Aug. 11, 1959 | P. P. COPPOLA | 2,899,592

THERMIONIC DISPENSER CATHODE

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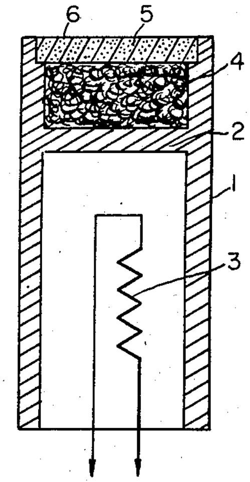


Fig. 1

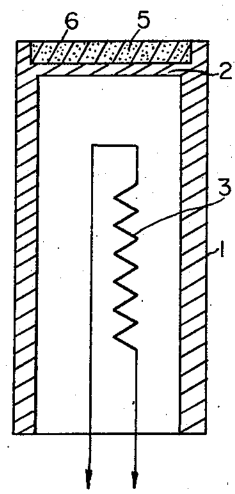


Fig. 2

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# THERMIONIC DISPENSER CATHODE

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2 Claims. (Cl. 313—346)

My invention relates to a thermionic dispenser cathode.

In a thermionic dispenser cathode, a supply of alkaline earth material is disposed within a body of refractory metal, e.g., tungsten, molybdenum, tantalum, hafnium, or niobium, having a porous wall portion through which alkaline earth metal produced by a reaction between the alkaline earth material and the refractory metal can pass and form an emissive layer on a surface of the body. The reaction between the refractory metal and the alkaline earth compound usually proceeds quite rapidly, and in many cases an excessive amount of alkaline earth metal is supplied to the emissive surface and is evaporated which is a disadvantage of the cathode for certain applications. Efforts have been made to reduce the rate at which the free alkaline earth metal is supplied to the emissive surface by decreasing the porosity of the porous wall. However, this not only makes the cathode more difficult to fabricate, e.g., higher sintering temperatures in fabricating the porous wall must be employed, but makes the porosity of the wall a critical factor in the performance of the cathode. Moreover, for certain types of dispenser cathodes, the porosity cannot be decreased sufficiently so that the rate of evaporation of alkaline earth metal still remains excessive.

A principal object of my invention is to provide a thermionic dispenser cathode having a reduced rate of evaporation of alkaline earth metal.

A still further object of my invention is to provide a cathode in which the porosity of the porous wall is not the controlling factor in determining the rate at which free alkaline earth metal is furnished to the emissive surface of the cathode.

A further object of my invention is to provide a thermionic dispenser cathode in which the initial rate of evaporation of alkaline earth metal during fabrication and activation is reduced.

Another object of my invention is to facilitate the fabrication of a thermionic dispenser cathode by employing a refractory metal alloy which can be sintered into a body at lower temperatures.

A further object of my invention is to provide a dispenser cathode employing a more readily machinable refractory metal whereby the cathode can be machined to close tolerances.

A further object of my invention is to employ a refractory metal alloy in which one of the constituents of the alloy will serve to bind some undesirable gaseous

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products which may be produced during the operation of the cathode.

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

I have found that the rate of evaporation of alkaline earth metal in a dispenser cathode can be reduced by substituting for the refractory metal, such as tungsten, in the porous wall of the cathode structure an alloy of at least two refractory metals one of which is active in reducing the alkaline earth material disposed in a cavity within the body and the other of which is more passive during the reaction.

By the term "active refractory metal" I mean a refractory metal which will react with certain alkaline earth compounds to furnish a supply of free alkaline earth metal in excess of that required to form a satisfactory emitter.

By the term "passive refractory metal" I mean a refractory metal which does not react or only reacts with those alkaline earth compounds to such an extent as to form an insufficient amount of free alkaline earth metal.

The refractory metals may be either passive or active depending upon which alkaline earth compounds are employed.

The passive refractory metal serves to limit the amount of active refractory metal available for reaction with the alkaline earth material in the cavity and also serves to limit the rate at which the active refractory metal is brought into contact with the alkaline earth material because the active refractory metal must diffuse through the passive refractory metal before contacting the alkaline earth material. Consequently, the alloy must contain the "active" and "passive" refractory metals in amounts sufficient to form the emissive surface while preventing excessive evaporation of alkaline earth metal.

The refractory metals, molybdenum, tungsten, tantalum, niobium, zirconium and hafnium, are more or less active in reducing certain alkaline earth compounds or compositions to free alkaline earth metal. More particularly, I have found that molybdenum is the least active of the refractory metals in its ability to reduce alkaline earth compounds or compositions to the free alkaline earth metal. By alloying molybdenum with tungsten, for example, I have found that the rate of reaction producing free alkaline earth metal from alkaline earth compounds is materially reduced so that the porosity of the porous wall portion is no longer a critical factor in controlling the rate at which the free alkaline earth metal is supplied to the electron-emissive surface.

