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THERMIONIC CATHODE AND METHOD OF MANUFACTURING SAME

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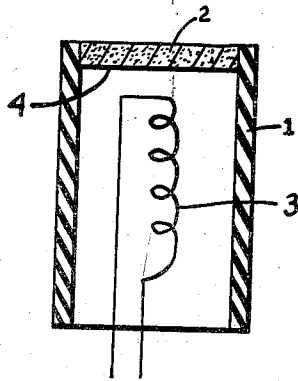


FIG. 1

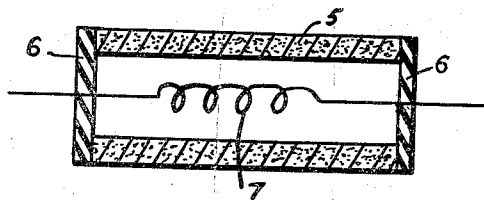


FIG. 2

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1

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**THERMIONIC CATHODE AND METHOD OF MANUFACTURING SAME**

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14 Claims. (Cl. 117—33.26)

Our invention relates to a thermionic cathode and to a method of making the same. In particular, our invention relates to cathode containing a supply of an alkaline earth composition capable of furnishing free alkaline earth metal to the cathode surface.

Cathodes of the type containing a supply of alkaline earth compounds have been described in U. S. Patent No. 2,543,728 to H. J. Lemmens et al. In the cathodes described in that patent the supply of alkaline earth compounds are contained in a tightly closed cavity of a body, one wall portion of which consists of porous refractory metal, the pores of the wall forming the largest passageways connecting the cavity to the exterior of the cathode.

It is a main object of our invention to permit prefabricated porous bodies to be rendered well-emissive without causing any alterations in shape or dimensions of the body and without requiring any additional tightly closed internal cavities.

It is a further object of our invention to provide a cathode which is easily manufactured to close mechanical tolerances and has a high degree of dimensional stability.

It is a still further object of our invention to provide cathodes having a flatness and smoothness of surface not obtainable by other techniques.

It is a still further object of our invention to provide a cathode which can be manufactured without restrictions as to shape or dimensions.

It is yet another object of our invention to provide a cathode using alkaline earth metal compositions which do not react unfavorably with the refractory metal during activating or processing of the cathode and which furnish a greater proportion of free alkaline earth metal to the external surface of the cathode than the alkaline earth compounds heretofore suggested.

It is still another object of our invention to provide a cathode which is relatively stable to air and atmospheric influences.

These and further objects of our invention will appear as the specification progresses.

In accordance with our invention we form a body of refractory metal having pores therein connecting the interior of the body to the surface and fill those pores with an alkaline earth composition which reacts with the refractory metal principally in a manner productive of free alkaline earth metal.

The body may be formed by pressing a finely-divided powdered refractory metal and heating to an elevated temperature at which the particles sinter together and form a cohesive mass which is dense yet porous, i. e., the particles are not melted in this process, but a process of "grain-growth" appears to take place and the body approaches but never reaches 100% of theoretical density. Preferably, sintering is effected at a temperature which will exceed the cathode operating temperature and the temperature at which the impregnant material melts and diffuses into the body.

Shaping of the body may be effected during the pressing operation but during subsequent heating the body tends to shrink and warp and close dimensional tolerances cannot be maintained. We therefore prefer to machine the body after it has been thusly formed by employing the technique disclosed in the co-pending U. S. application Serial No. 234,513 filed June 30, 1951, by Roberto Levi. In that process, the body is impregnated with a "filler" metal, i. e., a metal which does not alloy with the metal of the body, machined, and the

2

filler subsequently removed by volatilization at a temperature below the sintering temperature used in forming the body.

