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TUNGSTEN DISPENSER CATHODE HAVING EMISSION ENHANCING
COATING OF OSMIUM-IRIDIUM OR OSMIUM-RUTHENIUM
ALLOY FOR USE IN ELECTRON TUBE
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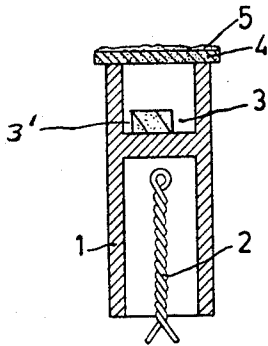


FIG. 1

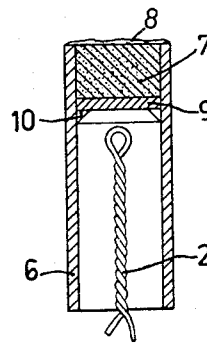


FIG. 2

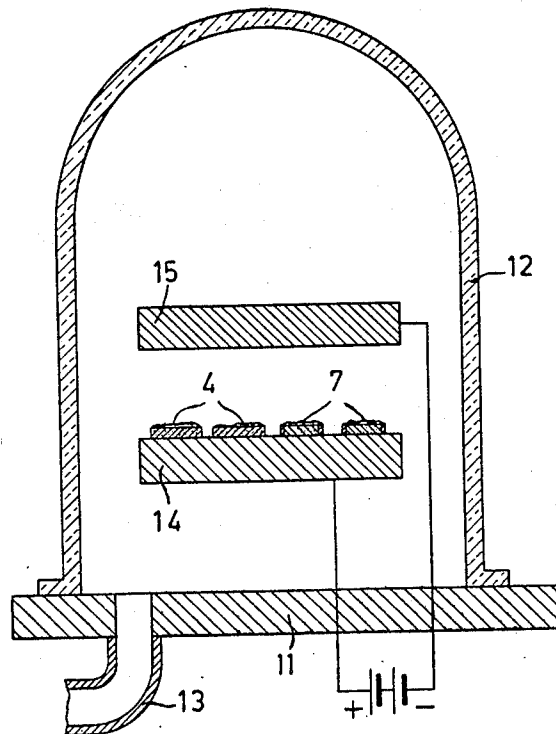


FIG. 3

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TUNGSTEN DISPENSER CATHODE HAVING EMISSION ENHANCING COATING OF OSMIUM-IRIDIUM OR OSMIUM-RUTHENIUM ALLOY FOR USE IN ELECTRON TUBE

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Int. Cl. H01j 1/14, 19/06

U.S. Cl. 313—346

6 Claims

ABSTRACT OF THE DISCLOSURE

An improved coated dispenser-type cathode comprising a metal matrix of tungsten or tungsten-molybdenum in reactive relationship with an alkaline earth metal compound which will supply barium or barium oxide to the emitting surface of the matrix. The matrix emitting surface is coated with a thin porous layer of an alloy of osmium and iridium or osmium and ruthenium to provide longer cathode lifetime and less danger during the manufacture of the cathode in comparison with prior art coated cathodes.

This application is a continuation of application Ser. No. 704,032 filed Feb. 8, 1968, which is now abandoned.

This invention relates to a dispenser cathode, and in particular to a thermionic dispenser cathode in which the emitting surface is constituted by a surface of a porous refractory metal matrix or body of tungsten or tungsten-molybdenum alloy in the pores of which or behind which a barium-containing alkaline earth metal compound or compounds which will react upon heating with the tungsten to generate free barium metal and/or barium oxide is provided.

In our prior Patent No. 3,373,307, the contents of which are hereby incorporated by reference, we describe an improvement over the prior art dispenser cathode obtained by coating the surface of the porous refractory metal body with a thin porous coating of a high work function refractory metal selected from the group of osmium, iridium, ruthenium and rhenium. The improved dispenser cathode described in our copending application has exhibited significantly improved properties over the prior art cathode, specifically, an electron emission level which is as much as four times higher than the prior art dispenser cathode at the same temperature, or more importantly, an emission level the same as the prior art cathode but at a significantly lower temperature. The best results with the improved cathode were obtained with a coating of osmium, of which has the highest work function of the four named coating metals. While such osmium-coated dispenser cathodes have proved successful, certain drawbacks were encountered whose avoidance is the main object of the present invention. In particular, it was found that the lifetime of the osmium-coated cathode was not as long as it should have been on the basis of the known theoretical understanding of such cathodes. For instance, it has not been possible to obtain cathodes with a lifetime of the order of 100,000 hours or longer. Another difficulty encountered is that osmium oxide is poisonous and an extremely dangerous material to work with. When the osmium is applied by the sputtering technique described in our aforementioned patent, fine particles of osmium are deposited in various areas of the apparatus. Upon opening

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of the apparatus to remove the coated cathode bodies, the finely-divided osmium metal readily oxidizes and thus becomes dangerous to persons who come in contact with it.

