Patented May 3, 1938 2,115,828

UNITED STATES PATENT OFFICE

2,115,828

ELECTRON EMITTING CATHODE AND METHOD OF PREPARATION

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No Drawing. Application April 13, 1935, Serial No. 16,260

11 Claims. (Cl. 250—27.5)

This invention relates to electron emitters and more particularly to composite coatings for said emitters and methods of preparing and activating the emissive coating matrix.

The oxide coated type cathode has been commercially practical for a number of years. Technical advances have materially increased its life and efficiency in operation and portrayed the complex character of the constituents of the matrix structure of the coating. However, such a cathode, usually called a "dull emitter", is limited in use by the current dissipated in the cathode and the power rating of the device in which it is used. In devices of high power consumption, it is more practical to employ a tungsten filament or a "thoriated" filament. The latter type filament, usually referred to as a "bright emitter", is generally prepared by an extrusion process in which the constituents are fabricated in the core of the filament and the active agent, thorium, diffused to the surface of the core. Such an emitter does not embody the complex matrix structure of the dull emitter.

An object of the invention is to control and reproduce the electron activity in emitters of the thoriated type.

Another object of the invention is to reproduce the structural characteristics of the dull emitter in a bright emitter and attain increased life and efficiency in operation.

A further object of the invention is to activate composite type emitters by direct chemical methods.

In accordance with this invention a metallic core or base capable of serving as a current conducting body is provided with a coating matrix including thorium as the active emitting component, a stable highly refractory metal, to serve as a repository component and a mass of inert separating material, preferably a compound of the active metal, such as thorium dioxide.

A specific example of an emitter according to this invention consists of a core or base of tungsten having a composite matrix coating of a large mass of thorium dioxide, in which finely divided particles of molybdenum, iridium, tungsten or similar metals are dispersed with an adsorbed layer of thorium on the surface of the coating and a supply of thorium associated or alloyed with the repository particles of the stable metal. This composite emitter exhibits the uniform characteristics of dull emitters both for operating life and efficiency, enables a wide range of control over the proportioning of the constituents of the matrix and provides an emitter which is easily reproducible for mass production.

The composite emitter may be activated in a hydrocarbon gas at a low pressure or, by including carbon or a carbonaceous compound in the matrix coating, to reduce some of the thorium dioxide to thorium metal to serve as the active component of the coating.

A feature of the invention is an activation process involving the chemical reduction of the highly refractory compound of active metal by a reducing agent incorporated in the coating matrix. The only necessary treatment is to heat the emitter in vacuum. This promotes a rapid and economical manufacturing process which is, furthermore, substantially controlled by the coating composition so that the product is of a uniform quality.

Another advantage is that this matrix may be applied and activated independently of the chemical constituents of the emitter base, its mechanical configuration or the relative configuration of the emitter and other electrodes or parts of the device.

Further features and advantages will appear in the following detailed description.

The composite matrix coating of this invention may be prepared by forming a mixture of a large mass of thorium dioxide with a small amount of finely divided particles of a highly refractory stable metal, such as molybdenum, tungsten, iridium, osmium, ruthenium, tantalum, hafnium, or rhenium, together with a reducing agent, such as carbon or a carbonaceous compound, preferably powdered graphite, cane sugar or lampblack. The mixture of the thorium compound, the stable metal particles, and the reducing agent may be commingled in a binder material of nitrocellulose and amyl acetate to form a viscous fluid suitable for coating. Instead of using the finely divided metallic particles of the stable metal, it may be more desirable to employ a compound or salt of the stable metal. For instance, molybdenum oxide is a satisfactory compound for the coating mixture. In another form of the invention when the activating or reducing agent used is cane sugar it may be more desirable to use water as the coating vehicle instead of the amyl acetate.

