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THORIATED CATHODES AND METHOD FOR MAKING THE SAME

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Fig. 1

Fig. 2

Fig. 3

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THORIATED CATHODES AND METHOD FOR MAKING THE SAME

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ABSTRACT OF THE DISCLOSURE

Thoriated hot cathodes in which the metal carbide such as W₂C or Mo₂C is transformed from hexagonal to body centered cubic modification. This is done at an elevated temperature by way of a solid-state reaction, in the presence of a suitable metal catalyst.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending application Ser. No. 384,500 filed July 22, 1964.

BACKGROUND OF THE INVENTION

The present invention relates to so-called "hot" cathodes for use in electric discharge vessels, particularly cathodes in which the active component is thorium, and to methods for making the same.

Cathodes containing thorium as the active component are well known in the art and are presently used in various pieces of electronic equipment, such as electron tubes, as well as in gas-filled discharge vessels.

Normally, thoriated cathodes fall into four types, as follows:

(1) So-called film cathodes, which are cathodes made of tungsten wire containing thorium oxide, the active emitter surface being formed by subjecting the incandescent filament to a high-temperature treatment.

(2) Thoriated tungsten cathodes having a carburized surface, which are made from tungsten wire containing thorium oxide. The wire is heated with carbon, or gaseous compounds of carbon, so as to form a carbide layer, the carbide layer being about 10 to 30% of the cross section and consisting of a hexagonal tungsten carbide which chemical formula is W₂C. The function which this carbide layer plays will be referred to below in detail.

(3) Massy cathodes, mainly pasty or reserve-type cathodes, whose active mass consists of thorium oxide, which may, if desired, be admixed with a metal that melts at a high temperature and with a reducing agent such as, for example, carbon.

(4) So-called "cernet" (ceramic-metallic) cathodes, that is to say, sintered cathodes, made up of a metal that is difficult to melt and thorium oxide, with or without reducing agents, according to powder-metallurgical techniques.

The film-type cathodes described in (1) are very sensitive in that they are easily poisoned by bombardment or by impurity gases, so that, for practical purposes, such cathodes are no longer in use.

The thoriated tungsten cathodes described in (2) have a long life expectancy but are very brittle and are quite sensitive to impurity gases. In general these cathodes have the same operating values insofar as maximum current density and power output are concerned as in the case of the film-type cathode described in (1). Therefore, the only significance that was assigned to the carbide layer was that it had better reducing properties with respect to thorium oxide, thereby to facilitate the diffusion of the thorium.

The massy cathodes described in (3) were developed based on the supposition that metallic thorium had to be present in order to obtain good emission, i.e., that part of the thorium oxide had to be reduced to the metallic thorium. It was assumed that heavy metals such as, for example, tungsten, molybdenum, as well as other difficult-to-melt metals, could reduce the thorium oxide to the metal. As is now known in the art, this is not so, or if such reduction does occur, it will, at the usual cathode temperatures, do so to a negligible extent.

The cernet cathodes described in (4), i.e., the sintered cathodes made in accordance with powdered metal techniques, are also based on thorium oxide and one or more difficult-to-melt metals. In general, these cathodes are made without carburizing, but in case there is carburizing, all that is obtained is the known hexagonal carbide phase.

SUMMARY OF THE INVENTION

It is the primary object of the present invention to provide a hot cathode which overcomes the drawbacks of heretofore known hot cathodes, namely, to provide a hot cathode which is capable of putting out high power, which has a high emission current density and a long life expectancy, which is insensitive to poisoning and which, moreover, has good mechanical strength and which is stable.

It is another object of the present invention to provide a new modification of metal carbides which is used as the constituent in a hot cathode, thereby to produce better emission, higher stability and better mechanical properties.

It is still a further object of the present invention to increase the maximum permissible current density — which, in the case of conventional thoriated cathodes is, at the usual operating temperature, about 2—3 A/cm²— to about double that which was heretofore possible, namely, to about 5—6 A/cm² at the same operating temperature, while simultaneously reducing the costs of the cathode.

In accordance with the present invention, the above objects are achieved by providing a cathode of the above type in which the conventional hexagonal carbide is transformed into a new body centered cubic (b.c.c.) modification.

