

UNITED STATES PATENT OFFICE.

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ELECTRON-EMITTING MATERIAL.

No Drawing.

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This invention relates to electron-emitting cathodes and more particularly to a cathode comprising a refractory metal body having incorporated therein, material having high electron-emitting properties.

In the present day manufacture of electron discharge devices, such as rectifier, X-ray devices, radio receiving and transmitting tubes, etc., it is the very common practice to employ as the cathode, a thermionically active body composed of a refractory metal, such as tungsten, impregnated or mixed with a small percentage of thoria or thorium. The present invention is especially concerned with an electron-emitting body of this nature.

One of the objects of this invention is to provide a cathode of the thoriated type having substantially increased electron emission and which will maintain such high electron emissivity over a long commercial life.

Another object is to provide a method of producing such an electron-emitting body.

A still further object is to produce a filamentary refractory metal body of increased strength and toughness.

Other objects and advantages will hereinafter appear.

The present invention is based upon the discovery that when an oxide of a rare earth metal of the cerium group is added in small proportions to a thoriated refractory metal body and the same subjected to the usual manufacturing and activating processes, that such material imparts to the body a very substantial increase in electron emission. This increased electron emission, moreover, is maintained for a much longer period than in the case of plain thoriated wire and the filaments to which this rare earth oxide has been added are stronger and tougher than ordinary thoriated tungsten wire.

While thoriated tungsten is the preferred electron-emitting material with which the present invention is concerned, it is to be understood that the invention is not so limited but may be employed with the same advantageous results to other refractory metal bodies, such as molybdenum, having other electron-emitting metals incorporated therein, such as zirconium, uranium, vanadium, etc.

In the manufacture of thoriated tungsten filaments for electron emission purposes it

is the usual practice to incorporate up to 3% of thorium oxide with the tungsten metal in powdered form and to fabricate the mixture into wire form by pressing, swaging, and drawing. The thorium oxide is converted, at least in part, to thorium metal, either during the fabrication process or subsequently and forms the active electron-emitting ingredient of the filament.

I have found, however, that when an oxide of a metal of the cerium group of rare earth metals is added to the thoriated-tungsten body in the proportion of about .5 to 4% of the rare earth oxide to the thorium oxide content that the electron emission obtained from the cathode is increased very substantially. For instance, with a thoriated tungsten filament containing 1% of thorium oxide and from .01 to .03% cerium oxide, an increase in emission over plain thoriated-tungsten filaments of from 10 to 40% was obtained. However, it was found that when the percentage of cerium oxide was increased to 5% or more of the thorium oxide content, it acted detrimentally rather than beneficially.

The action of the rare earth oxide in increasing electron emission is not clearly understood but one possible explanation may be that the cerium either in oxide or metallic form, forms an alloy or mixture with the thorium or thorium oxide and that such alloy or mixture has a greater efficiency for transforming heat energy into electronic emission than does the plain thorium. I do not desire to be limited by any particular theory, however, since other plausible theories might be suggested in explanation of the phenomena which I have observed.

Various methods may be employed for incorporating the cerium oxide or other oxide of the cerium group of rare earth metals into the thoriated tungsten body but the method I prefer to employ is to prepare a solution of thorium and cerium nitrates in such proportion as to produce, upon reduction, the desired amount of thorium oxide and cerium oxide. This solution may then be intimately mixed with the proper proportion of previously purified tungstic oxide. The proportions which I prefer to employ are 1% to 2% thorium oxide, with cerium oxide present in the proportion of 1% to 3% of the thorium oxide content and the remainder

tungsten. This mixture is then dried at about 110° C. until free from moisture in the usual manner. It is then crushed and sieved and the dried oxide fired in a muffle furnace at from 900 to 1000° for about three hours and the contents removed and again sieved. During this heat treatment the cerium nitrate and thorium nitrate are converted to the oxide. After sieving, the fired material is placed in a nickel boat and heated in a hydrogen furnace at about 1000° C. for a period of about two hours. The hydrogen effects a reduction of the tungsten oxide but does not reduce, to any extent, either the cerium or thorium oxide.

