therefore be concluded that there exists a correlation between the major surface structures of the coating and the form of the emission pattern and in particular the larger emission centres can be correlated with cracks in the surface of the coating.

Chapter 14 The causes of emission centres on oxide cathodes

14.1 The influence of surface structures

The experimental evidence presented in the previous chapter supports the view that surface cracks in the oxide cathode are a cause of emission centres. The reasons why a crack in the surface may give rise to a region of intense emission will now be considered.

One possible explanation of the increased emission at cracks may be that because of the form of the crack, the electric fields in the vicinity of the crack are such that the electrons emitted from the crack are bunched together and give a region of apparently high density of emitted electrons. Kemmnitz, Knoll and Walcher[3] have investigated this bunching effect. They prepared specially shaped cathodes with which to demonstrate that electron bunching can occur. Various forms of groove were cut in an otherwise smooth cathode and emission pictures were obtained for different positions of focus of the microscope. The groove appeared both as a bright region and also as a dark region depending on the position of the object plane. The appearance of the emission pattern thus depends on the focusing of the microscope. In order to demonstrate the bunching effect they used grooves of the order of 1 mm. depth and width. It is doubtful if the much smaller surface cracks in the oxide cathode would give any noticeable effect. In the case of emission centres no reversal of the intensities could be detected by changing the focus of the microscope. It is probable that the electron bunching effect is not a cause of emission centres but is in fact more likely to be the reason for the non-emitting regions such as that shown in plate 4. This region was found to alter its form with the change of focus of the microscope and thus behaves in the same manner as the electron bunching patterns investigated by Kemmnitz etc.

A different kind of electron bunching effect may occur. If a crack occurs such that the depth of the crack is very much greater than the width of the crack at the surface of the cathode, then the surface area of the walls of the crack will be much greater than the area of the crack in the plane of the cathode surface. If it is assumed that all boundaries between the oxide and the vacuum emit electrons at the same rate per unit area, and that all those electrons emitted from the walls of the crack will bunch together and pass out through the narrow opening of the crack in the plane of the cathode surface, then the emission from this region will be more intense than that from the surrounding regions in the plane of the cathode surface.

The saturated emission current from an oxide cathode has been found to conform to the emission equation

$$I = A_0 T^{\lambda} \exp \frac{-e\phi}{kT} \qquad (1)$$

The emission current is thus dependent on the temperature and the work function at the point on the cathode where the emission occurs. If either of these two quantities is different for different points of the cathode then variations in the emission will occur. We must therefore consider how the emission may be modified through the influence of surface structures and their effect on these quantities.

Consider the effect of temperature. Because of the construction of the cathode, there will be a temperature gradient in the coating; the highest temperature in the coating will occur at the metal to oxide interface. Therefore, if a crack occurs in the coating, the surface at the bottom of the crack will be at a higher temperature than the top surface of the cathode presented to the microscope lens. The emission will therefore be greater from the bottom of the crack than from the top surface and since the electrons emitted from the bottom of the crack will pass out through the crack in the top surface, this crack will appear to emit more strongly than the rest of the surrounding cathode surface.

The effect of changes of the work function and their relation to the surface cracks is less obvious than that of the temperature. It may be that the cracks will provide regions on the cathode where the contamination of the cathode by residual gases is less than for the surface exposed directly to the vacuum. There is therefore a possibility that the work function of the surface within the crack is lower than that of the rest of the cathode. The cracks would therefore emit more strongly than other parts of the cathode.

On the basis of the de Boer theory the increased emission from cracks can be explained in the following way. The number of adsorbed barium atoms will depend on the number of possible places available for the atoms to become adsorbed. Within a crack there is a large area available on which there will be places suitable for adsorbing an atom. Also the Van de Waals forces will be greater at crevices than on plane surfaces so that it would in any case be expected that atoms would be adsorbed in greater numbers at the cracks than at the rest of the surface. Since the emission current depends directly on the number of adsorbed atoms, then it follows that a greater emission current would be produced at the cracks than at the rest of the surface.

On the basis of the Loosje and Vink model, with the cathode running at the temperature sufficient to produce a visible emission picture, i.e. with cathode temperatures of 700°C and higher, the conduction mechanism will be mainly through the pores of the coating and thus since the cracks in the coating are large pores, it follows that the majority of the current will flow from the cracks and they will appear as bright regions in the emission picture.

Besides the major emission centres which can be correlated with the cracks in the surface, there are a number of smaller emission centres and unresolved brightly emitting regions which cannot, with any certainty, be correlated with surface structures. It is therefore necessary to retain the effect of orientation of the crystallites of the surface and the roughness of the surface as possible causes of emission centres, in order to account for these additional centres.

14.2 Discussion

In view of the fact that, in contradiction to Heinze and Wagener, a correlation between surface cracks and emission centres has been observed, it must be considered for what reasons Heinze and Wagener[2] were unable to observe the correlation.

The apparatus that they used was only capable of producing emission photographs which when printed had magnifications of x30. The specimens were cylindrical cathodes and the electron lens formed a plane image. Some distortion of the picture must occur and it may be that an equivalent distortion did not occur with the optical picture. The optical pictures in any case give the impression of much rougher cathode surfaces than were used in the present work. This roughness of the surface may have caused defocusing of the picture in the same manner as is observed with the coating in the vicinity of the grid bars in our specimens. It appears likely that oblique incident light was used to photograph the cathode. The optical picture may therefore not be a true record of the surface structures. Any one of the above possibilities may account for the fact that the correlation was not observed.

Any hypothesis concerning the mechanism for the formation of emission centres must be able to account for the experimental results of Heinze and Wagener[4] and Benjamin, Huck and Jenkins[5]. They found that the size of emission centres obtained from various cathodes was influenced by the size of the crystallites in the different emission pastes, which were used to coat the cathodes. In general the emission centres decrease in size with decreasing size of coating particle.

For the purpose of showing that the above experimental results are not inconsistent with the view that emission centres are formed at cracks in the cathode coating, it is convenient to draw an analogy between the oxide cathode and a coal fire. Various sizes of coal could be used; a fire with large lumps of coal burns so that the crevices between the lumps are bright while the central regions of the lumps remain dark. With smaller pieces of coal there are more crevices of a smaller size. The bright regions and the dark parts are therefore smaller with smaller lumps. With very fine coal the fire will glow evenly. If in the analogy the lumps of coal correspond to the crystallites in the coating, and the bright and dark regions of the fire correspond respectively to places of good and poor emission on the cathode, then the crevices of the coal fire will correspond to the emission centres on the cathode. It would therefore be expected that the emission centres will decrease in size with decreasing size of coating particle. The hypothesis is therefore consistent with the experimental result.

It is common knowledge that a coal fire will only smoulder if stoked with very fine coal dust. It is perhaps dangerous to carry the analogy to these limits but at the same time it provides a convenient explanation of the experimental results of Benjamin, Cosgrove and Warren[6] and Windsor[7] who find that there is an optimum density of the coating for the highest emission current density. It is to be expected that the density of the coating will increase with decreasing particle size due to the better packing and from the analogy with the fire there is an optimum particle size for the most uniform glow from the fire. It would therefore be consistent with the analogy to expect an optimum density of the coating for the highest emission current from a cathode.

In proposing mechanisms by which surface cracks may lead to emission centres, no account of space charge was taken. If the temperature of the cathode is raised, the emission becomes space charge limited and it is found that all the detail in the emission pattern is lost. It is therefore a necessary condition for obtaining detailed emission pictures that in general the emission from the cathode is not space charge limited. However, within the cracks it is conceivable that pockets of space charge will exist due to the higher temperatures at the bottom of the cracks and also the fact that the external fields will not penetrate into the depths of the cracks. It is thus probable that an equilibrium exists between the proposed mechanism for the increased emission at the cracks and the space charge which tends to decrease the emission. In considering the influence of the work function as a possible cause of emission centres we have so far only considered it in conjunction with surface structures. Heinze and Wagener[4] propose that the influence of the work function is, independent of the surface structure, in itself a reason for the formation of emission centres. They propose that the crystallographic orientations of the crystallite surfaces which form the cathode surface will vary for different crystallites and since they postulate that the work function will have different values for the various possible orientations, there will arise in the cathode, regions with various different values of work function which will consequently give rise to emission centres. In order to establish that the work function varies with the crystallographic orientation, they distributed a number of crystallites at random on a nickel ribbon. When examined under the emission microscope some crystallites emitted more strongly than others. They then argue that since the crystallites were distributed at random on the ribbon, not all the crystallites will present a similarly crystallographically orientated surface to the microscope. Therefore since the emission from the various crystallites was not the same they argue that differences occur because the work function varies with the crystallographic orientation. In the opinion of the writer their argument is not conclusive. Although they state that the crystallites were of similar sizes their experimental results could also be explained as an effect of different temperatures at the surfaces of the crystallites. It cannot be assumed that irregularly shaped crystallites placed on a heated nickel ribbon will present surfaces to the microscope which will all have the same temperature. Thermal contact between the ribbon and the crystallites must vary for the different specimens as indeed must also the thickness of the specimens. The explanation of Heinze and Wagener, although possible, cannot be regarded as definite evidence of a cause for the production of emission centres.

The other cause which Heinze and Wagener propose is important for the production of emission centres is the roughness of the surface. This is a rather ill-defined quantity. However, we have seen that large irregularities in the cathode surface lead to defocused regions, or in other cases to electron bunching effects. Both these defects in the emission patterns could be interpreted as emission centres if examined at low magnification. It is obvious, with higher magnification, that these defects are a function both of the microscope lens and also the cathode. They cannot therefore be regarded as true emission centres. The other possible influence of the roughness of the surface may be that it may cause a reduction of work function at sharp edges or protrusions on the cathode. It may happen that because of the structure, the electric field in the region of the structure is increased. Morgulis[8] has discussed the influence of strong fields on the work function of semiconductors. It appears that the work function may be reduced at regions on the surface where the field strength is high. The work function may therefore vary across the surface and thus emission centres will form. This mechanism could thus explain the formation of emission centres.

14.3 Conclusion

In the present work a correlation has been observed between cracks in the cathode surface and the emission centres observed from the cathode under the emission microscope. The possible reasons why cracks should give rise to emission centres have been considered. They can be enumerated as follows:-

(1) Electron bunching due to the distortion of the electric fields at the surface in the presence of the crack
(2) Electron bunching due to the emission out of the crack of electrons emitted from the inside walls of the crack
(3) Increased emission from the crack due to the higher temperature at the bottom of the crack
(4) Lower work function inside the crack
(5) On the basis of the de Boer theory, the cracks will

provide places for the adsorption of barium atoms.

(6) On the basis of the Loosjes and Vink model the conduction will occur through the cracks.

The first of the possible explanations is thought to be unlikely. There is no direct evidence to confirm the last three explanations, but they cannot be discarded as possible explanations.

Following the observation of the correlation, the work of Heinze and Wagener[2, 4]. has been re-examined and possible reasons to account for the fact that they did not observe a correlation have been suggested.

The causes of emission centres can therefore be set out as

(1) Cracks in the coating

(2) The effect of external fields on the work function at edges and protrusions on the cathode.

(3) The variation of the work function with crystallographic orientation of the surface elements.

The last of these possible causes requires experimental verification.

With the explanation of the causes of emission centres outlined above, the nature of emission pictures from oxide cathodes, as well as the influence of variations in the properties of the coatings, can be accounted for.

Part 6

COATINGS DEPOSITED BY AN EVAPORATION TECHNIQUE

Chapter 15 The reasons for adopting the technique

The earlier work reported above has shown that there exists a correlation between emission centres and surface structures on oxide cathodes. It would thus be a further proof of the influence of the surface on the formation of emission centres if, with a smooth surface, uniform emission were obtained.