More particularly, the present invention resides in a cathode in which the b.c.c. carbide is produced, in an appropriate process step, by catalytically reacting a metal. This new modification is the determining component of the finished cathode. The reaction of the b.c.c. carbide from a carbide of a difficult-to-melt metal, such as W or Mo, which carbide is produced by reaction with carbon or a hydrocarbon at high temperature. This carbide will have the conventional hexagonal crystal structure and is then transformed by way of a catalytic solid-state reaction which converts the hexagonal carbide in the new b.c.c. modification. This reaction is carried out at high temperature in the presence of a metal such as Pt, Pd, Ru, Os, Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Mn or Cu. This heat treat-
ment is continued until the original hexagonal carbide phase disappears and the new phase is formed. The solid-
state reaction takes place at a temperature which is be-
tween about 5% of the melting point of the metal and the melting point of the metal, and continues until the cata-
lytically acting metal has, for the most part, been vapor-
ized. Remaining traces become part of the crystal lattice and are then reacted by the remainder of catalyst which is vaporized from the surface. The new b.c.c. carbide phase can be pro-
duced at the surface of a wire, strip or the like. The wire
itself may be made in such a way as to contain the neces-
sary amount of thorium, or it can be made of the particu-
lar carbide and be added to a mixture containing thorium
or TlO.
This transformation can just as well be carried out in
the case of Mo or W wires which are alloyed with one or
more difficult-to-melt metals.
The exact way in which the new carbon phase accor-
ding to the present invention brings about the higher emis-
sion is not yet fully understood, but it is assumed that a
semiconductor mechanism is involved, and that the b.c.c.
carbide layer, acting as a semiconductive surface, brings
about the conditions conducive to the increased emission.
Actually, even the effect of the heretofore used hexagonal
75

carbide phase in thoriated cathodes is not completely
understood, and in order to investigate the question of
whether a typically increased emission of thoriated cath-
odes is possible without carbon, the following exper-
iment was carried out:
In order to explain the part played by the carbide com-
ponent in the emission, the original Langmuir measure-
ments were repeated, with the object of withholding car-
bon and its compounds as far as possible from the cath-
odode, i.e., of preventing the production of any carbide im-
purity on the tungsten surface. For this purpose, all the
metal parts, especially the indentescent wire, were heated
a number of times in a moist hydrogen atmosphere for
long periods of time. The pumping unit which was used
had no lubricated connections and valves. All the glass
parts were treated similarly. In addition, the carbon ra-
dues and especially carbonaceous gases were removed by
incandescent and also cold getters (titanium) of large area
having high affinity for carbon. Measurement of the work
function of a noncarburized, commercially obtainable
thoriated tungsten filament showed under the aforesaid
condition values of about 5.4-5.5 ev. which values corre-
responds approximately to the work function of metallic
thorium. However, when very small quantities of hydro-
carbons were added to the measuring arrangements by
way of a breakable seal, a characteristic value of about
2.6-2.8 ev. was measured without difficulty after activa-
tion.
It may be concluded from this that the production of
the low work function normally attributed to the system
of thorium on tungsten is dependent upon the possibility
of a carbon contamination. This impurity reacts with
tungsten to form tungsten carbide at the activation tem-
perature. It is concluded that the characteristic low
work function of thoriated cathodes is not a property of
the tungsten-thorium system but of the system tungsten-
carbo-thorium.
If it is indeed a semiconductor mechanism which is
responsible for the higher emission of a thoriated cath-
odode, it should be possible to influence the emission by vary-
ing the characteristics of the semiconductor. This is,
according to the present invention, achieved by trans-
forming the structure of the carbide and influencing the
semiconductor properties by the remainder of catalyst
which is vaporized from the surface.
The new b.c.c. carbide phase can be produced either
at the surface of a wire or the like, by converting the
hexagonal carbide, or this carbide phase can be produced
in a separate step from the hexagonal carbide, which can be
added to a thorium-containing active mass or to a mass
which is to be pressed into the shape of the cathode. This
new carbide phase, hereinafter referred to as the \( \gamma_2 \) car-
bide phase, is preferably at least 5% by weight of the
TlO, but may advantageously be increased to 50%.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The features of the thermionic cathode produced by
the process of the invention are illustrated in the draw-
ings, in which:

FIG. 1 shows the emission curves of a conventionally
carburized thoriated tungsten cathode and of a cathode
produced by the process according to the present in-
vention.