In a preferred embodiment of my invention I mix the alkaline earth material with powdered refractory metal alloy and press the mixture into a body which is sintered to produce a coherent body. During the sintering, some reduction of the alkaline earth material occurs but this reduction, I have found, is materially less than if tungsten alone is used as a refractory metal. Moreover, because such a cathode is likely to be quite porous, it would be expected that the rate of evaporation of free alkaline earth metal during operation will be relatively high. I have found, however, that the alloys according to my invention substantially reduce the rate of evaporation of the alkaline earth metal by inhibiting the rate of reduction of the alkaline earth material.

I have also found that by alloying a more active refractory metal, such as tantalum, zirconium or hafnium, with one of the less active metals, such as tungsten or molybdenum, it is possible to use alkaline earth compounds which are difficult or impossible to reduce with tungsten alone. For example, an alloy of tungsten and hafnium will reduce barium orthosilicate, which tungsten will not reduce at all, without excessive evaporation of barium which would be the case if hafnium alone were used.

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 dispenser cathode according to the invention; and

Fig. 2 is a sectional view of another embodiment of a dispenser cathode according to the invention.

The dispenser cathode shown in Fig. 1 comprises a tube **1** composed of refractory metal such as molybdenum having an internal partition **2** for separating the tube into two chambers. The lower chamber houses a conventional heater **3** while the upper chamber houses a supply of alkaline earth compounds **4** such as a mixture of barium and strontium carbonates. The upper chamber is closed by a porous disc **5** sealed to the end of the tube **1** by welding so that the pores in the wall constitute the only passageways connecting the cavity in which the alkaline earth compounds are disposed to the emissive surface **6**.

The porous disc **5** is made of an alloy composed of 25% of tungsten and 75% of molybdenum made by pressing the powdered alloy into a disc and sintering the same at a temperature of about 1600° to 1900° C. Since the resulting disc is porous, the alkaline earth metal obtained by reaction between the alkaline earth compounds in the cavity passes through the pores of the disc and forms an emissive layer on the surface of the cathode.

In this alloy tungsten is the active refractory metal which reacts with the barium and strontium oxides formed by thermal decomposition of the carbonates in the cavity to supply free barium to the emissive surface of the cathode. Since the tungsten is alloyed with molybdenum, not only is the amount of tungsten available for the reaction diminished but the rate at which it is made available for reaction is limited by its diffusion rate through the molybdenum.

If other alkaline earth compounds or mixtures or solid solutions thereof are substituted in the cavity for the barium and strontium carbonates, other refractory alloys may be used. The following table lists the most suitable refractory metal that should be used for various alkaline earth compositions in the cavity in order to obtain a sufficient but not excessive supply of barium for the emissive surface.

| Refractory Metal Alloy<br>Passive Ref. Metal—Active Ref. Metal | Alkaline Earth Material in Cavity |
|---|---|
| Mo—W, up to about 90% of W | $BaCO_3$.<br>BaO.<br>Basic barium silicates ($3BaO:Si_2$ or $4BaO \cdot SiO_2$). |
| Mo—Ta, up to about 10% Ta | Basic barium aluminates (excess BaO).<br>Normal and basic barium beryl-liates.<br>$BaCO_3$.<br>BaO.<br>Basic barium silicates. |
| W—Ta, up to about 10% | Basic barium aluminates.<br>Normal and basic barium beryl-liates. |
| Mo—Nb, up to about 10% Nb | $BaCO_3$.<br>BaO.<br>Basic barium aluminates.<br>Basic barium silicates.<br>Normal and basic barium beryl-liates. |

| Refractory Metal Alloy<br>Passive Ref. Metal—Active Ref. Metal | Alkaline Earth Material in Cavity |
|---|---|
| W—Nb, up to about 10% Nb | Basic barium aluminates.<br>Basic and normal barium beryl-liates. |
| Mo—Hf, less than about 5% Hf | $BaCO_3$.<br>BaO.<br>Basic barium aluminates.<br>Basic and normal barium beryl-liates.<br>Basic barium silicates. |
| W—Hf, less than about 5% Hf | Basic barium aluminates.<br>Basic and normal barium beryl-liates. |
| Mo—Zr, less than about 5% Hf | Barium orthosilicate.<br>Basic barium aluminates.<br>Normal and basic barium beryl-liates. |
| W—Zr, less than about 5% Hf | Barium orthosilicate.<br>Basic barium aluminates.<br>Normal and basic barium beryl-liates. |

In the cahtode shown in Fig. 2, the alkaline earth compounds are homogeneously distributed within the porous disc itself. In this construction, the disc **5** in which the alkaline earth compounds are disposed is sealed in one end of a tube **1** of refractory metal such as molybdenum and separated from the heater **3** by a partition **2** of refractory metal.