The methods usually employed for coating cathodes all give surfaces which give emission centres in the emission picture. It is, however, evident that the smoothest surfaces which are normally produced, i.e. those obtained by depositing colloidal particles by electrophoresis, lead to emission pictures with very small emission centres e.g. see Hermann and Wagener[1]. It is thus evident that the emission tends to become more uniform as the surface is made smoother.

The surfaces resulting from the evaporation of various substances on to polished surfaces are commonly found to be of the same type as the polished substrate and it was thus a possibility that a cathode with a smooth surface could be manufactured in this way. Nickel can be polished quite easily to give the necessary smooth substrate and an examination of the Critical tables showed that it should be possible to evaporate barium oxide from high melting point metals such as molybdenum or tungsten.

Chapter 16 The evaporation technique

16.1 Synopsis of previous work

The evaporation of barium oxide seems to have been carried out for the first time by Moissan[2]. He used barium carbonate as raw material and heated it in a crucible with an oxy-hydrogen flame. After decomposing the carbonate to the oxide a white or pale yellow residue is formed which fuses to a hard brittle substance. With a hot enough flame the substance can be made to boil. The temperature at which the boiling occurs is in the region of 2000°C.

The evaporation of barium oxide under vacuum conditions occurs when oxide cathodes are used at temperatures in the region of 1100°C. In the literature on evaporated barium oxide only very thin films are discussed and the term 'monolayer' is applied to the films obtained. According to the work of Russell and Eisenstein[3] a suitable definition of a monolayer is a layer having an average surface density of 10^{15} BaO molecules/cm^2. Films of up to twenty-five monolayers thickness have been obtained by Davisson and Pigeon[4]. The usual method of evaporating the films is to use a conventional oxide cathode as the source and with the cathode heated to around 1100°C a monolayer can be deposited on a substrate, directly facing the source, in about 30 minutes.

Various core metals were used; Hull[5] used molybdenum mesh stockings filled with a compound of barium and aluminium to evaporate barium oxide on to nickel, while Moore and Allison[6] used pure platinum. In the reports of work on thin evaporated films the evaporations always seem to be made from sources run at temperatures of the order of 1100°C and the resulting films are very thin even after long periods of evaporation.

There is a possibility that if the barium oxide can be made to melt as in the experiments reported by Moissan[2], then the rate of evaporation may be considerably increased and as a consequence much thicker layers may be deposited in shorter times. Some experiments were thus carried out to investigate the necessary conditions.

16.2 Apparatus

Following the example of Moore and Allison[6] a platinum filament was coated with a mixture of barium and calcium carbonates. Initially glass substrates were used. No appreciable deposit was obtained with the substrate 6cm. from the filament, even when the temperature was raised to such an extent that the filament burnt out. The platinum filament was discarded and a boat filament made from .006" molybdenum sheet was used. The filament was filled with a thick sludge of emission paste and the substrate was mounted directly above it at a distance of about 6cm. When the filament was heated in vacuum by passing a current of 120 amps through it a thin brown deposit was obtained on the glass substrate. During the evaporation large amounts of gas were given off and a considerable proportion of the material in the boat was ejected. No sign of melting of the paste was observed, even at the maximum available current of 150 amps. In order to increase the maximum temperature which the filament could attain, radiation shields were placed round the filament. Slots were cut in the top to allow the material to evaporate on to the substrate. With this apparatus there was a noticeable melting of the emission paste and films of the order of $1000A^{o}$ thick were obtained. The films were transparent and had glass like surfaces and thus were of the kind needed for the proposed experiments.

The technique of evaporation suffered from a number of teething troubles and modifications to the apparatus and the type of raw material used, were made during the development of the technique.

The main difficulty was the frequency with which the filaments burnt out. There were two main causes of trouble. During the heating the filament supports expanded and the filament twisted and shorted to the radiation shields, thus causing a burn out. To overcome this the support was spring

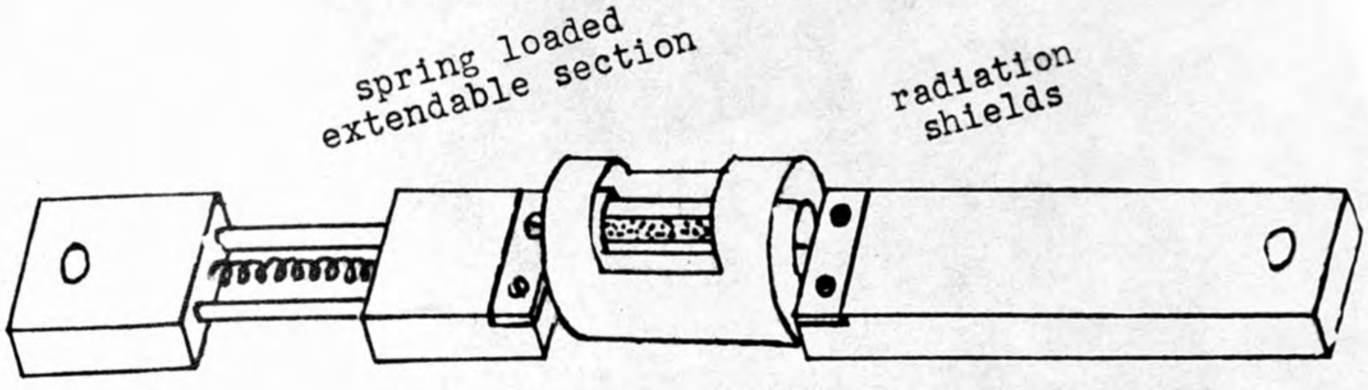


Fig. 16a A sketch of the apparatus

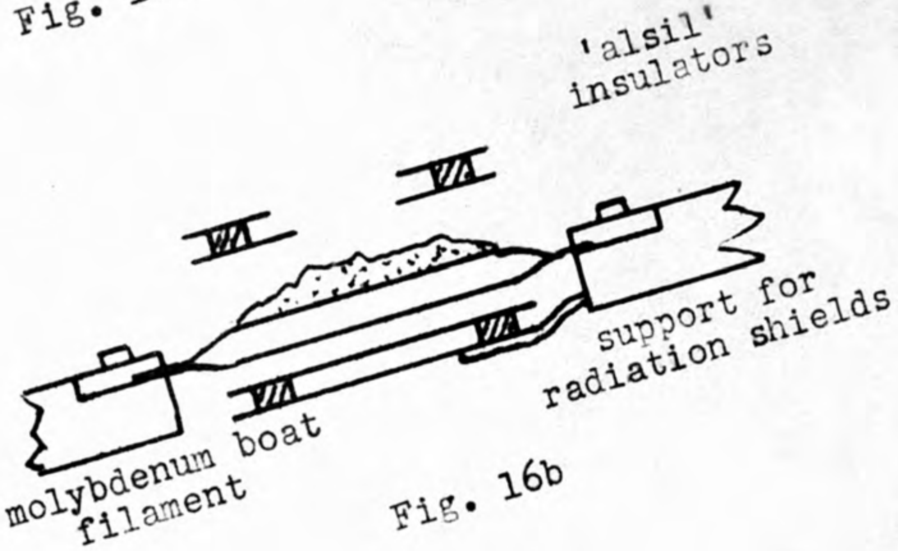


Fig. 16b

Fig. 16c

Fig. 16a, b and c Diagrams of the evaporation apparatus loaded and the inner radiation shield insulated from the rest of the apparatus. The apparatus as it was used in its final form is illustrated in Fig. 16.

The other cause of the burn outs was an apparent corrosion of the filament by the material in the boat. For reasons which will be discussed in the next chapter, the use of barium carbonate or a mixture of alkaline earth carbonates was found to be an unsatisfactory raw material. There was considerable advantage in using barium hydroxide and indeed, the corrosion effect was practically eliminated when this material was used. The indication is that the corrosion was probably due to the action of carbon monoxide.

16.3 Operation

The method finally adopted for the evaporation of films was as follows. A molybdenum boat was constructed from a strip of the .006" thick sheet. A piece about ¼" wide and 2" long tapered at the ends was used. A thick sludge of barium hydroxide and nitrocellulose binder was put in the boat and this was mounted in the apparatus as shown in Fig. 16. The supports were mounted in an Edwards standard evaporating plant with the 18" bell jar. The specimen and subsidiary pieces were mounted directly above the boat at a distance of about 6". The plant was pumped down and the boat heated up slowly. The temperature could only be raised slowly until the hydroxide had decomposed and the pressure in the chamber reduced to 10^{-4}mm. of Hg. The tendency for the material to be ejected from the boat is less after decomposition. After the decomposition the temperature can be increased more rapidly consistent with the pressure remaining below 10^{-4}mm. of Hg. Currents of between 120 and 150 amps through the filament are necessary to melt the oxide material. When the melting point is reached the oxide is seen to collapse into the boat and at the same time the pressure in the chamber improves and registers around 10^{-5}mm. of Hg. This effect is probably similar to the gettering effect used in the manufacture of radio valves. The time of the evaporation is only of the order of 5 minutes from the start of the melting. In this time films of thicknesses up to 14,000A° have been obtained.

Chapter 17 Characteristics of the coatings

17.1 Susceptibility of the coating to atmospheric attack

The coatings which were produced on glass substrates during the development of the process were all transparent when first removed from the evaporating plant, if a proper melting of the oxide occurred. The films soon turned milky and appeared much the same as finely ground glass. If one breathed on the film the change occurred very rapidly. A specimen film placed in a dessicator immediately after removal from the evaporating plant remained transparent indefinitely. On removal from the dessicator in one case after a fortnight, the film changed to the opaque state in a few minutes. It was therefore concluded that the change in appearance was due to the action of water vapour on the barium oxide.

The surface of the film when in the transparent state is glass like. The examination of films coated with a protecting layer of silver revealed, within the power of the optical microscope, no definite structure. In the course of measurements made on the films using multiple beam interference techniques the fringes obtained were practically of the same quality as those on glass surfaces. Thus there can be no structure on the surfaces of the transparent films which is detectable by these techniques, i.e. nothing larger than 50A°. above the general level of the surface. The surface of such a film will most probably contour that of the substrate and the final surface of a cathode prepared by evaporation of the oxide on to the core metal will be determined by the quality of the surface of the core metal. Since nickel can be prepared with a high polish, it is to be expected that, by the method of evaporation, cathodes with surfaces much smoother than those prepared by conventional methods, can be prepared. However, the effect of hydrolysis can produce surface structures visible to the naked eye and thus if it is desired to maintain the smooth cathode surface, precautions to avoid the hydrolysis must be taken.

17.2 Thickness measurements

The thickness of a film deposited on a glass substrate can be measured by multiple beam interferometry.[7] The method adopted was to coat only part of the substrate during the evaporation, thus leaving a step equal in height to the thickness of the film. The mask covering part of the substrate during the evaporation, was then removed and the specimen fully silvered. With a silvered glass flat, properly matched in the silvering, multiple beam fringes were obtained across the step, using the standard reflection method. The thickness of the film can then be determined from measurements on the fringes.

With films deposited on the nickel cores the direct measurement of the film thickness is not possible since it is not desirable to contaminate the cathode with silver. It was thus arranged that a piece of glass with a mask attached was suspended side by side with cathode during the evaporation at the same distance from the boat and the thickness of the film on the glass was taken as a measure of the cathode film thickness. Accurate determinations of the thicknesses were unnecesssary and all thicknesses are quoted only to the nearest 500A°.