The pores in the body thus obtained may now be filled with an alkaline earth composition which does not react with the refractory metal in a manner unproductive of free alkaline earth metal. The alkaline earth metal composition is first heated to a temperature at which the composition melts in a "neutral" atmosphere. By a neutral atmosphere we mean an atmosphere whose constituents do not react with either the refractory metal or the alkaline earth composition in a manner harmful to the operation of the cathode. In particular, the atmosphere should contain insignificant amounts of water-vapor, carbon dioxide and oxygen. Strongly reducing gases such as hydrogen should also be excluded from the atmosphere. Dry noble gases, i. e., helium, argon, neon, xenon, krypton, are examples of desirable neutral atmospheres. In some cases, we even prefer to heat the alkaline earth metal composition in a vacuum and we wish to have the term "neutral" atmosphere as employed in the specification and appended claims construed to cover not only atmospheres containing insignificant amounts of constituents harmful to the cathode but also to a vacuum. We then bring the porous body into intimate contact with the molten material, as, for example, by immersing the body in the molten material or by placing the material on the body and converting it to a molten state. While in a molten state, the material flows or diffuses into the pores of the body and completely or partially fills all voids and interstices accessible from the exterior of the body.

After cooling, the body is mounted in an evacuated envelope and activated by heating to a temperature at which the alkaline earth composition reacts with the refractory metal to supply a layer of alkaline earth metal substantially one molecule thick on the surface of the body. The cathode is now ready for operation.

Instead of machining the body in the manner described above, the body may be impregnated with a filler metal, swaged, or rolled and drawn to a reduced diameter in order to produce filaments which may be processed into cathodes. Likewise the body of refractory metal may be formed by extrusion and impregnated with filler metal or powdered refractory metal may be mixed with powdered filler metal and the body pressed and sintered.

As impregnant materials only those which are capable of reacting with the refractory metal principally in a manner productive of free alkaline earth metal are envisaged by this invention. As refractory metals, tungsten is preferred but molybdenum, hafnium, tantalum, niobium and rhenium among others, may be used. In the case of tungsten, certain alkaline earth compounds, notably the nitrates react therewith to form tungstates with a consequent diminution of the amount of free alkaline earth metal being made available in the free state. It is probable that similar reactions occur with the other refractory metals and for that reason we prefer to use no nitrates of the alkaline earth metals. We have found by extensive experimentation and by a study of the principles underlying the operation of cathodes of this type that impregnants having compositions of the type disclosed in the copending U. S. application Serial No. 258,892 filed November 29, 1951, by R. C. Hughes, P. P. Coppola and E. S. Rittner fulfill the essential condition outlined hereinbefore. Such preferred impregnants include fused mixtures of an alkaline earth oxide and one or more metal oxides, for instance, oxides of aluminum, beryllium, silicon, boron and thorium, which form materials having at least one phase different than an alkaline earth phase. We have also found that compositions of barium oxide, aluminum oxide and boric oxide are also very well suited to the invention. We also prefer to employ those impregnant materials which have a relatively low vapor pressure at their melting point to avoid excessive evaporation of the impregnant material, or any of its constituents.

The invention will now be described in connection with the accompanying drawing in which:

Fig. 1 is a sectional view of one embodiment of a cathode according to our invention; and

Fig. 2 is a sectional view of another embodiment of a cathode according to our invention; and in connection with the following illustrative examples.

Fig. 1 shows in section one form of a cathode according to our invention comprising a tube 1 of molybdenum closed at one end by a sintered tungsten disc 2 impregnated with a fused mixture of barium oxide and aluminum oxide in a 5:2 mol. ratio. The fused mixture completely or partly fills all voids and interstices between the tungsten accessible from the exterior surface of the cathode. A heater 3 is mounted within the tube for heating the cathode. In order to reduce evaporation of the alkaline earth metal and its composition into the molybdenum tube, the underside 4 of the disc was lapped to close the pores on that side prior to impregnation of the disc with the alkaline-earth metal composition.

Fig. 2 shows a typical cylindrical cathode suitable for use in tubes of the magnetron type wherein large emission currents and long life are desired. The cathode comprises a sintered tungsten tube 5 impregnated with a fused mixture of barium oxide, aluminum oxide and boric oxide containing in excess of 60% by weight of barium oxide with the proportions of the aluminum oxide and boric oxide varying as desired. The tungsten tube is closed at both ends by molybdenum caps 6 which are secured to the tungsten tube by welding. A heater 7 is enclosed by the tube, the lead-in wires extending through the molybdenum caps. In order to prevent evaporation of material internally into tube 5, the internal surface of the tungsten tube had been lapped or burnished prior to impregnation to close the pores of its internal wall.