The porous disc in which the alkaline earth compounds are disposed can be fabricated as follows. The disc may be made by mixing the refractory metal in powdered form with the alkaline earth material, e.g., a 5 to 2 mole ratio of a prefired mixture of BaO and $Al_2O_3$. This mixture is then pressed and sintered at a temperature of about 1650 to 1750° C. for about 30 seconds. The resulting body is mechanically coherent and relatively free of entrapped gases.

Alternatively, a porous disc obtained by pressing and sintering a powdered refractory metal alloy at relatively high temperatures, e.g., 1600–1900° C. but in any event no higher than a temperature slightly below the lowest melting point of either the alloy or any of its constituents. The porous disc thus obtained, which may be machined, if desired, is then impregnated with a suitable alkaline earth material as described in U.S. application Serial No. 273,607, filed February 27, 1952, now Patent 2,700,000 by R. Levi et al. If the sitered body of refractory metal alloy is impregnated from a melt, the alkaline earth material to be used must have a melting point below the temperature at which the porous disc was sintered in order to avoid further sintering thereof during impregnation.

In the cathodes in which the alkaline earth material is homogeneously distributed throughout the porous disc, the alkaline earth material must be selected so that it is readily reducible by the active refractory metal without deleteriously reacting therewith. Suitable alkaline earth materials and the criteria governing their selection for that type of cathode are disclosed in U.S. applications Serial Nos. 258,891, now Patent No. 2,716,716 and 258,892, now Patent 2,700,112 filed November 29, 1951, by R. C. Hughes et al. All of the compositions and mixtures of alkaline earth compounds disclosed therein may be used in the cathode according to my invention and the foregoing advantages enumerated hereinabove will be realized.

However, the selection of the particular alkaline earth material will to some extent determine the particular refractory metal alloy that should be used and I have listed in the table below the best combinations of refractory metal alloys and alkaline earth materials. In the table the terms "pressed powder" and "impregnated" refer, respectively, to cathodes made by mixing the alkaline earth material with the powdered metal alloy and forming a body therefrom, and to a cathode obtained by introducing the alkaline earth material into a porous disc by impregnation.

| Refractory Metal Alloy Passive Ref. Metal—Active Ref. Metal | Type of Cathode | Alkaline Earth Material |
|---|---|---|
| Mo—W, up to about 90% W | Impregnated and Pressed Powder. | Basic barium aluminates.<br>Basic barium silicates.<br>Basic barium berylliates. |
| Mo—Ta, up to about 10% Ta | Impregnated and Pressed Powder. | Basic barium aluminate.<br>Basic barium berylliates. |
| | Pressed Powder only | Normal barium berylliate. |
| Mo—Nb, up to about 10% Nb | Pressed Powder and Impregnated. | Basic barium aluminate.<br>Basic barium berylliates. |
| | Pressed Powder only | Normal barium berylliate. |
| Mo—Hf, less than about 5% Hf | Impregnated and Pressed Powder. | Mono-barium aluminate.<br>Basic barium aluminates.<br>Basic barium berylliates. |
| | Pressed Powder only | Barium orthosilicate.<br>Normal barium berylliate. |
| W—Hf, less than about 5% Hf | Impregnated and Pressed Powder. | Mono-barium aluminate. |
| | Pressed Powder only | Barium orthosilicate.<br>Normal barium berylliate. |
| Mo—Zr, less than about 5% Zr | Impregnated and Pressed Powder. | Mono-barium aluminates.<br>Basic barium berylliates. |
| | Pressed Powder only | Barium ortho-silicate.<br>Normal barium berylliate. |
| W—Zr, less than about 5% Zr | Impregnated and Pressed Powder. | Mono-barium aluminate.<br>Barium ortho-silicate. |
| | Pressed Powder only | Normal barium berylliate. |

The following tables indicate the emission and life of several cathodes of the pressed powder type pressed from a mixture of 10% by weight of a 5:2 mole ratio of prefired $BaO \cdot Al_2O_3$ and 90% by weight of a molybdenum-tungsten alloy. In Table I the alloy was composed of 90% of molybdenum and 10% of Tungsten; in Table II, the alloy was composed of 50% of molybdenum and 50% of tungsten; and in Table III the alloy was composed of 75% molybdenum and 25% of tungsten.

In order to test emission and life, the cathode was assembled in an evacuated envelope in which an anode was arranged. All emission measurements were taken at a cathode operating temperature of 950° C. brightness pulse-wise with 100 microsecond pulses at the rate of 20 per second at a 1000 volts on the anode. The cathode was held at 1050° C. brightness with 100 volts D.C. on the anode during life.