After the coating mixture is prepared it may be applied to a suitable base metal, such as tungsten, which is capable of carrying current of high amplitude without deleterious effects on the coating matrix applied thereto. After a coating of suitable thickness is secured on the base the coating

is permitted to dry to form a hard refractory body or matrix on the base or core. In order to accelerate the drying, the core may be passed through an oven or heated by passing an electric current through it to evaporate the binder material and form a closely adherent mass of the matrix constituents. The coated base or core is now ready to be inserted in an enclosing vessel and since the primary function of the coated core is to serve as an electron emitter, it is desirable to mount other associated electrodes in the vessel with the emitter, for instance, a control electrode or grid, and an anode or plate may be mounted in suitable spaced relation with respect to the emitter to form a complete discharge structure. However, since this invention is primarily concerned with the development of the coating matrix and the activation of the coating material to produce an electron emitting substance in and on the matrix, the following description will set forth the various steps for attaining this result and performing the direct chemical reduction for producing the electron emitter of this invention.

The preliminary procedure after the assembly of the cathode and other electrodes in the enclosing vessel, consists in sealing the vessel to an evacuating station, baking the glass vessel to remove water vapor and following this step with a thorough pumping of the vessel to remove all gases and other deleterious matter which might impair the succeeding steps of the process. When a low pressure is obtained in the vessel, generally of the order of 2×10^{-5} mm. of mercury, the initial processing of the cathode may be begun.

The technique of the process may be varied according to the initial material incorporated in the coating matrix. For instance, if the starting material of the matrix consists of thorium dioxide, molybdenum oxide and powdered graphite, it may be desirable to reduce the molybdenum oxide to metallic molybdenum by heating the emitter or cathode in hydrogen to a temperature above 1,000° C. to effect the reduction without loss of carbon and leave as a residue the finely divided particles of metallic molybdenum. The hydrogen is removed from the vessel by the pumps. The molybdenum metallic particles, after the reduction treatment, are quite stable since the melting point of this metal is sufficiently above the activation temperature encountered in following this invention and may be relied upon to maintain its metallic form during the succeeding steps of the process. It may be desirable to employ other compounds of molybdenum, such as ammonium molybdate. The conversion step may be eliminated entirely by incorporating finely divided particles of molybdenum in the coating suspension. In a similar manner, compounds of other stable metals, such as the oxides of tungsten, tantalum, hafnium or rhenium or ammonium salts, such as, tungstate, tantalate or chloroiridate, may be employed in the coating mixture. It is not essential that these compounds be reduced to the metallic form prior to continuing the activation process of this invention as adequate carbon may be employed to form by reduction both the stable and the active metals. But any compounds of the platinum metals will decompose spontaneously at relatively low temperatures. The prime requisite of the stable metal is to serve as a depository surface for the thermionically active metal, when developed, and this metal has a high melting point, which is sufficiently above the activation temperature, that it is not affected by subsequent treatment of the matrix and is sufficiently stable to perform the function of a repository material.

The cathode is then heated to an activating temperature of 1700° to 2200° C. to cause the powdered graphite in the matrix coating to react with some of the large mass of thorium dioxide in the matrix and reduce a portion of the thorium dioxide according to the following equation: $ThO_2+2C=Th+2CO$. If the molybdenum oxide is similarly reduced the equation will be $MoO_3+3C=Mo+3CO$. The carbon monoxide is evacuated by the pumping apparatus and the filament is heated to diffuse the active thorium throughout the matrix, that remaining near or at the surface serving as the primary source of electron emission for the cathode. Some of the active thorium within the matrix associates or alloys with the stable metal particles in the matrix or is adsorbed upon the surface thereof and forms a reservoir supply to replace the evaporated surface metal during the operation of the emitter.

In place of powdered graphite other reducing agents may be substituted, such as lampblack or cane sugar. When cane sugar is the reducing agent and also incidentally the binder material of the matrix, it is desirable to carbonize the sugar at a lower temperature prior to the activation process in order to avoid a too rapid evolution of gases.