It is essential that both the cerium and thorium oxides be retained in the oxide form since otherwise these metals would volatilize out of the tungsten during the subsequent heat treatment. The mixture is then pressed into slugs or ingots and the ingots heated in a hydrogen furnace at about 1200° for from one to two hours. This renders them sufficiently coherent to withstand the subsequent manipulations. The formed and baked ingots are then sintered in a treating bottle through which dry hydrogen gas continuously flows and gradually heated up by passage of electric current therethrough to around 90% of the fusion current. The sintered ingots are then swaged and drawn into wire form in accordance with the usual practice and after completion of the wire drawing process they may be activated by any of the approved processes for activating thoriated tungsten wire for electron emission purposes. In the case of small sized wires this activation may be accomplished by flashing the filament in hydrogen for a short interval as set forth in copending application Serial No. 110,047, filed May 19, 1926, Rich et al., entitled Electron-emitting devices and method of preparation. In the case of larger sized filaments it may be necessary to carbonize the filament by flashing the same in a hydrocarbon gas in accordance with the procedure set forth in U. S. Patent 1,529,597, Langmuir, entitled Electron-emitting device and method of preparation.

During this activation process or during the latter part of the wire drawing process the thorium oxide or a portion thereof and a portion of the cerium oxide appears to be reduced to the metal and apparently by some coaction of the cerium and thorium the electron emission obtained of the cathode is increased very substantially over that obtained from the plain thoriated-tungsten filaments.

In addition to the large increase in initial emission, an increase in life, in some cases amounting to several hundred per cent has been obtained, such life being based on the number of hours the filament may be continuously operated before the electron emission falls below a predetermined minimum.

This emission maintenance property of the present filament is of extreme importance since considerable difficulty has been experienced heretofore, due to early failure in emission of plain thoriated-tungsten cathodes.

It is obvious, of course, that many changes and modifications may be made in the process of producing the wire and various rare earth oxides, electron-emitting metals and refractory metal carriers may be employed without departing from the invention, but I do not desire to be limited to the exact details shown and described.

What is claimed is:

1. A thermionically active electrode comprising a refractory metal body having incorporated therewith a metal of good electron emissivity and a small proportion of a metal of the cerium group of rare earth metals.
2. An electron-emitting body comprising a refractory metal containing a small proportion of a metal of good electron emissivity and a metal of the cerium group of rare earth metals, the proportion of the latter metal being small in comparison to the electron-emitting metal.
3. An electron-emitting body comprising a thoriated-tungsten body containing a small proportion of a metal of the cerium group of rare earth metals.
4. A refractory metal body composed of tungsten containing a small percentage of thorium and cerium, said body having an electron emissivity at a given temperature substantially greater than plain thoriated-tungsten.
5. An electron-emitting body composed of a refractory metal containing from 1 to 3% of thorium or thorium oxide and from .005 to .12% of cerium or cerium oxide.
6. A thoriated refractory metal body for electron emission purposes containing cerium oxide in proportions of .5 to 4% of the total thorium oxide.
7. A refractory metal body adapted to be activated for electron emission purposes consisting of a refractory metal containing a small per cent of thorium oxide and cerium oxide.
8. A refractory metal body adapted to be activated for electron emission purposes consisting of tungsten containing from 1 to 3% of thorium oxide and from .5 to 4% of cerium oxide based on the thorium oxide content.
9. The method of increasing the electron emissivity of a thoriated refractory metal body which comprises adding to said body a small percentage of cerium oxide.
10. The method of making thermionically active electrodes which consists in incorporating cerium oxide and thorium oxide into a refractory metal body and subsequently re-

ducing a portion of the oxides to metallic form.

11. The method of producing filamentary bodies having high electron emissivity which comprises incorporating into a tungsten body from 1 to 3% of thorium oxide and from .5 to 4% of cerium oxide based on the thorium

oxide content and subsequently reducing, at least in part, said oxides to metallic form.

In testimony whereof, I have hereunto subscribed my name this 23rd day of February, 1927.

CHARLES V. IREDELL.