Since the technique according to the invention is applicable to either type of cathode or to any shape or form of cathode, it will be described generally. However, for practical considerations, the technique will be described in connection with the fabrication of an impregnated tungsten cathode but it is to be understood that the invention is not necessarily limited to tungsten or to the specific materials described herein but is defined in the claims appended to this specification.

The first step in the manufacture of the cathode is that of forming a dense, but porous, body of tungsten having the desired shape and dimensions. While various techniques can be used for this purpose as have been enumerated hereinabove, we prefer to form a tungsten body in accordance with the procedure specifically disclosed in U. S. application Serial No. 234,513 filed June 30, 1951 by Roberto Levi. We prefer to use the same particle size and distribution of tungsten powder disclosed therein and to press the powder and sinter at the stated pressure and temperature. This body can be machined after impregnation with copper and upon removal of the copper by subsequent volatilization at a temperature below that at which the body was sintered results in a body which has dimensional stability up to high temperatures, e. g., 2000° C., required porosity, and required density.

The tungsten body thus obtained is impregnated with an alkaline earth composition which has a melting point between 25° C. and a temperature below that at which the tungsten was sintered and which is capable of reacting with the tungsten principally in a manner productive of free alkaline earth metal such as compositions containing alkaline earth oxides or carbonates and aluminum oxide, boric oxide, thorium oxide, beryllium oxide and silicon dioxide. Compositions containing barium as the alkaline earth metal are preferred but strontium and/or calcium may be substituted for the barium in whole or in part.

In one embodiment of the invention, a quantity of barium carbonate and aluminum oxide in the mol. ratio 5:2 was placed on the surface of the tungsten body and the body heated in an electric furnace to a temperature of about 1700° C. in a vacuum. Up to and at that temperature the following steps probably occur. The barium carbonate is thermally dissociated into barium oxide and carbon dioxide, the latter being pumped out the furnace. The barium oxide and the aluminum oxide fuse into composite mass which can be loosely called barium aluminate. The mass liquifies and diffuses into the pores of the tungsten body filling all voids and interstices in whole or in part. The porous tungsten body is preferably kept in contact with the molten material for the shortest possible period of time consistent with impregnation of the body. After the furnace has cooled,

the body is removed and its outer surface lightly lapped or brushed to remove any excess barium aluminate on the surface.

After impregnation, a molybdenum supporting structure can be welded to the tungsten and the body mounted in an evacuated envelope. After degassing the envelope, the cathode is activated by operating the cathode at a temperature somewhat higher than normal operating temperature, e. g., 1000° C. to 1200° C. until the cathode emits satisfactorily.

We have made in addition to the foregoing cathode, cathodes which comprise a dense tungsten body having pores therein impregnated with a mixture barium oxide and boric oxide containing over 70% by weight of barium oxide and with mixtures of barium oxide, aluminum oxide and boric oxide with over 60% by weight of barium oxide with the proportions of the latter constituents varying over wide ranges.

The cathodes which we have made by our process have been tested for emission and life. Emission data indicates the cathode is capable of supplying about 1 amp./cm.<sup>2</sup> continuously (D.-C. emission) at 1000° C. with pulsed emissions of the order of 1 amp./cm.<sup>2</sup>. The indicated life of such cathodes is greater than 1000 hours.

The cathodes made by our process may be made to have exceptional dimensional stability because the tungsten body is not subject to shrinkage or warpage due to the high sintering temperatures employed.

We have been able to make, by our process, filamentary type cathodes, i. e. wire cathodes, merely by altering the shaping operation, for example, by swaging the sintered and copper impregnated tungsten body and drawing the body to required diameter.

