

UNITED STATES PATENT OFFICE

1,948,445

ELECTRON EMITTING BODY AND THE
PROCESS FOR ITS MANUFACTURE

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No Drawing. Application November 18, 1927,
Serial No. 234,289, and in Austria April 12,
1927

3 Claims. (Cl. 250—27.5)

This invention relates to an electron emitting body and the process for its manufacture.

In all kinds of discharge devices involving pure electron discharge, such as electron tubes for radio purposes, X-ray tubes, rectifiers etc. the glowing cathode consists of wires or filaments of highly refractory metals, principally, such as tungsten. For the purpose of increasing the electron emission the wires or filaments have contained thorium. Such thoriated tungsten wires are, as a rule, produced by working a mixture of tungsten metal and thorium oxide or a substance yielding thorium oxide into filaments or wires. However, the percentage of thorium never exceeds two percent, because, tungsten containing more than two percent thorium oxide cannot be worked into filaments or wires. Furthermore, it is not possible to use a tungsten wire containing thorium oxide for electron emission. For this purpose it is necessary to reduce the thorium oxide contained in the wire or filament material to thorium metal.

While the high emissivity of such bodies, due to the metallic thorium, would suggest the use of a body of pure thorium as a cathode, this is impossible in practice for the reason that in order to obtain ample electron emission from thorium it must be brought to a temperature of about 1800° K. (Kelvin) and, as its melting point lies at about 2000° K. it is evident that a thorium body could not for any length of time be subjected to a thermal strain so close below its melting point. It has therefore always been considered necessary to select for the thorium a carrier having a far higher melting point. However, in order to obtain coherent bodies meeting all requirements from a mechanical standpoint, only a comparatively small addition of thorium could be made.

The process by which the thorium oxide, incorporated into the tungsten, is converted into thorium metal, is, as a rule, carried out as follows: During the mechanical treatment the material consisting of tungsten and thorium oxide is heated continuously by gas burners and during the drawing process the wire is lubricated with graphite, so that, it is supposed, part of the thorium oxide contained in the tungsten is decomposed by the action of the carbon. Inasmuch as it is not certain that all of the thorium oxide is thus converted, the wires or filaments are subsequently heated to a temperature of about 2273° K. in hydrocarbons of low pressure, preferably in acetylene gas, in order to complete the reduction of the thorium oxide. The specific resistance of

such wire or filament is thus increased by about 10%. Owing to the content of carbon, however, the wires or filaments are brittle and cannot be used in this condition apart from the fact that thorium compounds have no emissivity. Therefore, a further treatment is necessary, which consists in subjecting such wires or filaments after insertion in their envelope, for a certain time to the so-called ageing or seasoning process, viz. to the action of an electric current. This seasoning process comprises three phases:

In the first phase the gas residues are removed to a great extent by excessive heating of the cathode which primarily consists of tungsten and reduced thorium oxide, and by applying a plate potential above normal. In the second phase the plate potential is disconnected and the cathode is heated to about 2800° K. whereby the thorium metal is separated so that the cathode filament will then consist of tungsten and thorium only. In the third phase the thorium metal is to be brought from the interior of the wire or filament to its surface which is effected by applying a current, 30–50% above the normal operation current.

The total duration of this seasoning process varies from 20 to 90 minutes according to the size of the tube and, as mentioned above, finished tubes are subject to it. Owing to the voltages used which exceed the normal operation current a loss of 25–50% of finished tubes occurs in manufacture.

The glowing cathodes obtained in this way consist of a tungsten wire or filament having a small amount of thorium metal on its surface and as this very small quantity of thorium volatilizes after a comparatively short time, resulting in an almost complete cessation of the electron emission, such glowing cathodes are effective as electron emitters for only a comparatively short time.

The present invention seeks to overcome the herein described disadvantages by the combination of thorium with a carrier substance which, even when admixed with a larger amount of thorium, will yield a material that can be worked into wires or filaments meeting all requirements from a mechanical standpoint and the physical properties of which carrier substance and of the wires or filaments made therewith are such that the favorable temperature for emission can be reached without causing a destruction of the wire.

Such carrier materials which are capable of absorbing an abundant quantity of thorium and

combined therewith, afford filaments and wires having the properties outlined above, are the metals of the platinum group, such as osmium, or alloys of such metals. For simplicity's sake only osmium will be mentioned, taken as an example of the carrying out of the invention in the following description.

I have found that bodies having a high emissivity can be produced of osmium with a content of thorium much in excess of that possible with tungsten. Ten or twenty percent or more of thorium oxide or other thorium compound which permits of being later converted into thorium metal can easily be incorporated with osmium and obviously such bodies contain more than 2% of metallic thorium which represents the maximum percentage when tungsten is used and the amount of thorium may be increased up to more than 50%. Inasmuch as a wire or filament of osmium with such quantities of thorium meets all requirements from a mechanical standpoint and the content of thorium is a big multiple of that of the well known tungsten wires, it is evident that the duration of the effectiveness of such a wire or filament exceed by far that of thoriated tungsten wires. A life of 5,000 to 15,000 hours may easily be attained. Inasmuch as such an osmium-thorium filament or wire is stronger than a filament consisting of tungsten and thorium compounds that has to be subjected to the above described seasoning process, there is less shrinkage than with the filaments known heretofore and moreover the whole seasoning process can be done away with. The osmium-thorium filament or wire, immediately after completion and insertion the tube may be put into operation.