During the course of experiments to produce the films some difficulty was experienced in silvering the films. The films were, as usual, transparent after evaporation but after silvering turned grey. The earliest experiments had been carried out with barium oxide, which was probably to a large extent converted to the hydroxide. This had been used with some emission paste to form the thick paste to fill the boat. At the time of the troubles with silvering the barium oxide had run out and barium carbonate was being used. During the evaporation of the paste large amounts of CO_2 were given off, and some of the gas was probably absorbed in the evaporated film. Although during the silvering the pressure recorded by the gauge was that normally used, i.e. about 5.10^{-5}mm. of Hg, it may have been that due to outgassing of the film, the pressure at the surface of the film was considerably higher and the silver consequently turned grey.

In order to overcome this trouble the carbonate was heated with an oxy-acetylene flame in a silica crucible and converted to the oxide. The fused residue resulting from this material was then crushed and mixed with binder for use as the filament paste. No further difficulties were experienced with the silvering process. The method was rather laborious and wasteful and as it appeared that the main cause of the trouble was the evolution of carbon dioxide it seemed that if barium hydroxide was used as the raw material, this difficulty would be removed. All that was then necessary was to drive off the water of crystallisation by heating over a bunsen flame and then crushing the material to a powder. On heating the mixture in vacuum the barium hydroxide decomposes at a temperature of approximately 400°C (see Haas and Jensen[8]) which is much lower than that required for the evaporation and thus all the water vapour can be pumped off before the evaporation starts and the pressure can easily be maintained below 10^{-4}mm. of Hg. Films deposited in this way gave good reflecting surfaces when silvered and were probably free from occluded gases.

The thickness of the films could not be controlled and films of varying thicknesses were produced. The majority of the films had thicknesses lying in the range of 2000 to 4000A°. The thickest film obtained was 14000A°.

17.3 Density measurements

The direct measurement of the density of an evaporated barium oxide film by weighing a film of known volume is difficult because the hydrolysis of the film not only invalidates the determination of the mass of the film but also makes the surface of the film unsuitable for the subsequent determination of the thickness by multiple beam interferometry. In order to overcome this difficulty density measurements were carried out by evaporating the films on to thin glass cover slips suitably masked to leave a step for the determination of the thickness. The film was then fully silvered but a further mask was kept in position so that the thickness of the silver coating could also be determined by measuring the step height. The increase in mass of the silvered film was found and the thickness of the barium oxide layer was measured using the reflection multiple beam interference method. The area of the oxide film and also that of the silver coating were measured. The specimen was then fully silvered, so that the step height of the silver coating could finally be found. Assuming the density of the evaporated silver layer to be the same as that of silver in bulk, the mass of the silver layer was calculated and hence the mass of the barium oxide was deduced. The density of the evaporated oxide films was then obtained.

In order to obtain a measureable increase in mass of the cover slip it was necessary to use large thin cover slips. It was therefore possible that the films were not uniform across the whole of the cover slip and thus an error of unknown size was introduced into the measurements. The results of six sets of separate measurements on different films gave values of the density of the films in the range 4.0-6.0 gm/cc.

The films are thus much more dense than the cathode coatings produced by other methods. Typical values for the sprayed coatings are in the range of 1-2gm./cc. With particular attention to the design of the spray gun, densities of the coatings have been increased up to 2.8gm./cc. (see Windsor[9]).

The density of barium oxide calculated from Xray data is 5.7gm./cc. and thus the evaporated films have densities approaching that of the perfect crystal. It is unlikely that these films are perfect crystals. Russell and Eisenstein[3], working with films up to 50 monolayers thick found that a preferred orientation of the barium oxide crystals occurred if a nickel substrate heated to 800°C was used. There was however, no sign of preferred orientation when the substrate was not heated. Thicker films of unspecified thickness showed clear rings in the electron diffraction patterns obtained from them, indicating quite well developed crystals with no preferred orientation. It is therefore probable that the films produced by my method of evaporation will be polycrystalline with no preferred orientation. The density of such a specimen would be expected to have a value close to that of the perfect crystal. The experimentally determined value of the density is in agreement with this expectation.

Part 7

EMISSION PHOTOGRAPHS FROM CATHODES WITH COATINGS DEPOSITED BY THE EVAPORATION PROCESS

Chapter 18

Emission photographs from cathodes with 'O' nickel cores

18.1 The initial emission photographs

There was found to be in general, a sequence of events which could be observed as variations in the form of the emission picture which was given by these cathodes.

The specimens were coated by the evaporation method described in the previous section. They were then transferred to the emission microscope and the emission picture obtained. The hydrolysis of the coating in the atmosphere was an obvious cause for producing irregularities on the cathode surface and in order to reduce this contamination the time required for mounting the specimen in the microscope had to be kept to a minimum. For this purpose the connections to the specimen and the lens were made through a plug and a spring contact respectively and it was possible to mount the specimen and close the chamber within three minutes.

The first attempts at obtaining emission pictures showed

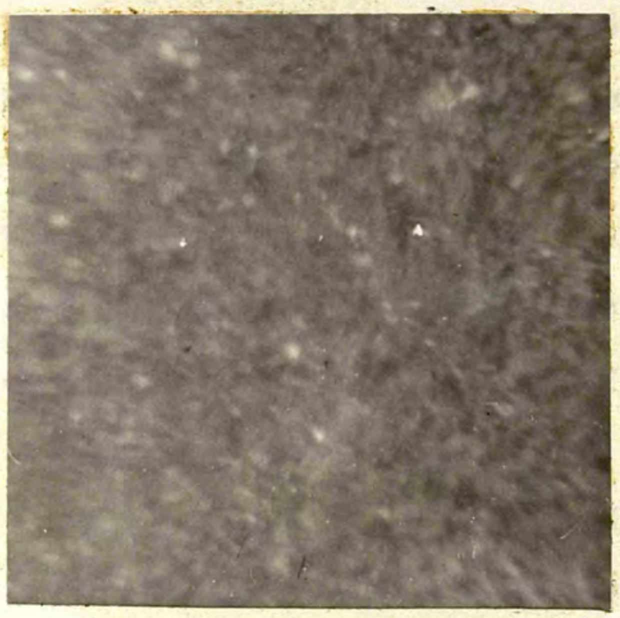


Plate 20 x 150

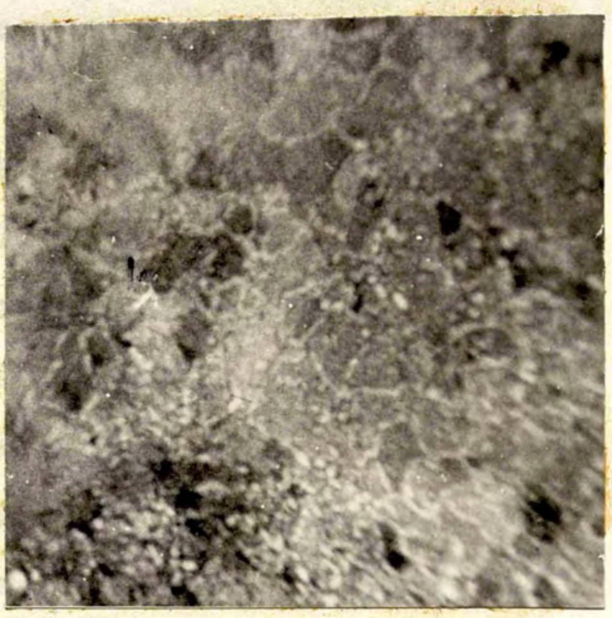


Plate 21 x 300

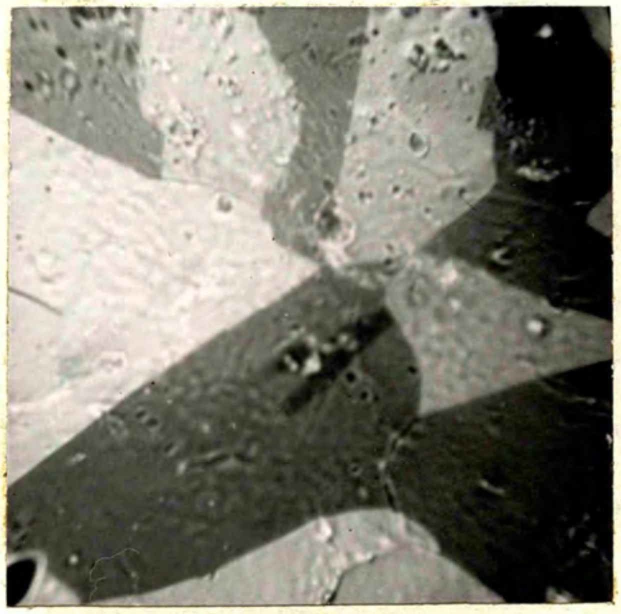


Plate 22 x 150

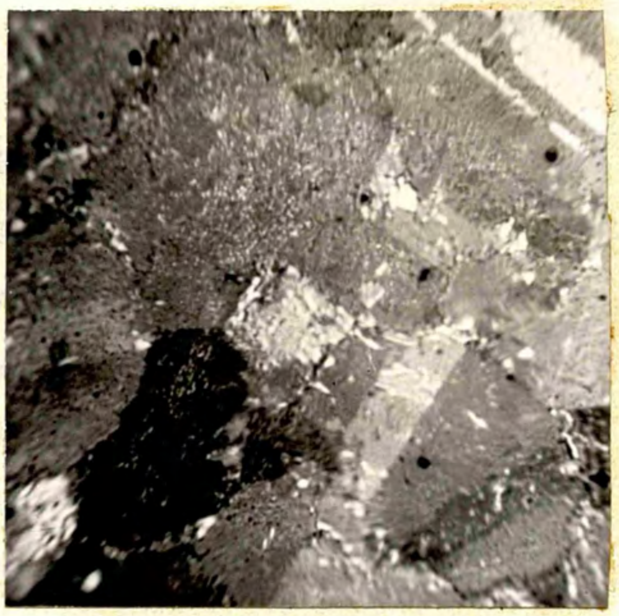


Plate 23 x 150

that an activation of the cathode by drawing current was not essential. It was possible to produce the pictures merely by heating the cathode to a temperature of about 800°C. The initial pictureswere usually of two types. If the specimen had been mounted before the hydrolysis of the coating in the atmosphere produced noticeable cracking, then the resulting emission picture was generally of the kind shown in plate 20. If, however, as was sometimes the case when the mounting operation did not go according to plan, the coating became crazed, and the emission pictures obtained from such coatings appear as in plate 21. The emission picture remains in this form for some time. After running the cathode at a temperature of between 800 and 900°C for two or three days a gradual change in the emission picture occurs.