The present invention is an improved high work function metal coated dispenser cathode in which the two mentioned drawbacks of the prior art coated cathode are minimized or eliminated. Briefly speaking, we have discovered that by constituting the coating of an alloy of two of the four named high work function metals in certain ranges of proportions, a coated cathode results which has practically all of the favorable characteristics of the osmium coated cathode while the aforementioned drawbacks are minimized or eliminated. In particular, the coating is constituted by an osmium-iridium alloy containing 30–70 atomic percent of osmium, or an osmium-ruthenium alloy containing 20–80 atomic percent of osmium.

The invention will now be described with greater detail with reference to the accompanying drawing in which several embodiments of dispenser cathodes in accordance with the invention are illustrated in cross-section in FIGS. 1 and 2, and in which FIG. 3 illustrates diagrammatically a suitable apparatus for providing the coating on the cathode. It will be noted that the drawing is essentially the same as the drawing of our aforementioned patent, as the present invention is basically the same as that of our previous invention as described in the patent except for the substitution of the alloy coating described above for the coating described in said patent.

As was described in the patent, the invention is applicable to dispenser cathodes of the type comprising a porous tungsten or molybdenum-tungsten alloy body in the pores of which or behind the pores of which is provided a barium-containing activating compound which upon the cathode being heated to its emission temperature reacts with the tungsten of the porous body to generate free barium metal and/or barium oxide which migrates as a vapor through the pores of the porous body to form on its emitting surface what is considered to be a substantially monatomic layer of barium, or of barium on oxygen, on tungsten or the tungsten-molybdenum alloy or the coating which reduces to a low level the work function of that surface enabling electrons to be emitted in copious amounts. As described in our patent, the barium compounds or compositions can be chosen from among a large group which are well known in the prior art, reference to which has been made in the patent. As is also mentioned therein, preferably the barium compound chosen is a barium aluminate or a barium calcium aluminate, which is formed by fusing a mixture of the constituents or their corresponding carbonates to produce the desired aluminates, which is also well known in the art. A preferred mole ratio of the constituents is between 2–3:1 of the barium oxide to the aluminum oxide with 1–3 of the calcium oxide. As previously mentioned, other suitable compositions are described in detail in our patent.

Reference is now made to FIG. 1 which illustrates a typical cavity-type dispenser cathode. It comprises an H-shaped cylindrical body 1, preferably of molybdenum, defining a lower cavity containing a heating filament 2 and an upper cavity 3 in which is provided a pellet 3' which may for example consist of 60% by weight of fine tungsten powder and 40% by weight of a barium calcium aluminate having a mole ratio of $\text{BaO}:\text{Al}_2\text{O}_3:\text{CaO}$ of 5:2:3. The upper cavity 3 is sealed off by means of a suitable weld by a porous tungsten wall 4 which is usually of densely sintered tungsten having a density of approximately 75% of solid tungsten. The upper surface of the tungsten wall 4 which constitutes the emitting surface of the cathode, which is a planar type intended to generate a

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cylindrical beam of electrons, is coated with a thin layer 5 of the alloy previously described, details of which will be later provided.

FIG. 2 illustrates a typical impregnated type dispenser cathode which comprises a cylindrical molybdenum body 6 provided with a molybdenum plate 9 to isolate a heating filament 2 from the active emitter part 7 of the cathode. Aluminum oxide 10 may be employed to seal the plate 9 to the molybdenum body 6. The emitting body 7 comprises a porous tungsten body 7, which is usually a densely sintered tungsten body having a porosity of about 80%, whose pores which are interconnected have been filled or impregnated from the melt with barium calcium aluminate, for example of the 5:2:3 mole ratio composition previously described. The impregnated body 7 can also be formed by compressing and sintering a mixture of tungsten powder and aluminate powder of the composition described, the sintering taking place at a temperature at which the aluminate melts, though to obtain best results we prefer to use the impregnated version in which the tungsten is preformed as a completely sintered body and later impregnated from the melt with the barium calcium aluminate. As in the FIG. 1 embodiment, the impregnated cathode illustrated in FIG. 2 also has on its emitting surface a coating 8 of the alloy previously mentioned.

Similarly to our patent, FIG. 3 illustrates a suitable apparatus for sputtering the alloy coating 5 of FIG. 1 and 8 of FIG. 2 onto the surfaces of the cathode bodies 4 and 7. In this case, the cathode bodies to be coated are supported on a lower plate 14 connected to one side of a voltage source, the other side of which is connected to an upper plate 15 which in this case is composed of an alloy of osmium and iridium or osmium and ruthenium in the proportions previously stated. The plate 14 preferably is of the same alloy. The plates may have a diameter of 3 cm. and are spaced apart by a distance of about 6 mm. The apparatus includes a base plate 11 and a bell jar 12, and the interior can be evacuated by means of an exhaust tube 13 and the usual pumping system not shown. After evacuation, the interior of the bell jar is filled with, for example, argon, at a pressure of approximately 1 mm. Hg and then the upper plate 15 which is connected as a cathode is sputtered by establishing a discharge of about 20 milliamperes between the two plates at a voltage of about 600 volts. The sputtered material of course deposits on the cathode bodies 4 and 7. In about 15 minutes under the conditions above mentioned, an alloy layer is formed on the cathode bodies with a thickness of about 1000 Å. If desired, the gas discharge may be confined to the center by means of an axial magnetic field. After the cathode bodies have been coated, they are preferably sintered in hydrogen of about one atmosphere pressure and at a temperature of approximately 1350° C. in order to improve the adhesion of the alloy coating to the bodies.