FIG. 2 is a graph illustrating the saturated emission
current data of a thoriated tungsten cathode, according
to the invention, during the useful life.

FIG. 3 illustrates the initial starting current of a tho-
riated tungsten cathode produced by the process of the
invention, at the exhaustion state as compared with the
behavior of a conventional thoriated cathode.

**DESCRIPTION OF THE PREFERRED
EMBDIMENT**

FIG. 1 illustrates the values of the emission current,
prompted against the heating power, obtained in compara-
tive measurements of two series of identical types of tubes
manufactured under normal production conditions, the
only difference between the two series residing in that
cathodes produced by the process of the invention were
used in one series and cathodes produced by the conven-
tional process were used in the other series.

The geometrical dimensions of the cathodes are the
same. Curve 1 of FIG. 1 shows the saturation current of
the tubes comprising the cathode according to the Inven-
tion, while curve 2 shows by way of comparison the emis-
sion values of the standard, normally carburized cath-
odes. At the rated power, the emission of the cathode
exceeds the standard value by 80%.

FIG. 2 shows the saturation current values, related to
a cathode area of one square centimeter, of three tubes
(curves 3, 4 and 5) comprising the cathode according
to the invention in the course of the life test. These tubes
were operated during the tests with the maximum rated
power in the 12 mHz range, class "C" operation.

Despite the high specific output which was approximately
twice that of normal cathodes—the tubes exhibit
no reduction of cathode activity during the normal useful
life.

FIG. 3 illustrates the behavior of the cathode accord-
ing to the invention at the pump (curve 6), as compared
with a conventional thoriated cathode (curve 7), at the
first heating of the cathode with applied anode voltage.

Curve 6 shows that in the case of the cathode produced
in accordance with the invention, a readily measurable
emission current is set up at a much lower temperature
than in the reference cathode, and this current remains
steady as the temperature rises without any sudden
changes in activation at higher temperature, as is appar-
ent, for example, from curve 7.

As set forth above, the cathodes according to the pre-
sent invention are produced by transforming the
hexagonal carbide phase into the \( \gamma_2 \) or b.c.c. modification.
This is done as follows:
The cathode which contains as active metal, thorium
and as a refractory metal, either W or Mo and a carbide
of the refractory metal, so that the chemical composition
is \( M_2C \) wherein M represents the refractory metal, has
the carbide in a hexagonal crystallographic structure. This
structure is transformed in the presence of Pt, Pd, Ru, Os,
Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Au, Mn or Cu by a solid-
state reaction at elevated temperature through a catalytic
action of one of these last-mentioned metals until the
hexagonal carbide is completely transformed to a body centered cubic modification. The temperature applied during the solid-state reaction is above 75 °C of the melting point of the used catalyst metal. Consequently, the catalyst metal evaporates substantially and disappears from the surface of the carbide.

In practice, the cathode may be in the form of a thoria-bonded filament and tungsten carbide, made by carburnizing the surface of the filament by heating in a carbon-containing media.

According to another embodiment of the invention, the cathode is made by providing a separately made fillet mass which includes the carbidic carbide in fine particle form, which is admixed with thorium (thorium oxide) and to a supporting metal powder. The thus-obtained mixture is then milled so as to homogeneously distribute the same, after which the mass is applied, with a conventional binder, to the supporting cathode body.

According to still another embodiment, the cathode is a sintered cermet cathode in which a ceramic sintered body, made of ThO₂, a refractory metal and a refractory metal carbide in hexagonal crystallographic structure, is made by mixing the components and sintering them to a ceramic body, which is preserved in a salt of Pt, Pd, Ru, Os, Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Au, Mn or Cu. The thus-prepared ceramic body is then dried and heat-treated, at a temperature above 75 °C of the melting temperature of the catalyst metal, to transform the hexagonal carbide into a b.c.c. modification.

Instead of immersing the sintered body, the same may, in accordance with another embodiment of the present invention, be exposed to a vapor of one of the catalyst metals and be heat-treated, as described above.

