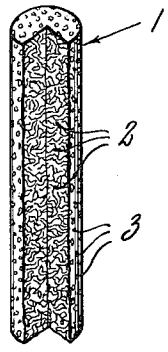
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REFRACTORY BODY OF HIGH ELECTRONIC EMISSION

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REFRACTORY BODY OF HIGH ELECTRONIC EMISSION

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The present invention relates to refractory bodies of high electronic emission and to methods of manufacturing the same. More particularly, it relates to such bodies as are intended for use as cathodes of radio tubes and similar electron discharge devices.

It is quite old in the art to employ cathodes that depend on coating a surface with electron emitting oxides such as thoria or the oxides of the alkaline earth metals—barium, strontium and calcium. Such cathodes may be heated either directly or indirectly and the value of the emission is directly proportional to the extent of the surface coated with the oxides.

A directly heated cathode is generally a filament of thoriated tungsten or it may be a nickel wire or ribbon having alkaline earth oxides coated thereon. Such filaments are great improvements over the pure tungsten filaments for whereas a pure tungsten filament may be heated to incandescence and even then give very small emission of electrons, a thoriated tungsten filament will operate at about 1700° C. and will give a considerably larger emission at that temperature. A nickel wire or ribbon coated with the alkaline earth oxides can be operated at about 700° to 750° C. and gives a very copious supply of electrons.

An indirectly heated cathode generally consists of a thin metal sleeve or tube coated externally with the electron emitting material. Within the sleeve is a heater which usually consists of a wire of tungsten or tungsten alloy. The heater is used only for the purpose of raising the cathode sleeve and the coating thereon to an electron emitting temperature, and no reliance is placed on the heater itself for the emission of electrons.

The cathodes above described which are in general use in the art at the present time are short lived and have a tendency to fall off in emission after a short period of use. In the case of indirectly heated cathodes, the effective surface adapted to carry the electron emitting material is also very small, and it is largely for this reason that the capacity for emitting electrons is very limited and is exhausted within a comparatively short time.

It is an object of the present invention to provide a cathode of refractory metal such as tungsten or molybdenum that depends for its electron emission on the surface coating of electron emitting materials, but which has an effective coated surface many times greater than that of the ordinary cathode of this type. Assuming, for instance, that the cathode of the present invention is tubular or sleevelike in form and that it has a diameter and length no greater than that of the type of such cathodes at present in use, it will have a considerably greater effective surface for the reason that it is porous or foraminate in structure and that not only the external surface of the tube or sleeve carries a coating of the electron emitting material, but this coating extends to the surfaces of the pores or foramina within the metal of the sleeve itself so that there is a considerable reservoir of electrons capable of being drawn upon through a very long period of operation. The effective surface of the sleeve of the present invention, therefore, includes not only the external surface thereof but the surfaces of the pores or foramina extending throughout the whole structure. The electron emitting material, as a matter of fact, is carried within and throughout the metal composing the sleeve.

The single figure of the drawing is a perspective view.

The structure thus described is not comparable to the structure of a thoriated tungsten filament, for instance, where also the electron emitting material is contained within the body of the filament, for in this latter case the electron emitting material is located in the crystal boundaries making up the filament, and it only slowly distils to the surface and gives rise to a very limited emission of electrons. In the case of the cathode of the present invention, the electron emitting materials are already on the surface and this surface extends into and throughout the body of the cathode in such a manner that it is at all times available for the emission of electrons in a large volume and continuous flow.

Where electron emitting materials have heretofore been incorporated into a tungsten cathode, it has always been considered that it is essential that electron emitting material should be introduced into the tungsten before it is sintered, and it is generally added to the tungsten oxide before reduction to metal powder and before forming the ingot which is later mechanically worked or drawn.

The method of the present invention departs radically from this procedure. Refractory metal powder, for example, tungsten or molybdenum powder, is mixed with a binder such as paraffin dissolved in carbon tetrachloride in a manner hereinafter described, pressed in a die to the form of a rod, and then heated in a furnace in an atmosphere of hydrogen at low temperature but sufficiently high completely to volatilize and

drive out the paraffin, care being taken to avoid decomposition or carbonization of the paraffin. The temperature is then raised sufficiently to cause partial sintering or pre-sintering of the body. The result is a rod which is extremely porous and this body is then soaked in an aqueous solution of the nitrate of one or more of the alkaline earth metals or thorium nitrate, until the limit of absorption is reached. The piece is then dried in the air to evaporate the water and the result is a porous body of tungsten having nitrate uniformly distributed through the mass. This body is then heated in a hydrogen furnace at a temperature just high enough to reduce the nitrate to the oxide, and when this process is complete, the temperature is then raised to a temperature of approximately 1500° to 2000° C. During this heat treatment a considerable shrinkage in volume takes place and the result is a strong, dense, refractory body, thoroughly impregnated with the emissive oxides. The material may also be formed into a tube, sleeve, or other shape according to the form of cathode desired or according to whether a directly heated cathode or indirectly heated cathode is to be employed.

