Oct. 26, 1937. M. F. JAMESON 2,097,157

ELECTRON EMITTING CATHODE AND METHOD OF DEVELOPING SAME

Filed March 9, 1935

FIG. 1

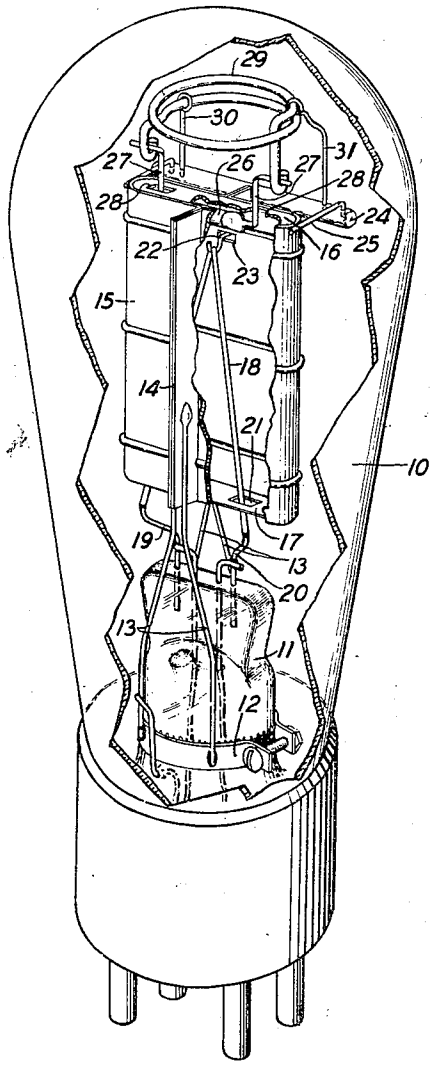
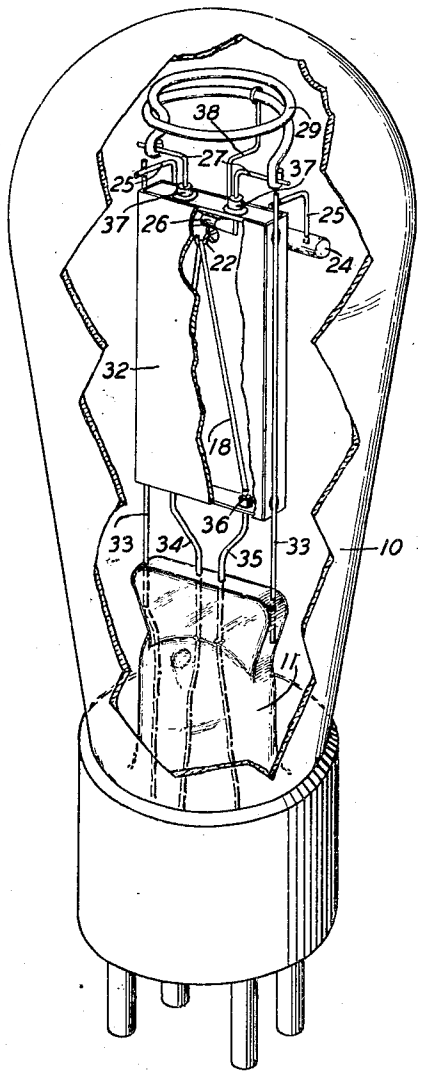


FIG. 2



INVENTOR
M. F. JAMESON

BY

Walter C. Kiesel
ATTORNEY

Patented Oct. 26, 1937

2,097,157

UNITED STATES PATENT OFFICE

2,097,157

ELECTRON EMITTING CATHODE AND METHOD OF DEVELOPING SAME

Malcolm F. Jameson, Chatham, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application March 9, 1935, Serial No. 10,237

15 Claims. (Cl. 250—27.5)

This invention relates to electron emitting cathodes of the complex coating matrix type and to methods of developing the electronic activity of such cathodes.

An object of the invention is to attain a stable combination matrix for cathodes.

Another object of the invention is to form the cathode under conditions which are reproducible and controllable.