According to yet another embodiment of the present invention, a sintered ceramic body consisting of ThO₂ of a refractory metal as supporting member, and of an already transformed metal carbide having the desired b.c.c. crystallographic structure is milled to a homogeneous powder mixture, after which the desired shape is obtained by conventional powder metallurgical methods and then sintered.

The following are illustrative and not limiting examples of the present invention.

**Example I**

A helical cathode, made of thoriated tungsten wire containing 2% thorium oxide and having a diameter of 1.0 mm, was first heated to a temperature of 75 °C, then sintered in a high vacuum, vapor, with a heating current of 6.5 A, until the temperature reaches 7.95 °C. The cathode is then sintered under a vacuum for 10 minutes at a temperature of 2200° K, and is afterwards coated with palladium, this being done with the use of the commercially available Palladium Plating Solution 3772 sold by Engelhard Industries. The current density during the plating was 10 ma./cm² and electrical energy was supplied at a rate of 1000 ma/sec/cm². This resulted in a coating of 0.2 mg/cm². The cathode was then washed and dried.

The thus-coated cathode was then subjected to diffusion heating, under a vacuum for one hour at a temperature of 1450° C for (the subscript "ppm" indicating pyrometer measurements) and then for two hours at a temperature of 2000° C to get a solid-state reaction. The cathode was then cooled under a high vacuum and mounted in the tube of the electrical discharge vessel, which was then evacuated in the usual manner.

Microscopic examination showed the cross section of the cathode filament to be homogeneous, there being a definite line of demarcation between the core and carbide layer. Only the b.c.c. γ₉ structure could be found by X-ray diffraction, while traces of palladium, of the order of ppm, were found spectrographically.

The thus-produced tube was then tested to yield a specific emission current of 5.2 A/cm².

**Example II**

A thoriated tungsten cathode having the same characteristics as the cathode described in Example I was carburnized and de-gassed, as described. After the degassing, the cathode was mounted in a glass envelope containing rhenium pentachloride. The temperature of the cathode was raised to 1900° C for 30 minutes and then cooled, de-gassed under a high vacuum and mounted in a conventional electron tube system.

The cathode was found to have the same desirable properties as those set forth in Example I. The hexagonal carbide phase was likewise found to have been eliminated.

**Example III**

An M-shaped filamentary cathode made of thoriated tungsten wire having a diameter of 216 μm, and having a rated heating current of 3.2 A and a voltage of 10 V, was carburnized in naphthalene vapor, the current applied being 4.75 A until the heating voltage rose from 17.2 V to 23.2 V. The cathode was then de-gassed under a high vacuum and subsequently coated cathaphorically with thorium oxide from a suspension containing 5 g ThO₂/100 cm³ until the thorium oxide attained a thickness of 30 μm. After this coating, the tube was assembled.

The thus-produced cathode was a tungsten cathode coated with thorium oxide. This oxide coating of the carburnized body, which consists of b.c.c. modification, retained while and produced a constant emission during its lifetime. This is in contrast to conventional thorium oxide cathodes which are applied on tungsten bodies and which turn black, either in the course of use or even while they are being manufactured.

**Example IV**

A molybdenum wire having a diameter of 1 mm, was recrystallized under a high vacuum at 2400° C for 30 minutes, and then annealed, to about 50% of its cross section, in a flowing atmosphere of xylene and hydrogen. The wire was then coated galvanically with nickel, in a conventional nickel-nickel solution, until the coating reached 0.3 mg/cm². The thus-coated wire was then annealed under a high vacuum for one hour at 1300° C for 30 minutes, and then for two hours at 1800° C for 30 minutes, after which the wire was cooled under high vacuum.

The wire was then broken into pieces and ground in a vibratory grinder until the average particle size of 30 μm was reached. This powder was then milled with thorium oxide (20 g powder to 15 g of thorium oxide) and this mass was added with a binder (pentafluorophenol, chloroform) and used as filament mass for reserve-type cathodes of mercury vapor lamps. The cathodes were found to have good stability and a long useful life.

