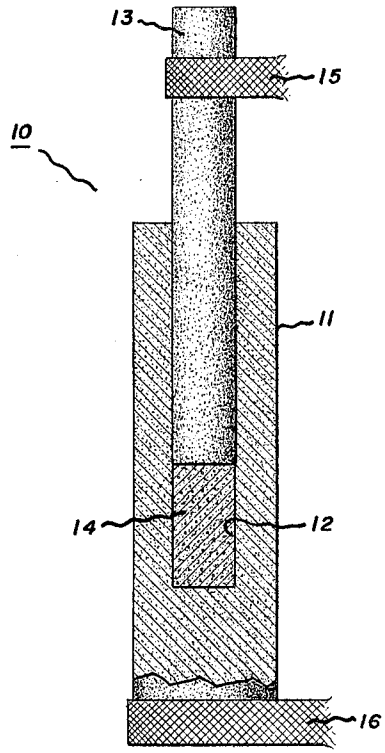
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DISPENSER CATHODE AND METHOD FOR THE PRODUCTION THEREOF

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DISPENSER CATHODE AND METHOD FOR THE PRODUCTION THEREOF

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This invention relates to a thermionic dispenser cathode comprising a sintered mixture of a refractory metal and an alkaline earth metal for use in various electrical apparatus as a source of electron emission, and more particularly to an improved method of simultaneous hot-pressing thermionic cathodes.

One example of a thermionic dispenser cathode is a cathode which comprises a porous refractory metal body, for example tungsten, which is impregnated with an alkaline earth metal compound such as a barium compound. Under operative high temperature conditions, the compound reacts with the refractory metal to produce free alkaline earth metal vapor. This vapor diffuses through the pores and forms a monatomic layer on the surface of the body. Such a surface constitutes an excellent source of primary electrons.

There are generally two commonly employed methods of fabrication of thermionic dispenser cathodes. One method consists of mixing the principal ingredients, for example a powdered combination of tungsten and a barium compound, and pressing the mixture at a very high pressure, for example, about 70 tons per square inch, to the required structural configuration. Thereafter the structure is usually fired in a reducing atmosphere such as hydrogen, at a high temperature of about 1700° C., in order that the pressed body is effectively sintered.

A second method of preparing thermionic dispenser cathodes includes the provision of a sintered block of a matrix metal, for example tungsten, by suitable compacting and sintering operations. The sintered tungsten is impregnated with copper to aid in subsequent machining to the desired configuration and the copper is then removed by vacuum firing. An alkaline earth metal compound such as barium aluminate is thereafter deposited in the porous tungsten matrix by vacuum impregnation.

It has been generally noted that many electron tubes are limited in life and performance by the thermionic cathode assembly. Examination of the many factors limiting frequency and power obtainable from electron tubes also reveals that cathode inadequacies are the more important of these limitations. Many of these inadequacies arise from production methods, from introduction of unknown variables from plural operations, and from the difficulty of predetermining optimum porosity and density under numerous operating conditions. A three-fold improvement over prior art thermionic dispenser cathodes involves selection of optimum materials and an improved method of repetitively producing high quality cathodes in one combined hot-pressing operation.

Accordingly, it is an object of this invention to provide an improved thermionic dispenser cathode.

It is another object of this invention to provide an improved high current density thermionic cathode.

It is a further object of this invention to provide a high current density cathode comprising a porous refractory metal, barium orthosilicate and calcium carbonate.

It is yet another object of this invention to provide an improved method for the production of thermionic dispenser cathodes.

It is a still further object of this invention to provide a combined pressing and sintering operation for the production of a thermionic emissive cathode.

It is yet another object of this invention to provide for the use of calcium carbonate ($CaCO_3$) in conjunction with a combined pressing and sintering operation to produce a thermionic cathode.

It is again another object of this invention to provide a simultaneous pressing and sintering operation, for the production of a thermionic dispenser cathode which combines a refractory metal, barium orthosilicate (Ba_2SiO_4), and calcium carbonate ($CaCO_3$), which is carried out in a carbon cylinder or crucible.