In accordance with certain aspects of this invention the electron emitter or cathode comprises a suitable core material or surface having a coating matrix including an electronically active metal, for instance, an alkaline earth or rare earth metal, such as barium or cerium, a depository or carrier metal which combines with or alloys with the active metal, such as zirconium or nickel or both, and an inert spongy refractory material, such as zirconium oxide alone, or associated with an oxide of the active metal, for instance, barium oxide. This class of compositions is suggestive of many workable permutations which are possible as direct analogs and corollaries from an understanding of the basic elements of the invention.

The methods of preparing the cathodes in accordance with this invention are fundamentally concerned with the deposition of the active metal on and in the coating matrix of the cathode in a high concentration of the vapor of the active metal within the confines of a relatively closed receptacle. In a specific application of the invention the cathode is in the form of a ribbon which is mounted in a box-like metallic anode which also encloses a pill or capsule containing the active metal, either in a pure state or as a compound associated with a reactive material, the capsule being supported by a wire loop which is mounted outside of the anode. The cathode is initially provided with a spongy matrix or coating, such as zirconium oxide or a combination of the oxide with finely divided metal, such as nickel particles dispersed throughout the oxide. The electrode assembly is enclosed in a vessel and the vessel evacuated to secure a high vacuum. The capsule is then flashed by high frequency induction heating and the active metal is evolved as a vapor which is concentrated in the limited area of the anode enclosure. The pressure of the vapor in the enclosure may be easily controlled to effect various chemical reactions in the coating matrix. For instance, the anode and cathode may be heated and the active metal vapor diffused through the spongy matrix to form a supply of active metal in the coating matrix and on the surface thereof.

A feature of the invention relates to a coating matrix of the spongy separating oxide and a reducible compound from which the depository metal is derived, the compound being reduced during the activating period by the active metallic vapor.

A further feature of the invention relates to a reaction process in which the active metallic vapor reacts with some of the spongy separating oxide under the influence of a bombarding arc to create a carrier metal in the matrix which combines with the active metal and forms a reservoir supply of active metal for replenishing the surface layer of active metal dissipated during operation.

These and other features of the invention will be explained in more detail in the following description which, in conjunction with the accompanying drawing, sets forth the manner in which the invention may be practiced.

Fig. 1 is a perspective view of a discharge device showing one form of the electrode structure to attain the results of this invention.

Fig. 2 is a perspective view of a device embodying a modified electrode structure similar to Fig. 1.

In practicing this invention, a wide variation of control may be realized since it is possible to obtain comparatively stable combination matrices on the cathodes by varying the procedure of activation. In order to comprehend the capabilities of this invention, the general scope of the procedure will be revealed, followed by more detailed disclosures including particular structural assemblies for obtaining the results of this invention.

The methods for producing the combination matrix cathodes of this invention may be classified into two general groups. In the first group are the procedures in which the active metal does not react with the refractory oxide matrix, while in the second group the conditions will cause a reaction between the active metal and the refractory oxide. In the non-reactive group the methods may be practiced as follows: The depository metal may be combined in the coating material in finely divided metallic form and thoroughly dispersed throughout the refractory oxide matrix when in place on the cathode core. The coated cathode is mounted in an evacuated vessel and the active metal is flashed from a pill enclosed in a box-like anode adjacent the cathode, the active metal being deposited on and diffused

through the matrix where it alloys with or otherwise combines with the depository metal.

In another form, the depository metal may be introduced into the coating mixture as an easily reducible salt or compound and after fixation on the cathode, the compound is decomposed to the oxide by heating the cathode. The oxide may be reduced by introducing hydrogen into an evacuated vessel in which the cathode is mounted, to form the fine particle sized depository metal in the refractory matrix. The active metal is then flashed to diffuse the active metal into the matrix to combine or alloy with the depository metal. In the final form of this group, the intermediate hydrogen reduction may be eliminated and the reduction of the easily reducible salt or oxide may be produced directly by a reaction with the active metallic vapor. The only difference in the final product of the matrix of these procedures occurs in the last instance in which an oxide of the active metal results from the reaction. This oxide merely becomes dispersed through the matrix and serves the same purpose as the refractory mass which is present in the matrix.