*Table I*

| Tube No. | Life—Hours [1] | Emission, Amps./cm.$^2$ |
|---|---|---|
| K 160 | 3,600 | 1.6 |
| K 163 | 3,590 | 2.2 |

[1] Results to date. Life test still continues.

*Table II*

| Tube No. | Life—Hours [1] | Emission, Amps./cm.$^2$ |
|---|---|---|
| A 164 | 5,232 | 2.2 |
| A 167 | 5,188 | 2.7 |
| A 168 | 5,188 | 2.7 |

[1] Results to date. Life test still continues.

*Table III*

| Tube No. | Life—Hours [1] | Emission, Amps./cm.$^2$ |
|---|---|---|
| K 155 | 4,210 | 2.4 |
| A 179 | 4,226 | 2.4 |

[1] Results to date. Life test still continues.

The reduction of the rate of evaporation of barium when using an alloy of two refractory metals rather than a pure refractory metal is illustrated by Table IV, which shows the total barium evaporation (Ba+BaO) determined for a pressed powder cathode prepared from mixtures by weight of a 5:2 mole ratio of prefired $BaO \cdot Al_2O_3$ and 90% by weight of tungsten and tungsten-molybdenum alloys.

*Table IV*

| Refractory Metal Composition | Average Total Barium Evaporation, Micrograms/cm.$^2$/hr. |
|---|---|
| Pure W | 9.5 |
| 50% W—50% Mo | 5.6 |
| 25% W—75% Mo | 3.8 |
| 10% W—90% Mo | 2.8 |

By alloying a refractory metal with gettering properties (which may also serve as either the passive or active refractory metal) with another refractory metal, alkaline earth compounds or mixtures thereof which evolve gas during activation may be used to advantage. More particularly, those mixtures of alkaline earth compounds which have been found to react together to form alkaline earth oxides which are then reduced by the refractory metal as disclosed in U. S. application, Serial No. 258,891, filed November 29, 1951, now Patent No. 2,716,716 by R. C. Hughes et al., while very advantageous, nevertheless evolve gas which must be pumped off while the cathode is activated in the tube. If a mixture of barium azide and barium formate is used as the alkaline earth material, using an alloy of at least two refractory metals one of which has inherent gettering properties such as molybdenum and zirconium not only achieves the principal advantage of the invention which is the reduction of excessive barium evaporation but also reduces the time required to pump off evolved gases during activation of the cathode. In this case, the zirconium is probably serving a dual function, i.e., it is the active refractory metal and it also scavenges the gas produced by the azide and formate. Zirconium is preferred because of its strong affinity for nitrogen and, secondly, because ZrN has a low dissociation pressure, namely, $1 \times 10^{-3}$ mm. Hg at 2046° C.

Several pressed powder cathodes employing an alloy of 99% Mo and 1% Zr were made and tested for emission and life. This data appears in Table V below. Those cathodes were prepared from a mixture containing 10% by weight of a 1:1 mole ratio of $Ba(N_3)_2+Ba(CHO_2)_2$ and 90% by weight of the molybdenum-tungsten alloy and assembled in diodes. The measurements were performed as in the foregoing tables.

*Table V*

| Tube No. | Life—Hours | Emission, Amps./cm.$^2$ |
|---|---|---|
| K 148 | 4,770 | 5.0 |
| K 149 | 4,770 | 5.0 |
| K 150 | 4,770 | 5.9 |

The time required on the pump for those cathodes was a fraction of that required when pure tungsten or pure molybdenum instead of the alloy was used.

This invention is not limited to cathodes having the shape shown but is applicable to dispenser cathodes of more complex construction. The cathode, for example, could have a cylindrical shape, or it could be a concave or planar type of cathode.

While I have therefore described my invention in connection with specific examples and applications, other modifications thereof will be apparent to those skilled in this art without departing from the spirit and scope of my invention as defined in the appended claims.

What I claim is:

1. A thermionic cathode comprising a structure consisting of refractory metal, a portion of the wall of said structure constituting the emissive surface thereof consisting of a homogeneously-porous sintered refractory metal alloy, and a supply of a fused mixture of 5 moles of barium oxide and 2 moles of aluminum oxide distributed within and only within the pores of said wall



portions and in intimate reactive relationship with said refractory metal alloy, said refractory metal alloy consisting of 75% by weight of molybdenum and 25% by weight of tungsten.

2. A thermionic cathode comprising a tubular structure consisting of refractory metal, a portion of the wall of said structure constituting the emissive surface thereof consisting of a sintered body composed of 90% by weight of an alloy consisting of 75% by weight of molybdenum and 25% by weight of tungsten, and 10% by weight of a fused mixture of 5 moles of barium oxide and 2 moles of aluminum oxide, the fused mixture of barium and aluminum oxide being contained within and only within said sintered body.


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