Briefly described, this invention comprises in one form the combining of a particulate refractory metal and barium orthosilicate in a ratio of about 90 weight percent to 10 weight percent respectively, and simultaneously pressing and sintering the mixture in a single operation in a reducing atmosphere. Very small amounts, about 1 weight percent or less of the body, of additives such as calcium carbonate are added to the mixture. In one preferred practice, this invention includes the combined pressing and sintering operation as carried out in a carbonaceous material crucible.

This invention will be better described when taken in connection with the following specification and drawings in which:

The figure is a cross-sectional illustration of a carbon piston-cylinder combination where the combined or simultaneous pressing and sintering operation may be carried out.

A common type of thermionic dispenser cathode to which this invention is particularly applicable is referred to as an internal dispensing cathode. Such a cathode may be defined as a cathode which gains its electron emissive pound dispersed therethrough to provide an emissive material dispensed from internally of the cathode to its surface. An internal dispensing cathode includes for example a sintered particulate tungsten matrix, and a barium compound dispersed therethrough to provide an emissive material as Ba or BaO. The emissive material is ideally one which uniformly covers the emitting surface and is about one monolayer thick. An important element in the operation of a dispenser cathode is to provide for the dispensing of the emissive material to the matrix surface so that a rather uniform layer is formed over the surface, resulting in a lowering of the work function.

At least four important factors are involved in this dispensing action and the maintenance of a uniform surface: (1) the production of the emissive material, usually an electro-positive atom, (2) the transport of the emissive material through the matrix to the surface, (3) the diffusing of the emissive material over the cathode surface, and (4) the evaporation of the emissive material from the cathode surface.

A consideration of these factors indicates that one common measure of cathode performance is its evaporation rate or loss of emissive material. A problem which is related to the above measure, in addition to choice of materials, is optimum pore size and density of the matrix, and the resultant dispersal throughout the matrix of the emissive material. It has been discovered that a particular choice of an activator material and a prescribed additive provides a salient improvement in the evaporation rate of a dispenser cathode. In combination therewith, a combined or simultaneous sintering and pressing operation on all materials as combined in the cathode not only improves the structure of the cathode, including porosity, but also provides a more improved cathode by eliminating potential introduction of unknown detrimental factors by separate operations.

The dispenser cathode of this invention in its preferred form includes a refractory metal in combination with a barium compound and additive materials. Various refractory metals may be employed in the practice of this

invention, including for example molybdenum, tantalum, tungsten, zirconium and hafnium. Best results have been obtained with the utilization of refractory metal powder of tantalum and tungsten of about 325 mesh.

Various barium compounds may be employed to provide the barium emissive surface, including for example the oxides, aluminates, silicates, beryliates and carbonates of barium. It has been discovered, however, that best results are obtained when barium is added by way of the compound barium orthosilicate (Ba_2SiO_4). Barium orthosilicate is added in particulate or powder form in about 325 mesh to the particulate refractory metal and intimately mixed therewith. In general these materials include a major or about 90 weight percent refractory and a minor or about 10 weight percent barium orthosilicate.

Specific additives may be employed to alter or improve the operating characteristics of the cathode. However, certain improvements are usually obtained only by accepting certain added disadvantages. Reducing the evaporation rate is a sought for improvement in dispenser cathodes. It has been discovered that the addition of calcium carbonate ($CaCO_3$) will reduce the evaporation rate of the dispenser of this invention with minimal, if any, added disadvantages. $CaCO_3$ is advantageously employed in amounts less than about 1 weight percent and preferably about 0.1 weight percent of the refractory metal which is a much more minor amount than the barium compound. The use of the calcium carbonate is believed to reduce the evaporation rate since calcium carbonate is converted to calcium oxide which fills the pores of the matrix and provides a structure which impedes the diffusion of barium to the emitter surface and thus aids in retaining the barium.

Other materials of an additive nature may be added to the initial basic mix for specific improvements in the cathode structure. For example, about 1 weight percent of the refractory metal, in the form of zirconium hydride (ZrH_2) may be added to the basic mix to serve as a reducing agent.