To illustrate the capabilities of the resultant cathode, the cavity type cathode illustrated in FIG. 1 when coated with an osmium-iridium porous layer (50-50 atomic percent) having a thickness of about 2000 Å. exhibited a saturation emission of 15 amperes/cm.² at an optically measured temperature of 950° C. (approximately 65 amperes/cm.² at 1050° C.). Very good results were also obtained with the osmium-ruthenium alloy with the proportions of 40% osmium to 60% ruthenium.

As has been earlier noted, the emission properties obtained of the two alloy coatings mentioned as the high work function metal coating of a dispenser cathode are substantially the same as those of a pure osmium coated cathode. However, they offer the important advantage over a cathode coated with pure iridium or pure ruthenium that due to the lower evaporation rate of the alloy coating, the lifetime of the cathode is considerably longer. Moreover, the tungsten diffuses less rapidly through the alloy coating than if it were constituted of pure osmium, which prolongs its lifetime in comparison with the osmi-

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um coated cathode. The alloys are applied as easily by cathode sputtering as the pure high work function metals alone, and other known application techniques should also prove equally satisfactory. The thickness range for the alloy coating is preferably from a few hundred, e.g. 200 to 10,000 Å.

In addition, the alloy coated cathodes offer the advantage over the single high work function metal coated cathodes that they can be operated at higher temperatures with reasonable lifetime more satisfactorily, up to, for instance, a pyrometrically obtained temperature of 1050° C. Both named alloys, offer the important advantage that toxic OsO₄ is not formed. They not only exhibit a higher resistance to reaction with oxygen, in comparison with osmium alone, but they also exhibit a higher resistance to other residual gases in the tube. The osmium-ruthenium alloy is readily pressed and sintered from powder to form plates or rods which can be employed in the apparatus illustrated in FIG. 3 as a sputtering source for coating the cathode bodies.

As is well known, such improved cathodes will prove useful in all applications where high electron emission densities at relatively low cathode temperatures are required, examples of which are camera tubes, cathode ray picture tubes, and various microwave tube applications.

While we have described our invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A dispenser cathode comprising a porous body of a refractory metal selected from the group consisting of tungsten and tungsten-molybdenum alloys, an alkaline earth metal compound in relative relationship with the body and capable when heated of releasing free barium metal which is capable of flowing through the pores to form a layer of barium on a surface of the body intended to serve as an emissive source of electrons, a thin layer of a refractory metal alloy having a work function higher than that of pure tungsten and selected from the group consisting of osmium-iridium containing 30-70 atomic percent of osmium, and osmium-ruthenium containing 20-80 atomic percent of osmium on the surface of said body from which electron emission is desired, said layer being porous to the barium flowing through the pores of the body, and means for heating said body at an elevated temperature whereby said cathode exhibits substantially the same emission level as a comparable cathode without the higher work function layer but at a much lower temperature.

2. A dispenser cathode as set forth in claim 1 wherein the cathode is a cavity-type cathode with the alkaline earth metal compound located in a cavity sealed off by the porous body.

3. A dispenser cathode as set forth in claim 1 wherein the cathode is an impregnated cathode with the alkaline earth metal compound melted into the pores of the porous body.

4. A dispenser cathode comprising a densely-sintered porous body of a refractory metal selected from the group consisting of tungsten and tungsten-molybdenum alloy, an alkaline earth metal compound in reactive relationship with the body and capable when heated of releasing free barium metal which is capable of flowing through the pores to form a layer of barium on a surface of the body intended to serve as an emissive source of electrons, a thin layer of a refractory metal alloy having a work function higher than that of pure tungsten and selected from the group consisting of osmium-iridium containing 30-70 atomic percent of osmium, and osmium-ruthenium containing 20-80 atomic percent of osmium on only the surface of said body from which electron emission is desired, said layer being porous to the barium flowing through the pores and

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having a thickness between about 200 and 10,000 Å., and means for heating said body at an elevated temperature whereby said cathode exhibits substantially the same emission level as a comparable cathode without the higher work function layer but at a much lower temperature.

5. A dispenser cathode as set forth in claim 4 wherein the alkaline earth metal compound includes barium aluminate.

6. A cathode as set forth in claim 5 wherein the compound is a barium-calcium-aluminate, and the alloy is osmium-iridium containing about 50 atomic percent of osmium.

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References Cited

UNITED STATES PATENTS

3,155,864	11/1964	Coppola	313—346
3,243,637	3/1966	Affleck	313—346
3,243,638	3/1966	Affleck	313—346
3,373,307	3/1968	Zaim et al.	313—346

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