18.2 The appearance of the patchwork pattern

The change in the emission pattern is first detected as a slight decrease in emission at some places on the specimen surface. The patches become gradually more distinct and sharp boundaries between dark and bright regions occur. Plate 22 is an example of the patchwork patterns that have been observed under the emission microscope. The pattern can be quite distinct, especially if the specimen has been mounted with the minimum of contamination. The contaminated coatings show the patchwork patterns as well but there is generally superimposed on this

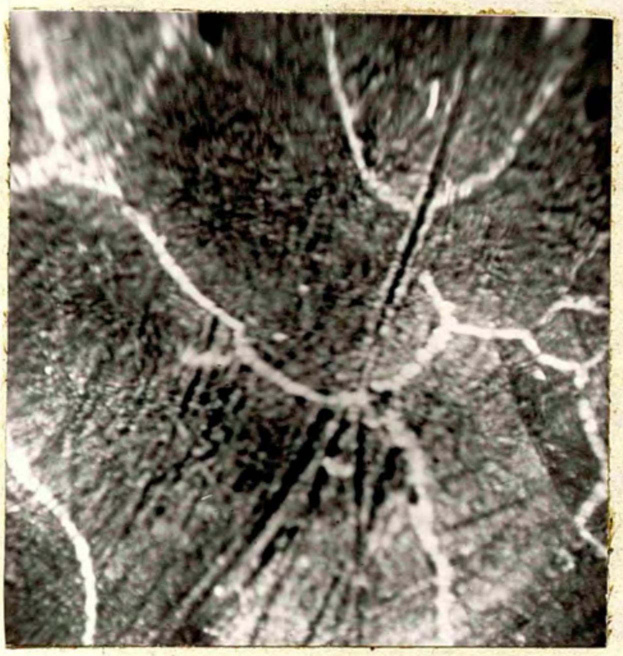


Plate 24 x 150

Plate 25 x 150

Plate 26 x 300

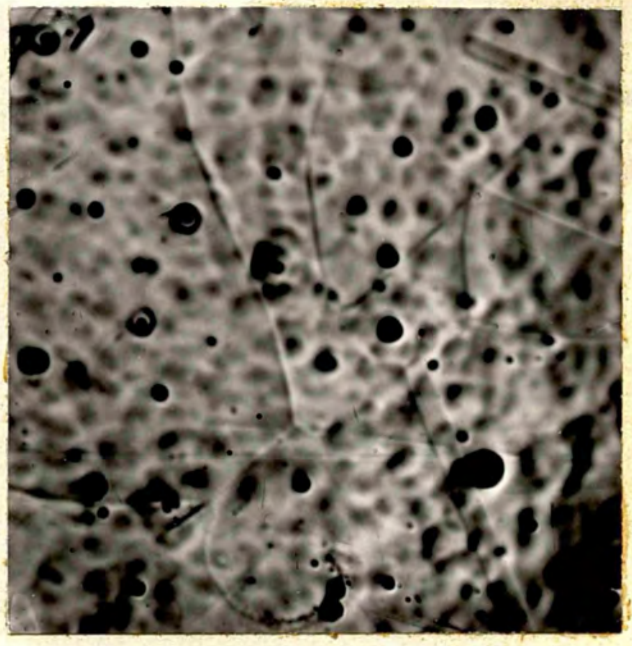


Plate 27 x 250

pattern the speckles resulting from emission from irregularities in the coating; plate 23 is an example of this type of pattern. This form of pattern can remain visible for a few days before gradually a further change in the emission picture occurs.

18.3 The appearance of grain boundary patterns

The patchwork patterns gradually fade and the emission becomes generally more uniform except at the boundaries between the patches where the emission appears more intense. Plate 24 is an example of this type of pattern.

During the life of the cathode the temperature has to be gradually raised in order to maintain sufficient intensity on the screen for visual observation of the patterns. The temperature at this stage of the life of the cathode is in the region of 950 to 1000°C. Even at this temperature the emission is such that the intensity of the picture on the screen makes the photographing of the phenomena difficult.

18.4 The decay of the emission

The final stages in the life of the cathode are not as definite as the sequence of events described above. Various different types of pattern have occurred and no conclusion which is generally valid can be drawn concerning the expected behaviour of the cathode.

The type of emission pattern appearing most frequently is shown in plate 25. The cathode appears to emit from spots distributed randomly on the surface. Another pattern which sometimes appeared is the apparent negative of the grain boundary pattern. The grain boundaries appear as poorly emitting regions compared with the surroundings. Plate 26 is an example of this type of emission picture. The emission is then usually so low that further examination of the specimen is not possible. It is, however, noticeable that the centre of the cathode usually becomes non-emitting at an earlier stage than the outer regions. The life of the cathodes varies but is generally around three weeks.

Chapter 19 Investigation into the causes of the different types of emission patterns

19.1 History

The patterns which have been designated as patchwork patterns in the previous chapter, bear a marked resemblance to the emission patterns which have been obtained at different times by some workers investigating metal surfaces activated with thin layers of barium oxide. The work of Bruche[1] with cathodes produced by evaporating barium from a barium azide cathode on to clean nickel surfaces, has shown that the patchwork pattern can be obtained in this way. There is also in this same paper mention of some work in collaboration with Johannson who found that when relatively thick coatings were used, the patchwork patterns were still obtained; no further details of this work were given. The work of Bruche was done at low magnifications in the range x5 to x60. More recently Heidenreich[2] using the improved electrostatic lens, has produced pictures at magnifications of x700. He activated various steel and nickel specimens with thin layers of barium formate which were decomposed by heating to form the oxide. In this way he was able to observe structure changes in the specimens. The main difference between the work of Bruche and Heidenreich and the present work is the fact that the patchwork patterns observed in the present work occur with films of barium oxide that are a factor of 100 times thicker than those reported by the other authors.

The explanation of the patchwork patterns according to Heidenreich[2] is, that the adsorption of the barium oxide on the nickel surface produces dipole layers which are orientated in such a manner that the work function of the grains are reduced. Either different densities of the adsorbed layers or different initial work function of the surfaces of the different grains would account for the variation of intensity from grain to grain.

If this explanation of the patches is valid for the thicker barium oxide films, then it would be expected that the patchwork pattern would appear as soon as the cathode was activated and would remain throughout the life of the cathode. The initial uniform emission from the uncontaminated cathode is in contrast to these expectations.

19.2 The effect of different methods of preparing the surface of the core metal

The first pictures which showed the uniform emission were obtained from specimens with mechanically polished surfaces. The specimens were turned up on a lathe and had a normal machine finish. After degreasing they were mounted in the specimen holder and electrical connections made as usual. These specimens were then abraded with two grades of carborundum powder finishing with grade 700. Microid polishing alumina was then used to produce the polished surface.

Specimens were washed, dried and then mounted in the coating unit. The thickness of the layer of barium oxide evaporated on to the specimen was determined and the emission picture obtained. Plate 21 is in fact the initial emission picture obtained from a mechanically polished specimen with a coating 2500A^{o} thick. The temperature of the cathode was 920^{o}C. There is no evidence in this picture of any patchwork pattern although after three days the patches appeared as in plate 23.

Because there was no evidence of patches in the initial pictures it may be argued that there were no well developed grains in the core metal and only after heat treatment had the grains become sufficiently large to form the characteristic patchwork pattern. In order to test this theory a cathode was selected which was known to have large grains. A specimen that had been used for a previous experiment was etched with concentrated nitric acid which revealed the grain structure. The specimen was then mechanically polished and subjected to a heat treatment in vacuum in an endeavour to remove the layer of amorphous material which, according to the ideas of Beilby[3] is formed at the surface during the polishing process. Clarebrough, Hargreaves and West[4] working with nickel specimens report that recrystallisation proceeds if the specimen is heated above 600°C. In the case of the 'O' nickel cathode a temperature of between 800 and 900°C was used. The cathode was maintained at the temperature for about 15 minutes and then allowed to cool. The evaporation of the barium oxide film on to the cathode was then carried out. With this treatment it was intended that the Beilby layer, if it existed, would be removed by the growth of the underlying grains. In spite of the treatment, the emission picture again showed no indication of the patchwork pattern until after two days continuous running.

Since electropolishing techniques can be employed and in this way the production of a Beilby layer can definitely be avoided, a more convincing experiment can be carried out with an electropolished specimen. A cathode with well developed grains was selected for the specimen.

The electrolytic polishing or etching was carried out in a small apparatus constructed to the design suggested on page 107 of the book Photomicrography with the V.P.M.[5] The electrolyte which was used was a mixture of two parts methyl alcohol and one part concentrated nitric acid. The cathode of the polishing tank was made of stainless steel. The 'O' nickel specimen was made the anode. By suitable adjustment of the voltage and current the specimen could be etched or polished. To prepare the specimen it was first etched until the grains were clearly visible and then a polished surface was obtained. The surface was not completely flat and had some small pits on it. Anoptical picture of the surface is shown in plate 27. The specimen was then coated with the evaporated film of barium oxide. The emission pattern was then obtained. As before the initial emission pattern was the usual uniformly emitting pattern with no sign of the patchwork pattern until after three days.

Since the core metal surface in the case of the last electropolished specimen was undoubtedly free from any amorphous or strained layer, the surface must have had patches of different crystallographic orientations depending on the orientation of the grains in the metal. If the explanation of the patchwork pattern given by Heidenreich[2] is true for these thick evaporated films, it would be expected that the patchwork pattern would appear at the start of the life of the cathode. It is, however, quite clear that there is always the uniform emitting picture before the patchwork pattern developes. Also, since the uniform picture occurs with different methods of preparation of the core metal surface, it is likely that the uniform pattern is dependent on the nature of the oxide coating rather than the core metal surface.

19.3 The patchwork pattern

The patchwork pattern has been explained in the earlier work, on the basis of the crystal structure of the surface of the core metal. There is ample evidence from experiments with the field emission microscope, first constructed by Muller[6], that the work function of a metal surface may vary according to the crystallographic orientation of the surface, and the contamination of the surface by surface films. As an example of this type of work see Benjamin and Jenkins[7]. The work function of the core metal surface at any point will thus depend on the particular orientation of the grain located there. The application of a thin layer of barium oxide is assumed to lower the work function of each of the grains and the intensity of the electron emission when the cathode is heated to about 800°C, becomes sufficient to enable the emission pattern to be formed which shows the grains dark or bright according to the value of the work function. In order to establish that the patches in the emission pattern were in actual fact related to the grains

Plate 28 x 200

Plate 29 x 200

Plate 30 x 200

Plate 31 x 200

in the core metal surface, Bruche[1] obtained a correlation between the emission pattern and the optical pattern obtained after cooling the cathode and then etching the surface to reveal the grains. In order to confirm that the core metal grains were related to the patches in the emission pattern obtained with the evaporation technique, a specimen was prepared which had been masked with an electron microscope grid during the evaporation of the barium oxide film. Plate 28 shows the patchwork emission pattern that was obtained. The patches are seen to be continuous across the narrow bars which correspond to the regions of the surface which were masked during the evaporation. Since the surface under the mask will not have been coated, the patches in these regions must be due to the grains in the metal surface and since these grains are carried through into the areas where the coating is much thicker, in this case 3500A, then it may be concluded that even in the case of the thick coatings, the patchwork pattern arises because of the influence of the underlying grains in the metal core.

19.4 The grain boundary pattern

The change from the patchwork pattern to the grain boundary pattern is very striking with the cathodes with '0' nickel cores. The intense emission which occurs from the boundary regions, even after the rest of the surface has become practically non-emitting, suggests that there must be some mechanism which maintains or even increases the activity of the coating in these regions.

It has already been noted that the 'O' nickel core metal is an alloy specially prepared to give high emission cathodes. Certain small amounts of impurities are added which react with the barium oxide to produce excess barium in the coating. A possible explanation of the enhanced emission from the grain boundaries could be that during the heating of the cathode, one or other of these impurities may diffuse into the grain boundaries, and due to the increased concentration of this impurity there, a greater quantity of excess barium would be produced in the region of the grain boundaries, than at the rest of the surface. Consequently, if it is assumed that the emission is dependent on the concentration of excess barium, the increased emission of the grain boundary could be explained.

If the added impurities in the core metal are in fact the cause of the grain boundary pattern, then an investigation of the emission patterns obtained with cathodes with pure nickel cores should provide a test of the theory, for in this case, the bright grain boundary pattern would not be expected.

Chapter 20 Cathodes with pure nickel cores

20.1 The sequence of emission pictures

The material from which the cathodes were made was spectroscopically purenickel rod obtained from Johnson and Mathey. The material has less than .001% impurity content and the main part of this is iron.

The specimens were mechanically polished and then coated as usual.

The emission pictures which were obtained were less intense at corresponding temperatures, than those on the '0' nickel cores. The initial picture was the same form as before, being uniformly emitting except for the brighter spots due to irregularities in the coating caused by the hydrolysis of the coating in the atmosphere. Plate 29 is an example of the initial picture from a pure nickel cathode at 890°C. The thickness of the coating was 2500A. Plate 30 is an emission pattern from a specimen which was mounted very quickly. There is practically no sign of contamination and the picture is uniform but for the polishing marks.