In the second group, the active metallic vapor reacts with the refractory mass to produce a supply of depository metal in the matrix. In the first variation of this group, the coating matrix consists exclusively of the refractory oxide mass, such as zirconium oxide. The coated cathode is sealed in an evacuated vessel also containing a box-like anode and the active metal pill. The active metal is flashed and the temperature conditions so controlled to produce a chemical reaction between the active metal and the refractory zirconium oxide and yield finely divided and highly dispersed free metallic zirconium throughout the refractory mass. The free zirconium metal then acts as the depository metal which, during the reaction period, combines with the active metal.

As additional ramifications of the second group, the coating matrix may contain free depository metal along with the refractory mass in which case two depository metals occur in the product, or, as in the first group, the depository metal may be introduced as a reducible salt which either may or may not be reduced by an intermediate hydrogen reduction step. In all the variations of the second group, an oxide of the active metal occurs in the complex matrix.

The procedure as applied to a specific case may be practiced in accordance with this invention by activating the cathode in a structure as shown in Fig. 1. This structure embodies a rectifier type discharge device comprising an enclosing vessel 10 having a stem 11 which carries a metallic band or collar 12. A plurality of wire braces 13 are attached to the collar and extend in converging pairs to flanged portions 14 on opposite sides of a flattened cylindrical anode 15 which is closed at opposite ends by plate inserts 16 and 17 to form a box-like enclosure. The cathode of the rectifier may be formed of a ribbon filament 18 which is coated with zirconium oxide with a paste binder, or a mixture of zirconium oxide and nickel carbonate applied as a water paste and dried on the filament. This coating forms a porous or spongy matrix for the reception of the active metal.

The filament 18 with the coating matrix thereon may be formed into an inverted V-shape and mounted within the anode 15 by connecting the ends to a pair of leading-in wires 19 and 20 in the stem with the legs of the filament passing through apertures 21 in the plate insert 17. The bight of the filament is supported by a hook 22 which extends through an aperture 23 in the side wall of the anode 15 near the top thereof. The hook 22 projects from a central point of an elongated glass bead 24 which is supported to the rear of the anode 15 as viewed in Fig. 1, by angular shaped wires 25 at each end, the wires being welded to the upper corners of the anode.

A capsule or pill 26 is enclosed within the anode 15 and is provided with angular shaped terminations 27 which project through apertures 28 in the plate insert 16. The capsule 26 is formed of a light, high resistance metal, such as molybdenum, with pinched ends to seal a slug of pure active metal, such as barium, or a reaction pellet of a mixture of aluminum and barium oxide or zirconium and barium oxide. The capsule 26 is joined to the ends of a heavy wire loop of low resistance material, such as copper, by clamping the ends around the terminations 27 of the capsule. The copper wire loop is supported by a pair of wire supports 30 and 31 which project from the bead 24. The loop 29 forms a secondary winding in which induced currents may be generated from a primary coil placed outside the vessel 10, to produce high frequency heating of the loop in a manner as disclosed in an application to C. H. Prescott, Jr., Serial No. 474,441, filed August 11, 1930.

In applying the methods of this invention in accordance with the structural assembly as shown in Fig. 1, the different complex coating compositions may be realized from the original compositions applied to the cathode core and the control of the pressure of the active metallic vapor, such as barium, in the enclosed anode of the device. For instance, if the filamentary cathode 18 is originally coated with a spongy matrix of zirconium oxide, it is possible to obtain several distinct complex end products in the matrix merely by varying the procedure of activation since the chemical reaction between the matrix and the active metal is reversible in accordance with the reaction $Ba+ZrO \rightleftharpoons BaO+Zr$ for which the equilibrium relation becomes $K=(\text{pressure of barium})^2$ where the constant K depends only on the temperature. The direction of the reaction is thus seen to be controlled at any given temperature by the pressure of the active metal.