Such osmium-thorium wires or filaments may, for instance, be produced as follows:

Very finely divided osmium metal is made up into a paste with very finely divided thorium oxide and a binding agent, such as collodion, tragacanth, gum and sugar or the like. From this paste filaments are squirted and the filaments are subjected to a heat treatment either by the passage of an electric current therethrough or by external heating in a suitable gas atmosphere at atmospheric or reduced pressure or in a high vacuum. If care is taken to exclude possibly occurring oxidizing gases or vapors (air or water vapor) and the heating is effected in substantially two steps, bodies consisting of pure metallic osmium and metallic thorium are obtained.

The paste may be prepared as follows:

10 parts by weight of finely divided osmium with 10 parts by weight of finely divided thorium oxide and 6 parts by weight of amyl acetate solution of collodion.

From this paste filaments are squirted as just described and then subjected to a heat treatment. The first phase of the heat treatment must take place at a temperature above the melting point of thorium metal, that is to say above about 2000° K. A favorable temperature is between 2400 and 2500° K. During this operation the reduction of the thorium oxide to metal apparently takes place and an alloy or compound of the thorium and the osmium is formed. Then follows the second phase of the heat treatment which goes up close to the melting point of osmium, viz, about 3000° K., whereby the osmium filament is consolidated and becomes perfectly uniform.

Although such a body may contain considerable quantities of thorium, it is found that the melt-

ing point of the finished filament material is not very different from that of pure osmium.

Resistance heating may also be used instead of heating the filaments by the external application of heat, say in a carbon monoxide atmosphere, preferably at low pressure of about 150 mm. of mercury. In this case also, care must be taken to avoid the presence of accidental oxygenous gases or water vapor. With this method also, the first limit of temperature of about 2400° K. should be observed, at which the reaction takes place, whereupon follows a further raise of temperature up to close to the melting point of osmium, for the purpose of consolidating the filament. It is not necessary to always start from thorium oxide; the same result may be obtained by incorporating thorium metal directly into the basic mass.

From the original material bodies of larger cross section may also be produced and worked into wires by mechanical treatment. If properly treated, such wires are pliable in a cold state.

Of course it is not necessary to start with pure osmium and pure thorium oxide. Osmium compounds which yield metallic osmium when heated may also be used and likewise such thorium compounds which yield metallic thorium after heating. As already mentioned it is not necessary to use osmium alone. It is not detrimental to use other metals of the platinum group along with it, provided these are not used in excessive amounts. With some care other highly refractory metals such as tungsten may also be added to the osmium but by no means in excessive quantities because even a mixture of about 2 parts osmium and 1 part tungsten with an addition of 20% thorium oxide has a considerably lower melting point than osmium with thorium.

Another method of producing electron emitting bodies according to the present invention consists in applying to a carrier of some highly refractory metal, such as tungsten, preferably in the form of a ribbon, a suspension of osmium metal and thorium oxide (or proper compounds) and by effecting the conversion thereof into an alloy of osmium and thorium by a heat treatment. The mass may also be deposited on the carrier electrolytically. In this way the desired effect is attained with less material consumption and such a body differs considerably from the known tungsten wires described in the foregoing which have a small amount of thorium on their surface where it was brought by the lengthy and very disadvantageous seasoning process. It is evident that a much more active amount of thorium and consequently a higher and more lasting emissivity can be obtained by a ribbon of an osmium-thorium alloy upon the tungsten wire. Also such a filament is much more uniform than that of filaments known heretofore.

The fact that the thorium oxide added to the osmium undergoes an alteration and apparently forms a very intimate compound with it can be proved by holding, in the oxidizing zone of a Bunsen burner, a finished filament consisting of osmium metal and thorium metal which filament originally consisted of a mixture of the powders of osmium and thorium oxide; both constituents will be oxidized in the flame. The osmium forms a very volatile oxide, viz. osmium tetroxide, the thorium is left as thorium oxide. If the glowing is continued for a sufficient length of time all of the osmium may be volatilized, leaving as may be distinctly seen under the microscope, a crystalline skeleton of thorium oxide which shows how

intimate the osmium-thorium compound has been.

Various modifications will occur to those skilled in the art in the composition and proportions of the material of which the filaments and the like are made as well as in the manner of preparing them and no limitation is intended in the broad aspect of the invention by the phraseology of the foregoing description except as indicated in the accompanying claims.

What I claim is:

1. The process of making an electron emissive cathode which has a more constant and more lasting electron emission than "thoriated tungsten", which process comprises forming an intimate mixture at least containing thorium and osmium of which there is between 100 and 50 times more osmium than there is thorium, heating said mixture in a non-oxidizing environment to a temperature above the melting point of thorium to form an intimate and uniform alloy between the thorium and osmium, and then raising the temperature close to the melting point of osmium

whereby the mixture is consolidated and becomes uniform to give a resulting body which is pliable in the cold state.

2. The process as claimed in claim 1, wherein the mixture is first heated to between 2400° and 2500° K. and is then heated to about 3000° K.

3. The process of making an electron emissive cathode which has a more constant and more lasting electron emission than "thoriated tungsten", comprising intimately mixing osmium with a thorium compound to produce a mixture containing more than 2% metallic thorium in relation to the osmium, heating said mixture in a non-oxidizing environment to a temperature of between 2400° and 2500° K. to reduce the thorium oxide and to form an intimate and uniform thorium-osmium alloy, and then increasing the temperature to about 3000° K. to produce a resulting body which is uniform and pliable in the cold state and which as a whole has a melting point substantially the same as that of osmium.

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