Our cathode has one distinct advantage over the internal cavity type of dispenser cathode in which the alkaline earth compounds are contained within a tightly sealed cavity closed by a porous wall portion. In order to tightly close the cavity it is generally necessary to fabricate a cup of refractory metal such as molybdenum and weld the porous tungsten member to the cup. Because our source of alkaline earth metal is contained wholly within pores of the tungsten body itself, it is no longer necessary to weld a closure member to the tungsten body or to use any other expedient to obtain a tight fit. Thus, the cost of manufacture of our cathodes is much less than other known types of dispenser cathodes.

While we have thus described our invention with specific examples and in specific embodiments thereof, we wish it to be understood that we are aware that cathodes of other shapes than those disclosed can be fabricated and that other alkaline earth compositions than those specifically disclosed hereinabove can be used. We wish, therefore, to have it understood that our invention is not to be limited by our disclosure but to be defined by the limits of the claims appended to this specification.

What we claim is:

1. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of refractory metal having at least one surface portion adapted to act as an electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide and aluminum oxide containing about 60 to 90% by weight of barium oxide.

2. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of refractory metal having at least one surface portion adapted to act as an electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide and aluminum oxide in a molecular ratio of about 5:2.

3. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of refractory metal, and impregnating the pores of said body with a molten mixture of barium oxide and aluminum oxide containing about 60 to 90% by weight of barium oxide.

4. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous body of densely-sintered refractory metal, and impregnating the pores of said body with

5

6

a fused mixture of barium oxide and aluminum oxide in a molecular ratio of about 5:2.

5. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of refractory metal having at least one surface portion adapted to act as an electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of an alkaline earth metal oxide and an oxide selected from the group consisting of aluminum oxide, silicon dioxide, boric oxide and beryllium oxide, the alkaline earth metal oxide forming a substantial amount of the mixture.

6. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of refractory metal having at least one surface portion adapted to act as an electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide and an oxide selected from the group consisting of aluminum oxide, silicon dioxide, boric oxide, and beryllium oxide, the barium oxide forming at least about 60% by weight of the mixture.

7. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of tungsten having at least one surface portion adapted to act as an electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide and an oxide selected from the group consisting of aluminum oxide, silicon dioxide, boric oxide, and beryllium oxide, the barium oxide forming at least about 60% by weight of the mixture.

8. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of refractory metal having at least one surface portion adapted to act as an electron-emissive surface and provided with a large surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide, boric oxide, beryllium oxide and aluminum oxide, the barium oxide forming at least about 60% by weight of the mixture.

9. A thermionic cathode adapted to operate at an elevated temperature comprising a sintered body of tungsten having at least one surface portion adapted to act as an

electron-emissive surface and provided with a large number of interconnected pores forming passageways between said surface portion and at least a portion of the interior of said body, said latter portion being impregnated with a fused mixture of barium oxide and aluminum oxide in a molecular ratio of about 5:2.

10. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of refractory metal, and impregnating the pores of said body with a molten mixture of an oxide selected from the group consisting of aluminum oxide, silicon dioxide, boric oxide, beryllium oxide and a substantial amount of an alkaline earth metal oxide.

11. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of refractory metal, and impregnating the pores of said body with a molten mixture of an oxide selected from the group consisting of aluminum oxide, silicon dioxide, boric oxide, beryllium oxide and at least about 60% by weight of barium oxide.

12. A method of manufacturing a thermionic dispenser cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of tungsten, and impregnating the pores of said body with a molten mixture of an oxide selected from the group consisting of aluminum oxide, boric oxide, silicon dioxide, and beryllium oxide and at least about 60% by weight of barium oxide.

13. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of refractory metal, and impregnating the pores of said body with a molten mixture of aluminum oxide and at least about 60% by weight of barium oxide.

14. A method of manufacturing a thermionic cathode adapted to operate at elevated temperatures which comprises forming a porous sintered body of tungsten, and impregnating the pores of said body with a molten mixture of barium oxide and aluminum oxide in a molecular ratio of about 5:2.

References Cited in the file of this patent

UNITED STATES PATENTS

1,735,080	Hertz	Nov. 12, 1929
2,389,060	Kurtz	Nov. 13, 1945
2,547,869	Keilholtz	Apr. 3, 1951