In following a specific procedure let it be assumed that it is desired to obtain a simple activated filament in accordance with the first group of this invention, namely, a stable filament in which the active metal does not react with the refractory oxide material. The electrode unit is sealed into the vessel 10 and while still on the pumping station, the vessel is baked in an oven at a temperature of 400° C., to remove water vapor and easily removable deleterious matter from the glass and the electrode assembly after which the vessel is evacuated, in a well-known manner, to secure a high vacuum. The filament 18 is heated to a normal temperature and the capsule or pill 26 is heated by high frequency current, to induce a strong heating effect in the loop 29, but since this loop is formed of low resistance material and the pill 26 of high resistance material, the pill becomes the hottest section of the series circuit. If the pill 26 contains an active metal slug, such as barium, the barium is evolved from the pill as a vapor, which, because of the confined space of the anode and the heating of the anode to a temperature of 500° C. or higher by the high frequency induction effect, produces the barium

vapor in a highly concentrated form and at a suitable pressure in the confined volume of the anode around the filament 18. The barium vapor is projected into the porous zirconium oxide matrix by straight diffusion to activate the filament by supplying a source of electronically emissive metal in the spongy matrix which retains the supply of active metal.

The same filament may be activated in accordance with a procedure in the second group by a supplemental step at the time of diffusion of the barium from the pill. In this method a bombarding arc is produced in the barium vapor by applying an ionizing potential to the anode, the arc facilitating the reaction between the barium and zirconium oxide by increasing the pressure within the anode, due to the rise in temperature to approximately 800° C. During the reaction some of the zirconium oxide is reduced to metallic zirconium according to the formula recited above. The metallic zirconium is dispersed throughout the spongy matrix and readily combines with the active barium metal in some manner not positively known, although it is believed it forms an alloy therewith or retains the barium as an adsorbed film or layer on the metallic zirconium particles. The zirconium metal, therefore, serves as a depository metal for the active metal, to replenish the supply on the surface which is the primary source of electrons in the operation of the device.

In a similar manner, the activation method of this invention may be utilized in processing a filament of the spongy matrix type in which a reducible salt or compound is incorporated in the coating matrix. For instance a proportional amount of nickel carbonate may be added to the zirconium oxide mixture and dried on the filament prior to mounting it in the vessel. The compound or salt may be decomposed by heating the filament, to convert the carbonate to oxide which is later reduced to metallic nickel by introducing hydrogen into the vessel, the metallic nickel being finely divided and well dispersed throughout the zirconium oxide, to serve as a depository metal in the matrix. By flashing the pill by high frequency while heating the anode a high pressure of barium vapor is developed in the anode and the vapor diffuses through the oxide to form an alloy with the free nickel in the matrix and also forms an adsorbed film or atomic layer on the surface of the oxide mixture. The above procedure may be varied by increasing the vapor pressure of the barium in a bombarding arc, the temperature being approximately 1100° C., to provide two dissimilar depository metals in the oxide matrix, namely, nickel and zirconium, to increase the reservoir of free active metal in the spongy matrix. It should be understood, as previously explained, that in this procedure a proportional amount of the oxide of the active metal, for instance, barium oxide, will be present in the matrix as a reaction product of the barium and zirconium oxide, but this oxide is substituted for the original zirconium oxide which it replaces and forms a separating component of the matrix.

Similarly, the intermediate hydrogen reduction step may be obviated and the nickel oxide directly reduced to metallic form by a reaction with the barium vapor generated in the enclosed anode space so that the reaction may be selectively instituted depending on the combination desired in the complex matrix of the filament.

The filamentary cathode matrix coating then comprises free metallic barium or barium alloyed or otherwise associated with metallic nickel or metallic zirconium, or both, dispersed through the remaining zirconium oxide or zirconium oxide and barium oxide, with an atomic layer of free barium adsorbed upon the surface of the spongy matrix of the coating. These complex matrices result in various final stable electron emitters which will have extensive life, due to the accumulation of reserve active material in the coating matrix. Furthermore, the cathode of this invention is easily reproducible and the many combinations may be attained by controlling the vapor pressure of the barium or active metal within the confines of the box-like anode.

While the above procedure have been described in connection with a pill containing a pure metal slug of barium it is to be understood that the active metallic vapor may be produced from various reaction mixtures, such as aluminum and barium oxide or zirconium and barium oxide. Furthermore, the active metal, in accordance with this invention need not be limited to barium since other alkaline earth metals or rare earth metals or compounds may be substituted for the barium or its compound. Similarly, the depository metals and the refractory spongy matrix material may comprise other substances which serve the same purpose, for instance, iron, tin, chromium or cobalt or other similar stable metals may be substituted for the nickel in the coating compositions, either as pure metals or as easily reducible compounds or salts and the zirconium oxide may be replaced by other highly refractory materials, such as aluminum oxide, chromium oxide and silicon dioxide. When silicon dioxide is employed as the spongy matrix material, the reaction with the active metal vapor may produce a deposition material in the matrix, such as barium adsorbed on silicon or a compound such as barium silicide.