In specific examples of the practice of this invention, dispenser cathodes were produced by the use of a high purity finely divided or particulate refractory metal in powder form passing through a 325 mesh sieve. In the dispenser cathode the refractory metal usually made up about 90 weight percent of the body. Barium orthosilicate and calcium carbonate were also utilized in high purity powder form passing through a 325 mesh sieve. Preferably the barium orthosilicate constituted about 9 weight percent of the body and the calcium carbonate less than about 1 percent. The mentioned materials are intimately mixed, placed in a suitable compressing and heating apparatus, and subjected to a pressure of about 1000 pounds per square inch for compacting purposes. At the same time, while the material is under compression, it is also heated in a vacuum or reducing atmosphere in order that the compact may be united in an integral high strength cohesive cathode compact. One of the difficulties which deterred the use of the foregoing method is that the sintering temperature of the required refractory metals is so high as to be detrimental to the included materials. It has been discovered that barium orthosilicate, and its combination with calcium carbonate, ameliorates the high temperture effects mentioned. Furthermore, it has been discovered that the simultaneous hot-pressing method may be carried out in the presence of a carbonaceous material, for example, in a carbon crucible or cylinder. The result is the production of CO and CO_2 about the mixture for reducing atmosphere effect and eliminating special atmospheres or vacuum conditions. Additionally, the carbon reacts with undesirable excess oxygen in the mix to provide the mentioned gases. This method and apparatus is better described in relation to the figure.

Referring now to the figure there is disclosed an apparatus **10** including a carbon block or crucible **11** which defines an open ended cylinder **12**. In cooperation with the cylinder **12** there is illustrated a carbon plunger or piston **13** operative in cyliner **12**. The carbon parts may also be liners for existing apparatus or corresponding parts, and consist primarily of hard carbon. This apparatus is employed to compact the materials to the desired density. The dispenser material mix **14** as above-described is placed in the bottom portion of cylinder **12** and the plunger **13** is operative to supply the suitable pressure to compact the dispenser material **14**. Such compressive pressure is maintained in one exemplary range of about 800–1600 pounds per square inch for effective dispenser cathode production.

The dispenser cathode compact **14** is subjected to concurrent high temperatures while being subjected to elevated pressure. For example, a suitable source of power (not shown) is connected by means of an electrical conductor **15** to plunger **13**. By the same token the suitable source of power is also connected by electrode **16** to crucible **11**. By this means a current path is established between piston **13** through material **14** through crucible **11** and through conductor **16**. Current flow may be established through or about the compact **14**. It is merely satisfactory that the electrical resistance through the apparatus **10** or between the conductors **15** and **16** be such as to raise the temperature of the compact **14** to the general range of 1400 to 2000° C. in order to integrally bond the compact **14**.

The high temperatures involved lead to the formation of carbon dioxide and carbon monoxide by causing carbon to react with air on excess oxygen in the compact **14** for oxygen clean-up. Carbon monoxide (CO) acts as a reducing atmosphere about the compact and thus special reducing atmospheres or vacuum conditions are unnecessary. Carbide formation is minimized by limiting the time at high temperatures. In one preferred method of this invention a pressure of 1000 pounds per square inch and a temperature of between about 1000° to 1800° C. for about one minute yields cathodes of from about 50% to 20% porosity. An exemplary size of a dispenser cathode produced by this invention weighs about 10 grams and is of cylindrical configuration of about ¼ inch diameter and ⅛ inch height.

It is an important feature of this invention that the carbon environment and resulting CO and CO_2 gas atmosphere provides an economical method for utilizing tantalum as a refractory material, since heretofore tantalum required a high degree of care in the selection of its environment and control conditions to prevent oxidation during fabrication for cathode purposes.

The following are representative practices of this invention:

Example 1.—Several dispenser cathodes were produced utilizing both tantalum and tungsten as refractory metal, and barium orthosilicate, in the range of 90 percent by weight refractory metal and 10 percent by weight, or the balance, of barium orthosilicate. This material was placed in the apparatus of the figure and pressed at about 1000 pounds per square inch while being concurrently heated to about 1400° C. for a period of about one minute. Thereafter the dispenser cathode was removed and tested revealing an apparent density of about 80%, a Knoop hardness (10 grams) 1800, and an emission (space charge limited) 150 ma./cm.^{2}.