After about two days continuous running at about 900°C the patchwork pattern appeared. The contrast of the picture was generally poor and photography of the patterns with the existing equipment was seldom possible. The plate camera and f4.5 lens which was used for the early work was therefore

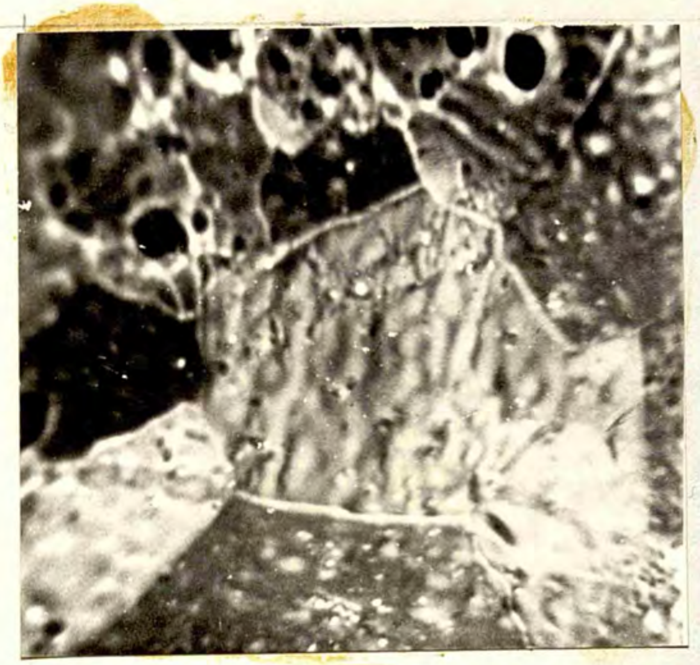


Plate 32 x 200

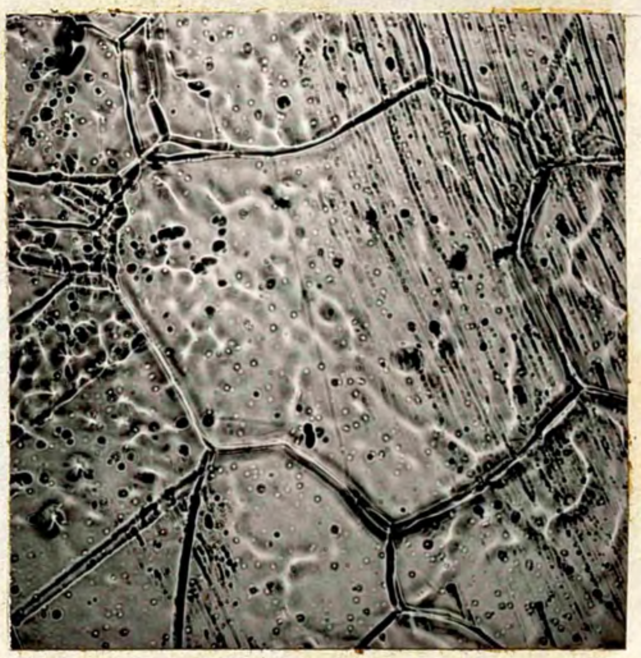


Plate 33 x 250

Plate 34 x 150

Plate 35 x 150

replaced with an f:2,35 mm. camera using Kodak R55 film.

The patchwork pattern was photographed and an example of this type of emission pattern is seen in plate 31. The specimen was running at 1000°C and the coating thickness was 3300A.

The patchwork pattern generally faded more quickly than with the '0' nickel cathodes. Usually it was visible for only about half a day. The type of pattern which was sometimes obtained after the patchwork had faded was different from that obtained previously with the '0' nickel cathodes. Plate 32 is an example of the pattern obtained from a pure nickel cathode at 1050°C; the coating thickness was 9500A. Although there are still bright regions linking up in the same manner as the grain boundary lines in the '0' nickel cathode pictures, the lines in these pure nickel cathodes are very much finer and much less intense than for the case of '0' nickel.

20.2 Comparison between emission pictures from cathodes with '0' nickel and pure nickel cores

The initial pictures from both these types of cathodes are similar in their appearance but the patterns from the '0' nickel cathodes are generally brighter at corresponding temperatures.

Both cathodes give patchwork patterns but the contrast of the '0' nickel pictures is better than that of the pure nickel. The patchwork pattern of the '0' nickel cathode is stable for periods of two or three days where as that of the pure nickel can only be observed for periods of about half a day. Although there is no strict correlation it was found that specimens with the thickest coatings generally took the longest times to change from one type of pattern to the other.

The grain boundary patterns of the '0' nickel are intense and the brightly emitting region of the boundary is a broad region compared with the sharp, much less intense type of boundary observed with the pure nickel specimens. This difference between the two patterns is so marked that it is quite likely that the two patterns arise because of two different effects. An inspection of the nickel cathode after demounting showed that the surface of the cathode had become marked during the heat treatment. Plate 33 is an optical photograph of a pure nickel cathode. There are a number of features which make a network on the cathode surface which appear of the same form as those seen under the emission microscope. It could be that these structures on the surface of the cathode are the cause of the fine brightly emitting regions in the pure nickel specimens.

The decay of the emission on pure nickel specimens is as with the '0' nickel, not a completely standard process. There is the type of pattern which developes big spots of bright emission, but more usually the grain boundary type of pattern merely fades until even at the maximum temperature available, there is insufficient intensity for visual observation of the emission pattern.

The study of the emission patterns has shown that although there is a tendency for the emission patterns to conform to the general pattern outlined above there have been isolated cases where specimens have shown types of patterns hitherto not discussed. Although these patterns are not consistently produced, there appearance has in some cases helped in the interpretation of the more common patterns. The following chapter deals with these special cases.

Chapter 21 Special effects observed under the emission microscope

21.1 Reversal of the patchwork patterns

On one of the specimens with an 'O' nickel core, a patchwork pattern had been observed. Plate 34 is the emission pattern obtained from a specimen with a coating 13,000A thick heated to 850°C. The patchwork pattern is quite clear. The temperature of the specimen was reduced to 500°C and the specimen left for three days. In order to take the emission photograph the temperature had then to be increased to 900°C. Plate 35 is the photograph which was obtained. A comparison between plate 34 and plate 35 clearly shows that the two plates are of the same portion of the cathode. It is also evident that a change in the relative intensities of the different grains has occurred and one plate is practically a complete negative of the other. This almost complete reversal of intensities of the different grains has only been recorded with these thick film specimens on this one occasion. A similar reversal of intensities was observed by Bruche[1] and also Heidenreich[2].

21.2 Reversal of the grain boundary pattern

The pattern with the grain boundaries showing as brightly emitting regions was found, on some occasions, to fade and at a later stage the grain boundary regions appeared less intense than the surroundings, so that the latter type of picture appeared as a negative of the former. The pattern with the poorly emitting grain boundary regions was generally not very stable. It only occurs at the stage of life of the cathode when the intensity of the emission is very low. Although the pattern is usually visible for about five minutes the intensity is so low that no successful photographs were obtained of any one grain boundary which reversed its intensity. However, plates 24 and 26 show the two different types of grain boundary patterns.

21.3 Reactivation of the coating

Since the emission microscope had been constructed so that the spacing between the cathode and the grid could be varied, it was not long before it was noticed that when the grid accidentally touched the cathode, a very large increase in the emission from the cathode occurred. Touching the cathode with the grid obviously resulted in a reactivation of the cathode.

This method of reactivation could be employed at any time during the life of the cathode and the effects on the emission picture could be observed. The study of these effects has given valuable information concerning the mechanism of the emission from the film cathodes.

If a cathode mounted and processed in the normal way is observed to have given the standard sequence of emission patterns, i.e. the uniform emitting pattern, the patchwork pattern and the grain boundary pattern, then reactivation of the cathode usually results in a repeat of the sequence of patterns. The time for the cathode to return to the state that it was in before the reactivation, is however, considerably less than the time that the cathode took to reach this state by the normal sequence of events. A cathode may for example, after reactivation, pass through all the stages of emission patterns within quarter of an hour compared with the six or so days that it would take for the normal sequence. If a further reactivation is attempted the sequence can again be repeated but in a still shorter time. The cathodes can normally not stand any further reactivation but the thicker the cathode is the more times one can bring about noticeable increases of emission by reactivation in this way.

The most striking result of this observation of the effects of reactivation is the evidence that the type of emission pattern obtained from a cathode depends on the state of activation of the cathode and not on the thickness of the coating.

Previous to the observation of the effects of activation, it may have been argued that the changes in the type of emission patterns obtained during the life of the cathode were due to the gradual evaporation of the barium oxide. The patchwork pattern could then be accounted for on the basis that when sufficient of the coating had evaporated, the conditions were such that the film was a dipole layer and an explanation similar to that given by Heidenreich would then be sufficient. Since, however, the sequence of emission patterns can be repeated merely by activation, it follows that the patterns cannot be explained on the basis of variations in thickness of the cathode coating. It also follows that even when the cathode emission first dies away there must still be a layer of barium oxide on the cathode which can then be reactivated by drawing current.

The observed sequence of emission patterns together with the effects of reactivation which have just been described all appear to be characteristic of the behaviour of the oxide coated cathode prepared by evaporation of the oxide on to the core metal. The behaviour of the cathode appears to be a more complicated sequence of events than that of the monolayer cathodes investigated by Bruche and Heidenreich. The theoretical explanation proposed for the monolayer cathodes cannot be directly applied to the much thicker cathodes at present under consideration and it is therefore necessary to consider an alternative explanation of these emission patterns.

Part 8

THE THEORY OF ELECTRON EMISSION FROM OXIDE COATED METALS

Chapter 22 Metal-semiconductor contacts

22.1 Introduction

In Part 2, where the theory of electron emission from oxide cathodes was considered, no account was taken of the influence of the metal on the emission. From the experimental results of Part 7 it is obvious that the theory is incomplete unless the metal is also considered. It has been shown that a theory of emission can be drawn which considers the oxide coating as a semiconductor. In this chapter the semiconductor model will be further developed to take into account the effect of the metal. The nature of the contact between the metal and the semiconductor must now be considered. Contacts of this kind have been extensively studied in the past in an attempt to provide a theoretical explanation of various forms of rectifying devices. As with the oxide coating theories, a number of models have been postulated and we shall therefore consider some of the more important models of the contact which will lead us to a theory of emission applicable to metals coated with barium oxide.