In the structure shown in Fig. 1 it will be noted that the legs of the filament and the terminations of the pill extend through apertures in the enclosing anode. The pressure of the active metal may be controlled more positively by a construction as shown in Fig. 2 in which a box-like anode 32 is supported from the stem 11 by upright wires 33 which also support the bead 24 by the angular wires 25. A pair of leading-in wires 34 and 35 extend from the stem and project into the anode 32 through two insulating bushings 36 and are attached to the legs of the ribbon filament 18. The hook 22 extends from the bead through a small aperture in the side of the anode similar to Fig. 1, and the capsule or pill 26 is supported within the anode by the terminations 27 which extend through two insulating bushings 37. The heavy copper wire loop 29 is supported in position above the anode structure by the terminations 27 of the pill and a single bent wire 38 which extends from the bead 24. In this arrangement the pressure of the barium vapor may be more easily maintained since the anode forms a completely closed structure except for the small opening through which the filament hook extends.

The structures of this invention as shown in Figs. 1 and 2 are intended to be utilized as rectifiers after the activation process is completed on the filament matrix and are intended to show examples of the construction of the device in accordance with this invention. However, it is apparent that an amplifier may be used for the same purpose merely by constructing the assembly to include one or more grids suitably insulated

from the anode to perform their function in operation after the activation process is completed on the filament. Therefore, in construing the scope of the appended claims, they should be interpreted to cover the various disclosures of the specification.

What is claimed is:

1. A composite matrix coating for an electron emitting surface comprising a mixture of an inert refractory separating oxide, an active earth metal, and a repository metal less volatile than said active metal distributed throughout the refractory oxide and alloyed with said active metal, said refractory oxide being an oxide of said repository metal.

2. A composite matrix coating for an electron emitting surface comprising a mixture of an inert mass of zirconium oxide, barium and strontium oxides scattered throughout the mass of zirconium oxide, finely divided particles of metallic zirconium dispersed throughout said oxides, and a supply of free barium associated with said metallic zirconium within said matrix.

3. A method of producing an active electron emitting cathode which comprises coating a suitable cathode support with a refractory oxide of the fourth group, placing said cathode within a box-shaped anode in an evacuated vessel, partially reducing the refractory oxide in a concentrated vapor of an active earth metal at a high pressure restricted to the space within said anode, and depositing the earth metal upon said cathode.

4. A method of producing an active electron emitting cathode which comprises coating a suitable cathode member with a mixture of a refractory oxide and a compound of a metal of the eighth group, placing said cathode within a confining enclosure in an evacuated vessel, reducing the compound of the eighth group to metallic form, and vaporizing a free earth metal in a high pressure area for the deposition of the free earth metal upon the cathode, the vapor being concentrated within the confining enclosure.

5. A method of producing an active electron emitting cathode which comprises coating a suitable cathode member with a mixture of a refractory and a finely divided metal of the eighth group, placing the cathode in an evacuated vessel, and activating the cathode in a high pressure of active metal vapor in such a manner that some of the active metal is alloyed or associated with the metal of the eighth group.

6. A method of producing an active electron emitting cathode which consists in coating a suitable cathode member with a mixture of zirconium oxide and finely divided metallic nickel, placing said cathode in an evacuated vessel, and depositing metallic barium condensed from barium vapor generated in a confined area upon said cathode.

7. A method of producing an active electron emitting cathode which comprises coating a suitable cathode member with a mixture of zirconium oxide and nickel carbonate, placing said cathode in an evacuated vessel, decomposing the carbonate to oxide by heating the cathode, reducing the nickel oxide to metallic nickel by heating the cathode in hydrogen, generating barium vapor at a high pressure, and diffusing the barium vapor into the cathode to alloy with or adsorb upon the finely divided nickel within the matrix of the coating.