The porosity of the refractory metal body, up to the time that it has been impregnated with the electron emitting materials, is a feature of great importance in the invention. I may, however, form this porous body of the hard dense alloy disclosed in copending application Serial No. 460,226 of Kurtz and Williams. According to the method therein described and claimed, the hard dense tungsten alloy of the aforesaid application is formed into a porous or foraminate body in the following manner:

Purified refractory metal powder, such as tungsten, having a particle size of approximately from 1 to 25 microns, is combined with a small but effective amount of powdered metals that result in the alloying, bonding and densifying of the ultimate body to be formed without mechanical working. The alloying, bonding and densifying metal mixture is first prepared by thoroughly mixing and ball milling approximately equal proportions by weight of pure finely divided nickel powder and pure finely divided platinum powder. Platinized nickel powder containing approximately 50% by weight of platinum, made by shaking nickel powder in a solution of chlorplatinic acid, may be used.

Then approximately ½% by weight of this prepared mixture is added to finely divided tungsten powder of a particle size of 1 to 25 microns, and is thoroughly mixed therewith. It may be ball milled for a period of several hours or at least long enough to insure the uniform distribution of the small amount of alloying powders throughout the mass of tungsten powder. This mixture of metal powders is then thoroughly mixed with a bonding material, such as paraffin dissolved in carbon tetrachloride, and the whole is then formed into the shape desired for the final cathode body in a die or other known manner. When so formed, the body is heat treated to a temperature sufficient to volatilize the bonding material and drive it out of the body without leaving any carbon residue.

The temperature is then increased to a presintering temperature of about 800° to 1200° C. and the result is an exceedingly hard, dense metal structure of foraminate or sponge-like type characterized by numerous intercommunicating channels or pores. This foraminate body is then soaked in an aqueous solution of thorium nitrate or of nitrates of one or more of the alkaline earth metals such as barium, strontium and calcium, or a mixture of two or more of these.

The invention will be more clearly understood by reference to the drawing which represents a wire of the invention, greatly enlarged, with a portion cut away to show the foraminate structure.

In the drawing, 1 represents the wire or filament. In the interior of the filamentary body, passages 2 are shown intercommunicating with each other and coming out on the surface as holes or pores 3. In the finished body the electron emitting oxides are deposited within the foramina or passages of the interior as well as on the surface thereof.

Instead of soaking the body in the nitrate solution, the nitrate may be added by slowly pouring the solution drop by drop upon this porous intermediate body until a desired measured amount has been completely absorbed or until the porous tungsten body has absorbed the nitrate solution to its full capacity. The piece is then dried in the air to evaporate the water and at this stage the nitrate is distributed throughout the pores of the entire piece as a dry film. The body is then heated in a hydrogen furnace at a temperature just sufficient to decompose the nitrate to the oxide, and when this conversion is complete the temperature is raised to a temperature of approximately 1500° to 2000° C. A very considerable shrinkage takes place and the body becomes a strong, porous body of hard dense metal, thoroughly impregnated with the electron emitting oxides.

Instead of the above described tungsten, nickel, platinum alloy, an alloy consisting of 99% of metal of the group consisting of tungsten and molybdenum, 0.25% of nickel, 0.25% of beryllium and 0.50% of platinum may be employed, the same being formed into the porous or foraminate body in the same manner as above described. It will be further understood that in specific examples above given which illustrate the invention by the tungsten metal specifically, molybdenum may be used instead of tungsten, the procedure and temperatures specified being the same.

It will be apparent that in the manner hereinabove described, electron emitting bodies either of the directly heated type or of the indirectly heated type may be formed as desired.

Having thus described my invention, what I claim is:

1. Refractory body having high electronic emission when heated consisting of refractory metal of the group consisting of tungsten and molybdenum and their alloys of foraminate structure coated with electron emitting oxides both on the external surfaces and on the surfaces of the foramina of said body.

2. Refractory body having high electronic emission when heated consisting of tungsten metal of foraminate structure coated with electron-emitting oxides of alkaline earth metals both on the external surfaces and on the surfaces of the foramina of said body.

3. Refractory body having high electronic emission when heated consisting of tungsten metal of foraminate structure coated with thorium oxide both on the external surfaces and on the surfaces of the foramina of said body.

4. Refractory body having high electronic emission when heated consisting of hard dense

tungsten alloy of foraminate structure coated with electron emitting oxides both on the external surfaces of said body and on the surfaces of the foramina within the same.

5. Refractory metal body having high electronic emission when heated which comprises an alloy consisting of 99.5% of metal of the group consisting of tungsten and molybdenum, 0.25% of nickel and 0.25% of platinum; said alloy body having a foraminate structure and a coating of electron emitting oxides both on the external surfaces of said body and on the surfaces of the foramina within said body.

6. Refractory metal body having high electronic emission when heated which comprises an alloy consisting of 99% of metal of the group tungsten and molybdenum, 0.25% nickel, 0.25% beryllium, and 0.50% of platinum; said alloy body having a foraminate structure and a coating of electron emitting oxides both on the external surfaces of said body and on the surfaces of the foramina within said body.

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