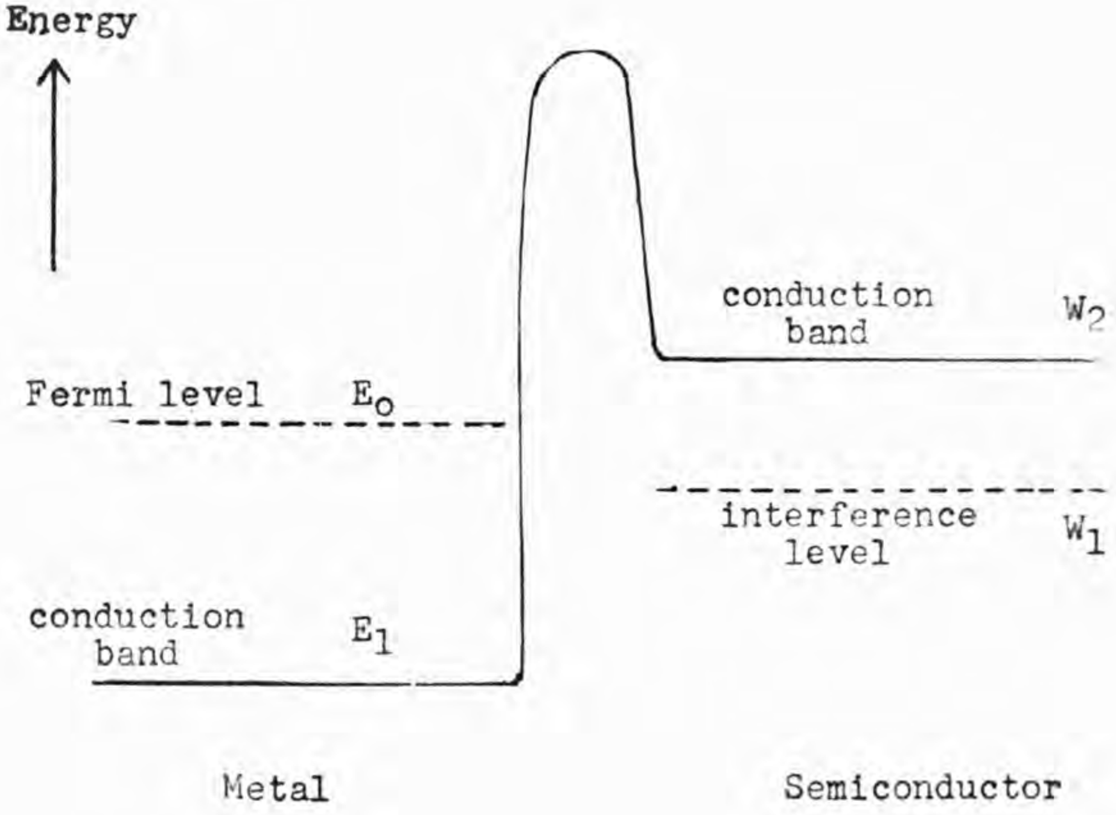


Fig. 17 Plot of the potential energy of a conduction electron

22.2 The Wilson model

The theories of rectification which have been developed are dependent to a large extent on the ideas originally put forward by Schottky[1]. Following the theories of intrinsic and impurity semiconduction given by Wilson[2 & 3] there appeared, independently of one another, due to Nordheim[4], Frenkel and Joffe[5] and Wilson[6], a theory of rectification at metal semiconductor contacts. In the model of the contact used, it was assumed that there was a small gap between the metal and the semiconductor. In equilibrium, the potential energy of a conduction electron as a function of its position in the system is shown in Fig. 17. E_o, the Fermi level in the metal and W_1, the interference level of the semiconductor, are shown as dotted lines. In equilibrium, E_o lies approximately halfway between W_1 and W_2 (see Wilson[6]). When a potential difference is set up between the ends of the combination they assume that a potential V appears across the gap and E_1 and E_o are increased by an amount eV where e is the charge on an electron. The main assumption in assessing the resulting current in the combination is, that the electrons pass through the hump according to the wave mechanical tunnel effect, and on account of the field in the gap, the transmission coefficient of the hump is altered from the equilibrium value and consequently a current flows. The Wilson theory leads to a relation between the voltage V across the gap and the resulting current I which can take the form

$$I = \text{const}\left[\exp\left(\frac{eV}{kT}\right) - 1\right]\exp -aV \qquad (1)$$

where a is a constant which is independent of V and is determined by the shape of the hump. Although the theory predicts a rectifying effect, there seemed to be some doubt as to what would be the direction of easy flow for the current.

For the particular case of a defect semiconductor in contact with a metal the above theory appears to be wrong. In a defect semiconductor, the interference levels are empty levels lying just above the valence band. When electrons gain sufficient energy to pass from the valence band into the interference level, holes are left in the valence band and conduction can then occur in this band. For contacts between defect semiconductors and a metal Mott[7] states that the above theory leads to an easy direction of flow of current in the opposite direction to that experimentally observed. The Wilson theory required a gap with a width of the order of 10^{-7} cm. so that the theoretically predicted curves of I against V would best fit the experimental curves. Mott quotes the experimental result of Waibel[8], who finds interface layers of the order of 10^{-3} cm, as further reason for modification of the above theory.

22.3 The Mott model

Mott[7] proposed a model of the contact which differed from

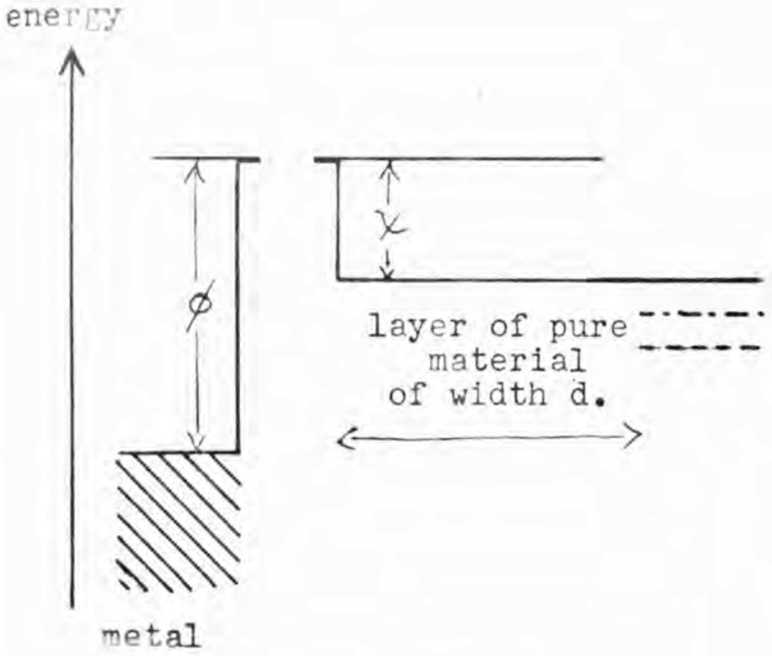


Fig. 18a.

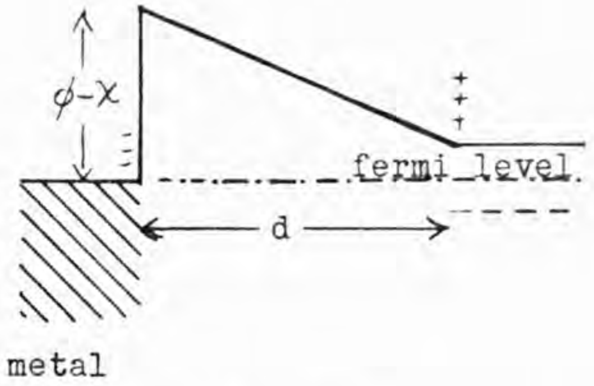


Fig. 18b.

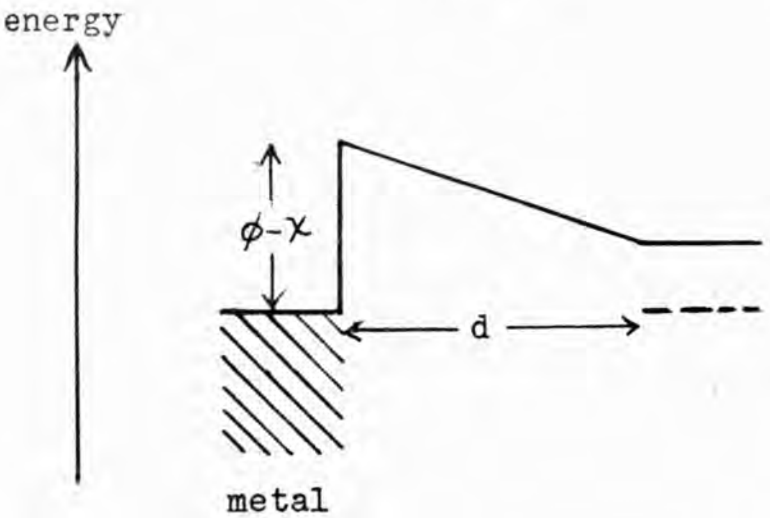


Fig. 18c.

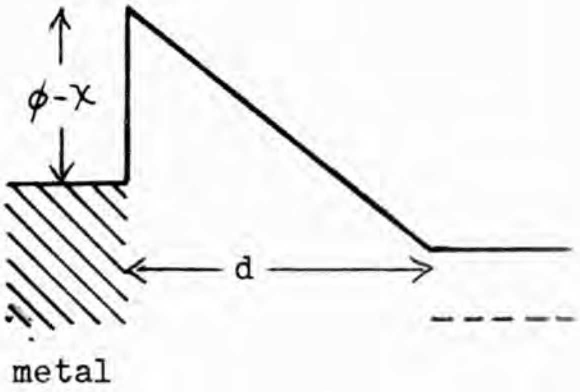


Fig. 18d.

the above model in one respect. Instead of a gap between the metal and the semiconductor he proposed that there was a layer of semiconducting material which differed from the bulk of the semiconductor in that the layer contained no impurities and thus the resistance of the boundary layer would be much higher than that of the bulk semiconductor or the metal. Therefore when a potential difference was applied between the two ends of the combinations, the majority of the p.d. appeared across the boundary layer. This boundary layer could then be assumed to be of the correct order of magnitude to satisfy the experimental results. Mott then assumed, contrary to Wilson etc, that only those electrons with sufficient thermal energy to pass over the hump could pass from one side of the layer to the other.

The energy plot of a conduction electron for this system is shown in Fig. 18. Fig. 18a shows the metal and the semiconductor separated. In Fig. 18b contact is made and the equilibrium condition has been established i.e. the Fermi level is the same throughout the contact. In Fig. 18c the effect of a potential applied to the contact is shown. Fig. 18d illustrates the case for an applied potential of opposite polarity. With this model Mott has obtained an expression for the current through the contact as a function of the voltage across the boundary in the form

$$I \simeq \frac{evn_1}{d}\left(V_0 - V_1\right)\left(1 - \exp\frac{eV}{kT}\right) \qquad (2)$$

where n_1 is the density of electronic states in the metal near the boundary, V is the applied potential, V_0 is given by the relation $\phi - \chi = eV_0$ where ϕ is the work function of the metal and $-\chi$ is the energy of an electron in the lowest state in the conduction band; v is the mobility of electrons in the boundary layer.

The assumption of a high resistance barrier layer is, for the case of a Cu-Cu_2O rectifier, probably a close approximation to the facts. One must enquire more deeply into the reasons for the appearance of such a region in the case of an oxide coated cathode, for even if such a region were present, it would be expected that the excess barium would diffuse into the boundary region and thus remove it. Barriers of high resistance material could be formed by chemical reaction between the core metal and the coating. For example Mutter[9] reports interface layers in commercial oxide cathodes. However, in the cases where there is no chemical reaction, or particular method of forming which would lead to the production of such a barrier, the Mott model of the contact between the metal and the semiconductor is unsatisfactory and an alternative explanation of the production of a potential barrier which will account for the behaviour of the contact, is therefore necessary.

22.4 The Schottky space charge region

Schottky[10] has proposed that when a contact is made between

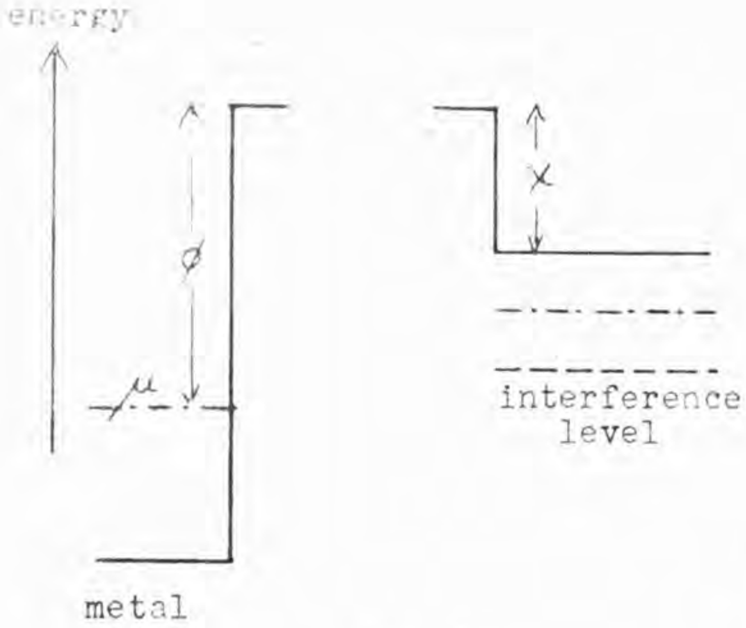


Fig. 19a.

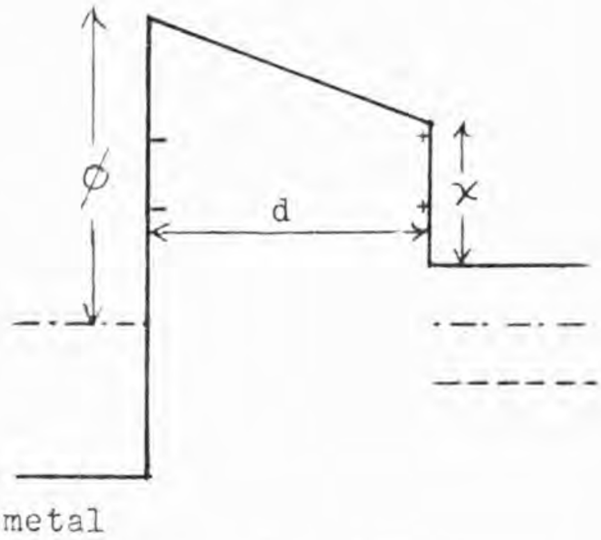


Fig. 19b.

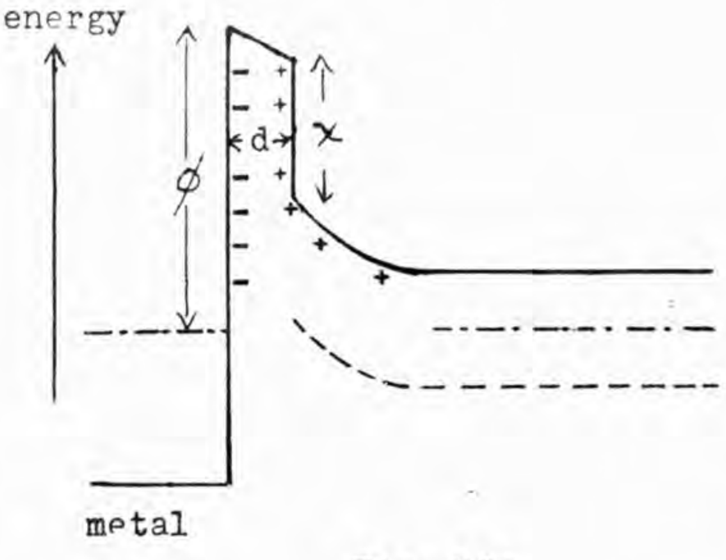


Fig. 19c.

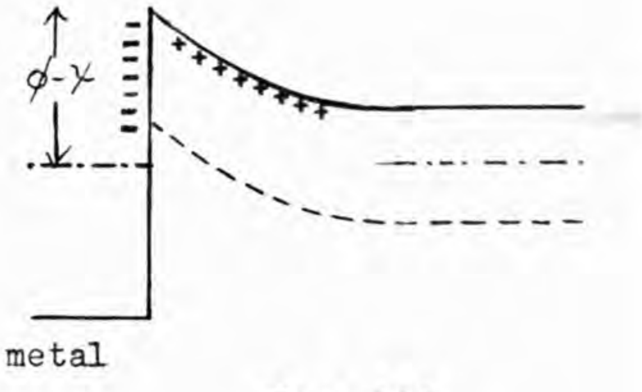


Fig. 19d.

a metal and a semiconductor with differing work functions, a potential barrier arises due to space charge effects.

In Fig. 19a the energy level diagram is shown for the case of an n-type or excess semiconductor separated from a metal by a large distance. An electron in free space must be in equilibrium with both the metal and the semiconductor and thus the potential at their surfaces must be the same. If contact is made between the metal and the semiconductor at some surface not shown in the diagram, then on thermodynamic grounds the chemical potential[11] of the two substances must be the same when thermal equilibrium is maintained[12]; previously it has been assumed that the potential inside the semiconductor was zero, and thus the Fermi level E_0 and the chemical potential μ, being related by the equation

$$\mu = E_0 + eV \tag{3}$$

where V is the potential in the semiconductor, were identical. It is now most convenient to take the zero of potential inside the metal. The energy level diagram will therefore appear as in Fig. 19b when such a contact is made. For large values of the separation d, the field in the gap, arising because of the different potentials of the surfaces, will be small, and the charge necessarily induced on the opposing surfaces will be small. When the gap is decreased, so increasing the field, the charge density increases and the energy level diagram appears as in Fig. 19c. The charge arising in the metal makes very little difference to the density of electrons and the effect on the energy levels is practically negligible. According to Ehrenberg[13] the necessary charge can all be accommodated in a layer at the metal surface of about 1A^0 width. In the semiconductor, where the density of conduction electrons is much less, the charge may have much more noticeable effects. The charge may be distributed over a wider region and appreciably influence the energy levels near the contact.

Various calculations of the potential distribution in the semiconductor have been made taking into account the effect of the space charge. Mott[14] gave a solution which involved making a number of assumptions. A more rigorous treatment has been given by Ehrenberg[13] and will be used here. Consider an excess semiconductor with N interference states per cm^3. The assumption will be made that these states are fully ionised at the temperature considered. If the density of electrons in the semiconductor is n, the charge density in the semiconductor is e(n-N). Let the semiconductor extend from the boundary at $x=0$ to $x=\infty$

Inside the semiconductor we must satisfy Poisson's equation

$$\text{ie} \quad K\frac{d^2V}{dx^2} = -4\pi e(n-N) \tag{4}$$

where k is the permitivity of the semiconductor, and V the potential.

Now the density of electrons in the semiconductor, according to Fermi Dirac statistics can be determined from an equation of the form

$$n = \frac{4\pi(2m)^{\frac{3}{2}}}{h^3}\int_0^\infty \frac{E^{\frac{1}{2}}dE}{\exp\left(\frac{E-E_0}{kT}\right)+1} \qquad (5)$$

As we have already seen this equation can only be solved approximately under certain conditions. It will be assumed that the density of electrons in the semiconductor is such that the condition $\exp\left(\frac{E-E_0}{kT}\right) \gg 1$ applies, *i.e.* $\exp\left(\frac{E+eV-\mu}{kT}\right) \gg 1$. For large negative values of $\frac{eV}{kT}$ the assumption may be invalidated and then metal statistics would have to be used. The assumption is, however, certainly justified if $\frac{eV}{kT}$ is positive which is the case under consideration. In this case the density of electrons is low and the effect of space charge will be greatest. We then obtain

$$n = 2\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}} \exp \frac{E_0}{kT} \qquad (6)$$

where the symbols have there usual meanings.

Now as $x \to \infty$ the effect of the contact will diminish and conditions in the semiconductor will be the same as for a normal piece of semiconductor in bulk. Thus the potential V and also $\frac{dV}{dx}$ will tend to zero as $x \to \infty$; since we assumed the interference states to be fully ionised the density of electrons will tend to N as $x \to \infty$.

Then

$$n_{x=0} - n_{x=\infty} = 2\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\left[\exp\left(\frac{\mu - eV}{kT}\right) - \exp\frac{\mu}{kT}\right] \qquad (7)$$

i.e.

$$n - N = N\left[\exp\left(-\frac{eV}{kT}\right) - 1\right] \qquad (8)$$

Substituting in (4) for (n-N) we obtain

$$\frac{d^2V}{dx^2} = -\frac{4\pi e N}{K}\left[\exp\left(-\frac{eV}{kT}\right) - 1\right] \qquad (9)$$

From this equation the distribution of potential in the semiconductor can be determined in conjunction with the above boundary conditions. As an approximate solution to equation (9) Ehrenberg[13] gives a curve showing the distribution of potential for the case where T=300°C, $N=10^{15}$ and V = 0.6 volts. In this case, for an n-type semiconductor with a positive space charge, the space charge region extends for 11,000A° into the bulk of the semiconductor.

When contact is made between the metal and the semiconductor as in Fig. 19d, the distribution of potential energy of an electron in the conduction band will follow a law of the type given by equation (9) in the vicinity of the contact. The distribution is illustrated in Fig. 19d.

The extent of the space charge region is determined by the number of ionised impurity centres in the semiconductor. In the case of a well activated oxide cathode, which according to Hermann and Wagener[15] contains 10^{19} excess barium atoms per unit volume, the space charge region would extend for a distance of approximately 10A into the semiconductor. This will only be a small fraction of the total thickness of the coating and therefore the space charge region will not effect the properties of the oxide in the region of the oxide to vacuum surface. The work function of the oxide surface will therefore be independent of the nature of the contact. The emission current will therefore be given by one of the expressions derived in Part 2 depending on which model of the semiconductor is used.

Tolpygo[16] has considered the emission from very thin film cathodes. The model he uses for the contact takes into account the effect of space charge. The emission equation which he derives shows that the work function of the coating may under certain conditions be dependent on the contact. If the height $\phi-\psi$ of the barrier in Fig. 19d is such that the space charge induced in the semiconductor would occupy a region of width d, then obviously if the width of the film is less than d, the boundary conditions used to derive the potential distribution, i.e. equation (9), will no longer be valid. Tolpygo has derived the relation between the emission current and the width of the coating for thin film coatings. The work function is found to depend on the thickness of the film.

It has already been pointed out that the width of the space charge region depends on the number of ionised interference states in the semiconductor. Therefore for a fixed width of the coating, the space charge region may or may not extend the full width of the coating depending on whether or not the cathode is well activated. When the state of activation of the cathode is such that the space charge region does extend the full width of the coating then the work function of the coating to vacuum surface will no longer be equal to that of the semiconductor in bulk but will instead be dependent on the space charge. Since the space charge is itself dependent on the difference of potential $\phi - \psi$, it follows that the work function of the coating to vacuum surface will be a function of the work function ϕ of the metal.

In the case of evaporated cathodes it is intended to show in the next chapter that the experimentally observed emission pictures may possibly be accounted for on the basis of the space charge model of the contact between a metal and a semiconductor.

Part 9

PROBABLE MECHANISM OF THE FORMATION OF EMISSION PICTURES

Chapter 23 Emission pictures from cathodes coated by evaporation

23.1 The initial uniform emission picture

It is the opinion of the author that the phenomena which have been observed on cathodes of this kind and which have been reported in Section 7 can best be accounted for on the basis of the semiconductor model of the oxide cathode. The explanation of the various forms of emission pattern will therefore be attempted on the basis of this model and other possible explanations considered later.

It has been seen that providing the specimen is mounted before atmospheric conditions can cause the cathode surface to become crazed, the initial picture obtained from the cathode is one of uniform emission. The uniform picture occurs independent of the method of preparation of the core metal surface, provided the coated specimen has a smooth polished surface. The surface structures due to crazing of the coating or irregularities of the core lead to slight local variations of the emission which can give the spotted pattern initially obtained from exposed cathodes.