**Example V**

The powder consisting of Mo and Mo₃C as described in Example IV was mixed with thorium oxide, two parts by weight of this metal-carbide powder to one part by weight of ThO₂, as described and as well as with 8 parts by weight of Mo powder. The mixing was done in a ball mill. The cathode body—in this case a cylindrical body—was pressed from this powder by means of conventional metallicurgical processes. The cathode body was sintered under high vacuum at 2300° C for 30 minutes and then finished by grinding and built in as the finished cathode.

**Example VI**

A conventionally carburnitized tungsten wire containing 2% ThO₂ was coated with platinum to 5.1 mg/cm² and then annealed for one hour at 1450° C for 20 minutes, and for two hours at 1950° C for 30 minutes. The wire was then broken into pieces and ground and then milled with ThO₂, 10 parts by weight of the Mo powder to 1 part by weight of ThO₂. The mixture was then processed further as described in Example V.
Hexagonal tungsten carbide was provided, which was made by any of several known methods—in this case, by carburizing tungsten wire. One part by weight of this carbide was admixed with 1 part by weight of thorium oxide and 1 part by weight of tungsten powder; this mixture then being ground and thereafter pressed into the desired shape. The pressed body was sintered at 2600°C in an argon atmosphere until the body was self-supporting but still contained 15% by volume of pores. This pre-fabricated body was then finished and thereafter soaked in a 5% solution of manganese chloride. After this impregnation, the body was dried and then annealed under high vacuum for one hour at 1100°C, and then for ½ hour at 2100°C. The cathode was then ready to be built into the electrical discharge vessel.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

1. A method for producing hot cathodes for electric discharge vessels containing as active metal thorium and as a refractory metal a material selected from the group consisting of W and Mo and a carbide of said refractory metals having a chemical composition MXC, wherein M represents said refractory metal, said carbide being in a hexagonal crystalllographic structure; transforming said structure in the presence of one of the metals selected from the group consisting of Pt, Pd, Ru, Os, Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Au, Mn, Cu by a solid-state reaction at elevated temperature through a catalytic action of one of the metals of said group, until said hexagonal carbide is completely transformed to a body centered cubic modification, the temperature applied during said solid-state reaction being above ¾ of the melting point of the used catalyst metal, whereby the catalyst metal evaporates substantially and disappears from the surface of said carbide.

2. A method for producing hot cathodes for electric discharge vessels containing as active metal thorium and as a refractory metal thoriated tungsten filament and tungsten carbide made by carburizing the surface of the tungsten filament by heating in a carbon-containing media to a carbide of a chemical composition W₂C, said carbide being in a hexagonal crystalllographic structure; transforming said structure in the presence of one of the metals selected from the group consisting of Pt, Pd, Ru, Os, Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Au, Mn, Cu by a solid-state reaction at elevated temperature through a catalytic action of one of the metals of said group, until said hexagonal W₂C carbide is completely transformed to the body centered cubic modification, the temperature applied during said solid state reaction being above ¾ of the melting point of the used catalyst metal, whereby the catalyst metal evaporates substantially and disappears from the surface of said tungsten filament.

3. A method for producing hot cathodes having a filler mass containing thorium as active metal and consisting of thorium and of an arbitrary refractory metal powder as a supporting agent, and of a refractory metal carbide, wherein said refractory metal is selected from the group consisting of W and Mo and a carbide of said refractory metals; said carbide being made by carburizing the refractory metal component by heating in a carbon-containing media to a carbide of a chemical composition MXC, wherein M represents the said refractory metal, said carbide being in a hexagonal crystalllographic structure; transforming said structure in the presence of one of the metals selected from the group consisting of Pt, Pd, Ru, Os, Ir, Rh, Re, Fe, Ni, Co, Cr, Ag, Au, Mn, Cu by a solid state reaction at elevated temperature through a catalytic action of one of the metals of said group, until said hexagonal carbide is completely transformed to a body centered cubic modification, the temperature applied during said solid state reaction being above ¾ of the melting point of the used catalyst metal, whereby the catalyst metal evaporates substantially and disappears from the surface of said tungsten carbide.
9 refractory metal, the improvement that said carbide has a body centered cubic crystallographic structure.

10. A sintered body of refractory metal selected from the group consisting of W and Mo, said body further containing ThO₂ and carbide of said refractory metal having a composition MₓC, where M represents said refractory metal, the MₓC having a body centered cubic crystallographic structure.

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