After the activating treatment has been completed and a high vacuum secured in the device by pumping out the residual gases generated during the activating period the device may be finally sealed off the pumping station. However, in order to stabilize the activity it may be desirable to reheat the cathode to a temperature of about 1700° C. for a period of one-half hour. This treatment facilitates the disperson of the finely divided stable particle metal and the associated active thorium metal adhering to the particles of the stable metal. It will be apparent that the preparation of the cathode in accordance with this invention produces a thoriated type emitter for use in high power devices having characteristics simulating those of the dull emitter. Furthermore, the activation of such an emitter may be effected by direct chemical methods in accordance with this invention to produce an emitter having high efficiency and long life and capable of filling a gap in the range of uses heretofore unattainable with the well-known oxide type emitter and the thoriated type emitter. Furthermore, the proportions of the coating matrix may be more easily controlled than is possible with the alloy type in which the thorium is diffused from the core.

The complex matrix type emitter of this invention may also be activated by a method disclosed in U. S. Patent 2,019,504, to C. H. Prescott, Jr., issued November 5, 1935, in which a hydrocarbon gas of the paraffin series, namely, methane, is introduced into the vessel under reduced pressure to activate the emitter substance and form a reservoir supply in the coating matrix. In the later method, it is to be understood that the reducing agent of this invention may be omitted from the coating solution and the gas carbonizing substituted in accordance with the above application.

What is claimed is:

1. A coating composition comprising a highly refractory compound of an electronically active metal, a carbonaceous substance, and a compound of a stable refractory metal having a melting point above the temperature of activation.

2. A coating composition comprising thorium dioxide, powdered graphite, and a molybdenum compound.

3. A coating composition comprising thorium dioxide, cane sugar, and molybdenum oxide.

4. An electron emitter comprising a refractory metallic base, a composite matrix coating thereon including a mass of thorium dioxide, finely divided particles of a stable refractory metal dispersed throughout said mass, and a refractory electronically active metal adsorbed on the surface of said mass and associated with said stable metal particles.

5. An electron emitter comprising a core having a composite coating composed of thorium, molybdenum, and thorium dioxide.

6. A thoriated emitter comprising a core of tungsten, a composite matrix coating thereon including a mass of thorium dioxide, finely divided particles of molybdenum, and metallic thorium adsorbed on the surface of said mass and alloyed with said molybdenum particles in said matrix.

7. A method of activating an electron emitter coating comprising a compound of molybdenum, a reducing agent, and thorium dioxide, which comprises heating said coating in vacuum, causing a chemical reaction to form metallic molybdenum and metallic thorium, and associating said thorium with said molybdenum.

8. A method of activating an electron emitter coating comprising a compound of molybdenum, a reducing agent, and thorium dioxide, which comprises reducing said molybdenum compound to metallic molybdenum, heating said coating in vacuum, causing a reaction between said reducing agent and said thorium dioxide to produce metallic thorium, and associating said thorium with said metallic molybdenum.

9. A method of activating an electron emitter coating comprising molybdenum and thorium compounds which comprises heating said emitter to decompose the compounds to oxides, reducing the molybdenum oxide to metallic molybdenum, heating said emitter in a hydrocarbon atmosphere to reduce a portion of thorium oxide to metallic thorium, and alloying the thorium with the molybdenum in vacuum by heating.

10. A method of activating an electron emitter coating comprising molybdenum oxide dispersed throughout a matrix of thorium dioxide including powdered graphite which comprises reducing said oxide to metallic molybdenum, heating said emitter in vacuum to chemically combine said graphite with a portion of said thorium dioxide to form free metallic thorium, and adsorbing said thorium upon said metallic molybdenum particles.

11. A method of activating an electron emitter coating comprising molybdenum oxide dispersed throughout a matrix of thorium dioxide including powdered graphite which comprises reducing said molybdenum oxide to metallic molybdenum, heating said emitter in vacuum, forming a reaction between said graphite and a portion of said thorium dioxide to form free metallic thorium diffusing some of said thorium to the surface of said matrix and associating the remainder of thorium with the finely dispersed particles of molybdenum in said matrix.

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