It has been pointed out in the previous section, that a fully activated oxide coating on a metal base would be expected to have a work function for the emission of an electron from the coating to the vacuum, equal to that of the bulk semiconductor and the work function would be independent of the metal, providing the cathode was sufficiently well activated and thick enough to contain the space charge region.

According to the results of Aldrich[1], who evaporated barium oxide from molybdenum filaments, the evaporant consisted of 50% BaO and 50% Ba. Although the conditions of evaporation were not identical to those used during the preparation of the coatings, it nevertheless seems reasonable to assume that the coatings will contain an excess of barium. With an excess of barium, on the basis of the semiconductor theory, the coating must be at least partially activated, and thus the fact that an emission picture can be obtained merely by heating the specimen can be explained. If it is now assumed that the activation of the cathode is sufficiently good that the space charge region arising at the interface can be contained in a layer of the coating only a few angstroms thick, then the cathodes, being of the order of $1000A^o$ thick, should emit so that the work function is characteristic of the bulk oxide. With no surface structures to produce local variation of the emission, it would then be expected that the coating would give uniform emission.

23.2 The patchwork pattern

The decay of the early uniformly emitting picture and the subsequent formation of the patchwork pattern has been described above. It has been established that the pattern is dependent on the core metal surface and in agreement with Bruche[2] and Heidenreich[3] it is concluded that the patches correspond to the crystalline structure in the core metal surface.

The results of work with the field emission microscope have shown that the intensity of emission obtained from a metal depends markedly on the crystallographic orientation of the emitting surface. It is also apparent that contamination of the metal by films with thicknesses of atomic dimensions, can cause major differences in the intensity of emission so that strongly emitting regions can, after contamination, become non-emitting. It may therefore be concluded that surfaces with different crystallographic orientations may possess work functions of different magnitude and the magnitude of the work function will be strongly dependent on the nature of the layer in contact with the metal.

In order to explain the formation of the patchwork pattern it is now only necessary to make the postulation that the activation of the cathode has diminished to such an extent that the space charge affects the work function of the coating. Those grains having work functions which differ from that of the oxide by the greatest amount will require the largest amount of space charge to reach equilibrium. Thus the space charge region in front of these grains will extend the furthest into the coating. As the state of activation of the cathode decreases, either due to evaporation of excess barium or poisoning, the space charge regions will gradually spread into the cathode until the widest regions can no longer be accommodated in the coating of the cathode. At this stage the work function of the coating opposite the grains with the highest work function will start to be affected and begin to increase. Since the regions of the coating opposite grains of smaller work function will not yet be affected because the coating is still thick enough to support the space charge region, then there will result patches of the coating, which have differing work functions corresponding in shape and size to the grains at the surface of the core. Therefore the emission will differ from patch to patch and hence the emission picture will consist of patches corresponding in shape and size to the grains of the core metal surface.

With this proposed mechanism for the formation of the patchwork pattern it is obvious that should the cathode be reactivated e.g. by drawing current, then if the activation was sufficient, the emission picture should return to the original uniform picture and then as deactivation proceeds the patchwork pattern should reappear. Thus the theory can explain the experimental observation that the sequence of patterns is repeated by reactivation of the coating.

23.3 The effects of impurities in the core metal

Continuing with the explanation in terms of the semiconductor model, the grain boundary patterns may be accounted for in the following way. It is known that the 'O' nickel contains active impurities which react with the coating to produce free barium. One of these impurities, namely magnesium is particularly effective in this process. According to the phase equilibrium diagram for a Mg-Ni alloy[4] magnesium is insoluble in nickel and above 1080°C it would be possible to obtain an alloy consisting of nickel crystals in a liquid of Magnesium and nickel. On cooling the alloy below 1080°C a solid will form consisting of large grains of pure nickel surrounded by a eutectic matrix of alternate crystals of pure nickel and $MgNi_2$ crystals. Since the concentration of the magnesium is very small the initial primary crystals of the alloy will occupy the majority of the volume of the alloy and the eutectic matrix will most probably appear in small quantities lying between the grains of pure nickel. Thus it will be expected that there will be quantities of magnesium present at the grain boundaries in the surface of the core metal in the form $MgNi_2$ crystals. If we obtain an emission picture from a core coated with oxide we may expect to see the patchwork pattern corresponding to the large grains of nickel. As the state of activation of the cathode decreases, the intensity of the emission would decrease over the surface of the grains. If, however, there is a chemical reaction between the $MgNi_2$ in the grain boundaries and the oxide coating which leads to the production of barium, then there would be a supply of excess barium which could maintain the state of activation of the coating above the grain boundary. The emission current from these regions would therefore be maintained while that from other parts of the cathode would gradually decrease since there is no mechanism for the replacement of the barium lost by evaporation from parts of the coating lying above the pure nickel crystals. In time the emission current from the grain boundary regions would therefore be greater than that from other regions and the grain boundaries will therefore appear as brightly emitting regions in the emission picture. The excess barium may even diffuse through the coating thus activating a region in the vicinity of the grain boundary of greater width than the boundary. In this way the relatively broad intense regions of emission can be explained. The fact that the grain boundary pattern on pure nickel specimens has only fine bright grain boundary patterns, much less intense than those of 'O' nickel specimens lends support to the view that the impurities play an important role in the formation of the pattern on '0' nickel specimens.

It is still necessary to account for the reversal of the grain boundary pattern on '0' nickel specimens. If chemical reactions occur between impurities in the grain boundaries and the oxide coating, then products of the reactions may lead to interface layers at the boundaries. After all the reactions leading to production of excess barium have run to completion due to one or other of the reaction products being exhausted, the activation of the coating in the vicinity of the grain boundary will decrease. Conditions could then arise such that, due to the formation of the interface layers, the work function of the core metal in the region of the boundaries is so much higher than the rest of the core metal surface, that the boundary regions emit with lower intensity than the rest of the surface. The boundary regions would then appear as dark regions in the emission picture.

The observation that fine bright grain boundary patterns occur with pure nickel specimens has yet to be explained. Since the grain boundary pattern on the pure nickel specimens is only obtained after prolonged heating at the highest temperatures available i.e. 1050 - 1100°C it may be that evaporation of the coating has occurred and it is merely surface structures on the core that give rise to the fine grain boundary pattern. It is known that polycrystalline metal surfaces which are originally polished will, after heating, develope grooves at grain boundaries. The theory of the formation of the grooves has been given by Mullins[5 & 6]. The optical picture of the surface of a nickel cathode after use in the emission microscope is shown in plate 33 and the surface structures at the grain boundaries are clearly seen. It has already been established that surface structures can modify the emission. It is therefore possible to account for the fine bright lines seen on pure nickel cathodes as due to surface structures on the cathode. The same kind of structures can form on nickel with impurities[7] but the activation process, since it may give rise to a prolific emission, will probably obscure the surface structure effect. The two forms of brightly emitting grain boundary patterns can thus be accounted for.

23.4 The final emission pattern

The last stage in the emission picture was not at all predictable. In view of the high temperature required to obtain sufficient emission for visual observation of these patterns it is quite likely that the coatings had cracked or even evaporated so that the emission pattern may not be characteristic of a smooth oxide cathode. The conditions of the experiment are so uncertain that there is little point in attempting to explain the various forms of pattern.

23.5 Discussion

In this chapter an explanation of the various stages in the appearance of the emission patterns from cathodes coated by evaporation has been given on the basis of a semiconductor model of the oxide coating. This model appears to be able to account most satisfactorily for the phenomena observed.

The model of Loosjes and Vink cannot be considered as applicable to the evaporated cathode because the pores through which conduction is supposed to occur do not exist. The mechanism of conduction through the oxide must therefore be predominant and therefore it is only of interest to decide the nature of this mechanism.

The de Boer model of the oxide cathode depends on the transfer of electrons from atoms of barium absorbed at internal sites in the coating to ions adsorbed at sites on the surface. A similar argument to that employed in the theory for the semiconductor will lead to the conclusion that on contact with the metal a space charge will accumulate in the coating. A possible explanation for the way in which the space charge occurs in the coating may be as follows. When contact is made between the oxide and the metal the chemical potential of both must be the same. Therefore assuming a work function of the oxide less than that of the metal, electrons will be attracted into the metal leaving the oxide with a positive charge sufficient to maintain equilibrium. It could be assumed that the electrons attracted into the metal are relinquished from absorbed barium atoms. Thus if the number of adsorbed atoms is insufficient to supply the necessary number of electrons a potential gradient will occur in the coating which will affect the potential of the surface between the coating and the vacuum. Fig. 6 showing the potential energy of adsorbed atoms and ions as a function of the distance from the surface will therefore be altered. The shape of the curve for the adsorbed atom would be expected to remain the same. The shape of the curve for the ion will obviously be changed but the final form of the curve is uncertain. Since work must be done in order to bring a positive ion from infinity towards a positively charged surface, the potential energy of the ion should increase with decreasing distance from the surface. If the forces of attraction are sufficiently large to overcome the repulsion due to the electrostatic forces, then it may be possible to obtain a minimum in the curve before the potential rises again at interatomic distances due to repulsive forces of the interacting atoms. If the forces of attraction are not sufficiently great, then no minimum would occur in the potential curve and the condition for adsorbtion of an ion would not exist. If the theory is to explain the effects of space charge on emission, it is essential to assume that a minimum does exist in the potential energy curve.

If then the assumption is made that a potential minimum exists at a small distance from the surface, then an ion can be adsorbed and there will be a certain probability that an atom can form an ion by emission of the electron. The energy required to make the transition will depend on the shape and position of the curve about which we have no details. It can be deduced, however, that since the forces of repulsion have been increased by the amount corresponding to the electrostatic repulsion force, then the minimum of the curve will most probably occur further from the surface. If the de Boer theory is to predict a decrease of emission with the onset of space charge effects, then the curves for the potential energy of an adsorbed atom and ion must be displaced relative to one another in such a way that the value of $\Delta\phi$ will be increased. The de Boer theory can thus only offer an explanation of the patchwork pattern if the shape of the curves happens to satisfy these conditions. There is insufficient evidence to decide whether the de Boer theory is valid in the case of space charge layers. The choice of which theory of the mechanism of emission is correct must therefore still be open to doubt. Friedenstein, Martin and Munday[8] are in favour of the de Boer theory on the ground that there is no experimental evidence to confirm the basic assumption of the semiconductor model that excess barium can exist in the barium oxide lattice due to vacancies at oxygen ion sites. In view of the assumptions that must be made in order that the de Boer theory may provide an explanation of space charge effects there now seems no grounds for favouring the de Boer model. With the success of semiconductor models in other fields, and the ample experimental evidence with simple ionic compounds of the effects of an excess of one of the constituents, the more quantitative theory provided by the semiconductor model seems, at the present time, a more satisfactory approach to the problem of the emission from oxide cathodes.

23.6 Conclusion

The method of coating cathodes by evaporating barium oxide on to polished metal cores has provided cathodes with coating whose widths were intermediate to those of the monolayer cathodes investigated by Bruche[2] and Heidenreich[3], and the conventional cathodes coated by spraying, dipping or other such methods. The work has shown that a semiconductor model of the oxide coating can be used to explain the various forms of emission pattern obtained from all forms of the oxide cathode. The various forms of the emission pattern observed from the cathodes coated by evaporation can be accounted for, on the basis of the semiconductor model, as effects due to the influence of the core metal and its impurities, the state of activation of the oxide coating and the surface structure of the coating. The form of the emission patterns from the smooth cathodes coated by evaporation, confirms the earlier conclusion of Part 5 that surface structures are a cause of irregularities in the emission from oxide cathodes.

The cathode coated by evaporation of barium on to the core is capable of providing a uniformly emitting surface. The precautions that must be taken to attain this end and the relatively poor emission of such cathodes compared with conventional cathodes limit the potential uses of this type of cathode.

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