8. A method of producing an active electron emitting cathode which comprises coating a suitable cathode member with a mixture of zirconium oxide and nickel carbonate, placing said cathode within a confining anode in an evacuated vessel, decomposing the nickel carbonate to oxide by heating the cathode, reducing the nickel oxide to metallic nickel by heating in hydrogen, generating free barium vapor in said anode, and propelling the barium vapor into the cathode coating mixture by the action of a bombarding arc between said cathode and anode, thereby causing a reaction between some of the barium and some of the zirconium oxide to form a reservoir of barium alloyed with or adsorbed upon the finely divided nickel and zirconium dispersed throughout the matrix of the coating.

9. A method of producing an active electron emitting cathode which comprises coating a suitable cathode member with silicon dioxide, placing said cathode in an enclosing anode, mounting the assembly in an evacuated vessel, generating metallic barium by high frequency heating from a pull enclosed in said anode, diffusing the barium vapor under the influence of a bombarding arc into the cathode coating, thereby causing some of the barium to react with some of the silicon dioxide to form metallic silicon or a silicide of barium or both and barium oxide, and combining the metallic barium with the metallic silicon or by-product dispersed throughout the coating matrix.

10. An electron discharge device comprising an evacuated vessel, an electrode assembly therein including an electron emitting cathode, an anode completely enclosing said cathode, insulating bushings in one end of said anode for the terminations of said cathode, a metallic helix situated exterior to the other end of said anode, said helix having extensions projecting into said anode, insulating bushings separating said extensions from said anode, a metallic receptacle connected to said extensions, and an activating substance enclosed within said receptacle.

11. A method of producing an electron discharge device which comprises enclosing a cathode having a refractory coating matrix in an anode structure, supporting a metallic receptacle containing an electron activating substance within said anode, connecting said receptacle to a metallic helix situated outside the anode, enclosing the assembly in an evacuated vessel, generating a vapor of the activating substance by heating the metal receptacle by high frequency current induced in the metallic helix, controlling the pressure of the vapor of the activating substance confined in the enclosed anode structure, and causing some of the activating substance to diffuse through the cathode coating material to become associated therewith and form a reservoir of active material dispersed through and adsorbed on the coating.

12. A method of producing an electron emitting cathode which consists in coating a suitable cathode core with a highly refractory oxide of the fourth group and a finely divided metal of the eighth group of the Periodic Table, mounting said coated cathode in a metallic closed anode receptacle within an evacuated vessel, inserting a capsule containing an active earth metal within said anode receptacle adjacent said cathode, vaporizing said active metal, heating said anode to a temperature between 500° C. and 1100° C. to create a high pressure in the vapor within said anode, diffusing said active metal vapor into said refractory oxide to convert some of the oxide to metallic form, and depositing said active metal on said refractory metal and the metal of the

eighth group to serve as a reservoir of active metal for replenishing the surface supply of active metal.

13. A method of producing an electron emitting cathode which comprises coating a suitable cathode core with a highly refractory oxide of the fourth group and a finely divided metal of the eighth group of the Periodic Table, mounting said coated cathode in a closed metallic anode receptacle within an evacuated vessel, inserting a capsule containing an active earth metal within said anode receptacle adjacent said cathode, heating said capsule to vaporize said active metal, heating said anode to a temperature of 800° C. to diffuse the active metal vapor into said refractory oxide, and depositing said active metal on said metal of the eighth group to serve as a reservoir of active metal for replenishing the surface supply of active metal.

14. A method of producing an electron emitting cathode which comprises coating a suitable cathode core with a highly refractory oxide of the fourth group of the Periodic Table, mounting said coated cathode in a closed metallic anode receptacle within an evacuated vessel, inserting a capsule containing an active earth metal within said anode receptacle adjacent said cathode, heating said capsule by high frequency induction to vaporize said active metal, applying a potential to said anode for producing a bombarding arc in the active metal vapor, simultaneously converting some of the refractory oxide to free metal and some of the active metal to an oxide at the reaction temperature, and combining the active metal with the converted refractory metal within the matrix.

15. An electron emitting cathode having a complex matrix comprising a highly refractory oxide mass, finely divided particles of a free repository metal commingled throughout said mass, and a free earth metal associated with said particles and forming an atomic layer on the surface of said oxide mass.

MALCOLM F. JAMESON.