Example 2.—A mixture of 88 weight percent tungsten, 10 weight percent barium orthosilicate, 0.1 weight percent $CaCO_3$ and 1 weight percent ZrH_2, was hot-pressed in the apparatus of the figure by the method described. This cathode was found to have a work function of about 2.23 ev. at about 1250° K.

The above examples are representative of numerous cathodes produced by the practices of this invention. Cathodes were produced both with and without $CaCO_3$ as an additive. It was found that with otherwise identical cathodes (by materials and process) the cathodes which

included $CaCO_3$ had a much lower evaporation rate. Comparable values are for example 3.5×10^{-10} evaporation rate (gm./cm.^{2}/sec.) for a W, Ba_2SiO_4, ZrH_2 cathode, and 2.7×10^{-11} for a W, Ba_2SiO_4, ZrH_2, $CaCO_3$ cathode, in accordance with the teaching of this invention.

It has been shown by the foregoing description that improved thermionic dispenser cathodes may be provided through the simultaneous application of heat and pressure. The basic method includes hot-pressing a refractory metal powder, a barium compound powder and an additive in a reducing atmosphere or carbon environment. Best results are obtained where the refractory metal-barium compound mix includes $CaCO_3$, and also ZrH_2 when desirable as a reducing agent.

While a specific method and apparatus has been described and illustrated, it is not desired that this invention be limited to the particular form shown or to the method described and it is intended by the appended claims to cover all modifications within the spirit and scope of this invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. An integral cohesive thermionic dispenser cathode comprising a hot pressed fused mixture of
(a) at least about 8 weight percent Ba_2SiO_4,
(b) less than about 1 weight percent $CaCO_3$,
(c) the balance of said cathode being a refractory metal as a porous matrix which constitutes a substantial major proportion of the weight of said cathode,
(d) said Ba_2SiO_4 and $CaCO_3$ being dispersed throughout the refractory metal matrix.

2. The invention as recited in claim **1** wherein said mixture consists essentially of
(a) at least about 88 weight percent refractory metal,
(b) at least about 8 weight percent Ba_2SiO_4,
(c) about 1 weight percent ZrH_2 and
(d) less than about 1 weight percent $CaCO_3$.

3. The invention as recited in claim **1** wherein said refractory metal is tungsten.

4. The invention as recited in claim **1** wherein said refractory metal is tantalum.

5. A method of producing a thermionic dispenser cathode comprising in combination
(a) intimately mixing a refractory metal, a barium compound, and less than about 1.0 weight percent $CaCO_3$,
(b) providing a reducing atmosphere in a heating and pressing apparatus,
(c) compressing said mixture to above about 800–2000 pounds per square inch, and

(d) simultaneously heating said mixture in the range of about 1000° to 2000° C. to provide a sintered cohesive integral thermionic dispenser.

6. The invention as recited in claim **5** wherein said mixture comprises
(a) at least about 8 weight percent Ba_2SiO_4,
(b) less than about 1 weight percent $CaCO_3$, and
(c) the balance of said cathode being a refractory metal which constitutes a substantial major proportion of the weight of said body.

7. A method of producing a thermionic dispenser cathode which comprises in combination
(a) intimately mixing a refractory metal and a barium compound, and
(b) hot-pressing said mixture in the presence of a carbonaceous material to produce a reducing atmosphere of carbon monoxide,
(c) said pressure being in the range of about 800–2000 pounds per square inch, and said temperature being in the range of about 1000° to 2000° C.

8. The invention as recited in claim **7** wherein said carbonaceous material is carbon.

9. The invention as recited in claim **7** wherein said carbonaceous material is a carbon crucible wherein said hot-pressing is carried out.

10. The invention as recited in claim **9** wherein said mixture comprises at least about 88 weight percent tantalum, at least about 8 weight percent of Ba_2SiO_4, and at least about .05 weight percent $CaCO_3$.

11. The invention as recited in claim **9** wherein said mixture comprises at least about 88 weight percent tungsten, at least about 8 weight percent of Ba_2SiO_4, and at least about .05 weight percent $CaCO_3$.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,269,804 August 30, 1966

John H. Affleck III, et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 33, strike out "pound dispersed therethrough to provide an emissive" and insert instead -- power by virtue of an activator cathode or emitting --.

Signed and sealed this 1st day of August 1967.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents