Jan. 11, 1966 J. H. AFFLECK III 3,229,147

THERMIONIC EMITTER AND METHOD OF MAKING SAME

Filed Sept. 1, 1961

FIG.1.

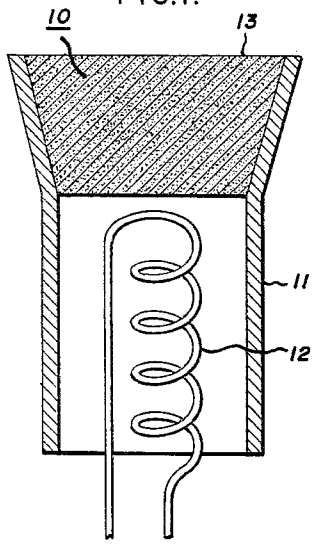


FIG.2.

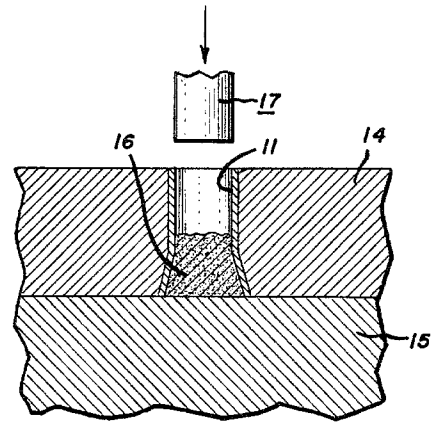


FIG.3.

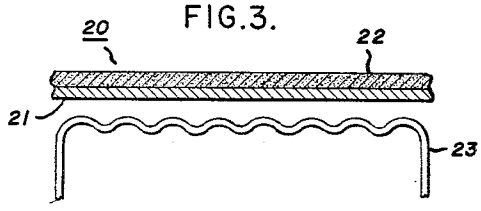
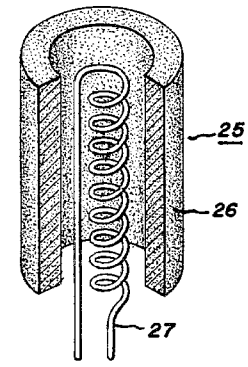


FIG.4.



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THERMIONIC EMITTER AND METHOD OF MAKING SAME

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11 Claims. (Cl. 313—337)

My invention relates to electron emitters and pertains more particularly to a new and improved thermionic emitter of the dispenser type and a new and improved method of making same.

Dispenser-type emitters usually comprise a porous refractory metal matrix impregnated with an activator compound adapted upon thermal dissociation of the compound to provide an elemental alkaline earth metal which migrates to the surface of the matrix and thus is available as an emissive film. Much of the effort devoted to the development of dispenser-type emitters heretofore has been for the provision of systems characterized by low effective work functions and, thus, adapted for high density electron emission within a given operating temperature range. Much development effort has also been directed toward the provision of emitters characterized by low evaporation rates of the activator material in the mentioned operating range, thereby to provide for prolonged operating life.

Disclosed and claimed in my copending U.S. application Serial No. 135,549, now Patent No. 3,176,180, filed concurrently herewith and assigned to the same assignee as the present invention are thermionic emitters and a method of manufacturing same which are adapted for providing dispenser type emitters characterized by low effective work functions and reduced evaporation rates. My present invention contemplates improved emitters and a method of manufacturing same effective for affording a dispenser type emitter characterized by a low effective work function and further reduced evaporation rates.

Accordingly, a primary object of my invention is to provide a new and improved thermionic emitter of the dispenser type.

Another object of my invention is to provide new and improved dispenser-type emitters characterized by low effective work functions and low evaporation rates of the activator materials during operation of the devices incorporating the emitters.

Another object of my invention is to provide new and improved dispenser-type emitters involving a new and improved system of constituents effective for thermally controlling the rate of production of an activator material in the matrix and thereby controlling the rate of evaporation of the activator.

Another object of my invention is to provide new and improved thermionic emitters of the dispenser type which are adapted for prolonged high density emission operation.

Another object of my invention is to provide new and improved thermionic emitters of the dispenser type which can be easily manufactured and which are not subject to the evolution of undesirable gases during manufacture or subsequent use.

Still another object of my invention is to provide a new and improved method of manufacturing a dispenser-type thermionic emitter.

Further objects and advantages of my invention will become apparent as the following description proceeds and the features of novelty which characterize my invention will be pointed out with particularity in the claims annexed to and forming part of this specification.

Briefly, my invention contemplates a new and improved emitter of the dispenser type comprising a compressed fused body of powdered constituents consisting essentially of (1) a refractory matrix material selected preferably from the group consisting of tungsten, tantalum and molybdenum and the silicides, carbides and borides of these materials and combinations thereof; (2) an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate; and (3) a reducing agent selected from the group consisting of aluminum, zirconium and titanium and combinations thereof. The emitter is preferably manufactured by admixing uniformly the powdered constituents and then compressing the mixture with a predetermined pressure effective for fusing the powdered constituents into a compressed coherent body having a consistency and internal structure whereby the body is adapted for uniform migration to the surface thereof of elemental activator upon chemical reduction of the activator compound. The reducing agent and operating temperature control the rate of activator production in the body and thus control the rate of evaporation of the activator.

For a better understanding of my invention reference may be had to the accompanying drawing wherein:

FIGURE 1 is a sectional view of a dispenser-type emitter constructed according to an embodiment of my invention;

FIGURE 2 is a fragmentary somewhat schematic illustration of apparatus and the method employable in manufacturing my improved emitter;

FIGURE 3 is a fragmentary sectional view illustrating another modified form of my invention; and

FIGURE 4 is a fragmentary sectionalized view illustrating still another modified form of my invention.

Referring to the drawing, there is shown in FIGURE 1 a thermionic emitter of the dispenser type generally designated **10** and constructed according to an embodiment of my invention. The emitter **10** is supported in a flared end of a cathode holder **11** which can be formed of a refractory metal such as tungsten, tantalum or molybdenum. It is to be understood that the cathode holder **11** need not be flared and can comprise a straight-walled cylindrical or tubular member of any desired cross-sectional configuration. A heating element **12** is contained in the holder **11** and is adapted when energized to heat the emitter **10**, thereby to effect a desired reaction between an activator compound and a reducing agent contained in the emitter **10** and for thereby effecting reduction of the activator compound and production of elemental barium for migration thereof to an active surface of the emitter designated **13**.

The emitter **10** comprises a compressed fused body of powdered constituents of approximately 325 mesh and consisting essentially of (1) a refractory matrix material preferably selected from the group consisting of tungsten, tantalum and molybdenum, the silicides, carbides and borides of tungsten, tantalum and molybdenum and combinations thereof; (2) an activator compound selected from the group consisting of barium orthosilicate (Ba_2SiO_4) and barium orthotitanate (Ba_2TiO_4) and combinations thereof, and (3) a reducing agent selected from the group consisting of aluminum, zirconium and titanium.

More specifically, the emitter **10** is preferably formed of a uniform, compressed fused mixture of powders of one of the mentioned refractory materials, one of the mentioned activator compounds and one of the reducing agents. However, it is to be understood that combinations of the refractory materials as well as combinations of the active compounds can be employed in practicing my invention. Additionally, while aluminum, zirconium and titanium can be effectively employed as the reducing agent in practicing my invention, aluminum is

preferred. Also, in the embodiment incorporating barium orthotitanate the use of titanium as a reducing agent should be avoided.

The above-discussed mixture is compressed at approximately 70 to 80 tons per square inch to a desired shape and whereby the particles constituting the powdered constituents are fused together to provide a coherent unitary body. In the present disclosure the term "fused" is used to mean that the particles constituting the body are blended together or joined as the result of pressure applied to the mixture in much the same way that metal members can be joined or fused by the application of pressure in the manner generally referred to in the art as "cold welding."

Illustrated in FIGURE 2 is apparatus whereby the device of FIGURE 1 can be constructed. This apparatus comprises a female die **14** adapted for holding the cathode holder **11** firmly in an inverted position against a smooth surface die **15** while a quantity of the mixture of the above-discussed metal powders designated **16** is compressed by activation of a ramrod **17**. The rod **17** is actuated with a force effective for compressing the mixture at the mentioned 70 to 80 tons per square inch. In this manner, the desired plug-like form of the emitter illustrated in FIGURE 1 is obtained and the emitter is formed as a compressed fused body having a desired consistency and porosity which contributes to the effectiveness of the emitter in providing a desired low effective work function and insuring uniform coverage of the active surface **13** with elemental barium during energization of a heater **12**.

Upon heating of the emitter **10** in a vacuum, as by incorporation of the emitter in a vacuum discharge device and energization of the heater **12**, the reducing agent in the emitter is effective for chemically reducing the activator compound and thereby producing elemental barium for diffusion through the body and migration uniformly to the active surface **13**. Thus is provided an emitter having a refractory matrix bearing an active surface **13** substantially uniformly covered with elemental barium for providing a high density source of electrons and characterized by a substantially reduced effective work function. Additionally, in this structure the amount of barium produced is dependent upon the chemical reduction of the activator compound by the reducing agent. Thus, only through the continued operation of the device and energization of the heater **12** can the reducing agent be rendered effective for chemically reducing the barium compound and thus producing elemental barium. As a result, the amount of barium appearing at the active surface **13** is controlled and, thus, is not subject to rapid evaporation. However, the reducing agent is effective when heated for continuously causing the production of barium from the activator compound and, thus, the device is adapted for continuous replenishment of the active surface with barium to maintain the active surface for high density emission operation and a substantially reduced effective work function. Included below are the reactions obtained in the present device when tungsten is the refractory metal and aluminum is utilized as the reducing agent and whereby the production of barium results:

$$W+Ba_2SiO_4+2Al \rightarrow W+BaAl_2O_4+Si+Ba$$
$$W+Ba_2TiO_4+2Al \rightarrow W+BaAl_2O_4+Ti+Ba$$

It will be understood that, while the foregoing reactions indicate the use of tungsten (W) as the refractory matrix material, any one of the above-mentioned matrix materials can be substituted therefor. Additionally, while in the reactions indicated above aluminum (Al) is indicated as the reducing agent employed, any one of the above-noted reducing agents may be alternatively employed except, however, in the case of barium orthotitanate where the use of titanium as a reducing agent should be avoided.

For the purpose of demonstrating the effective work functions and activator evaporation rates obtainable with the present invention, I have listed in the chart below some of the emitter systems tested at a given operating temperature of 1250° K. and the emission and evaporation properties observed:

System In Weight Percentages	Effective Work Function at 1,250° K., ev.	Evaporation Rate in Grams per cm.^{2} per sec.
Tungsten+Barium Orthosilicate+Aluminum.		
$W+Ba_2SiO_4(9.5\%)+Al(.5\%)$	2.21	4×10^{-10}
Tantalum+Barium Orthosilicate+Aluminum.		
$Ta+Ba_2SiO_4(9.5\%)+Al(.5\%)$	2.85	4.3×10^{-8}
Tungsten+Barium Orthotitanate+Aluminum.		
$W+Ba_2TiO_4(9.5\%)+Al(.5\%)$	2.20	1.8×10^{-8}
Tantalum+Barium Orthotitanate+Aluminum.		
$Ta+Ba_2TiO_4(9.5\%)+Al(.5\%)$	2.22	----------

It is to be understood that, while I have not listed in the above chart all of the systems falling within the purview of my invention as disclosed above, the other systems which are encompassed by my invention including, for example, those involving the admixture of activator compounds with molybdenum and the carbides, silicides and borides of tungsten, tantalum and molybdenum are equally effective in providing a low effective work function and low evaporation rate emitters having characteristics comparable to those indicated in the chart. Additionally, it is to be noted that the above chart shows no evaporation rate for one of the systems. Such datum was not prepared; however, it is expected that such datum would not be substantially different from that noted in respect to the other systems indicated.

Further, while the activator compound was in each case in the systems included in the above chart 9.5% and the reducing agent was 0.5% of the composition of the system under test, it is to be understood that the percentage compositions of the systems can vary and still be characterized by desirably low effective work function and evaporation rates, although the indicated percentage composition in the chart has been found highly satisfactory.

Additionally, in conducting the test whereby the above-listed information was obtained the temperature 1250° K. was arbitrarily selected for test purposes, and the effective work functions and the activator evaporation rates indicated are those calculated for this temperature. The effective work functions and evaporation rates will vary, of course, with different temperatures and can be determined by use of calculations well-known to those skilled in the art.

However, it can be seen from the data included in the above chart that the described systems are adapted for affording work functions which are considerably lower than the work functions of most metals. Additionally, the effective work functions approach closely the work functions of alkaline earth oxide cathodes which latter type cathodes have lower work functions but are limited in applications since they cannot withstand high operating temperatures and electron bombardment without deteriorating.

Illustrated in FIGURE 3 is a modified form of my invention in which the emitter is generally designated **20**. In this embodiment a base member **21** is provided which is preferably formed of a refractory metal such as tungsten, stantalum or molybdenum. The base member **21** carries as a coating thereon a body of the compressed fused mixture employed in forming the emitter **10** in FIGURE 1. In this embodiment the coating **22** is fused to the base member **21** and the formation of the coating **22** and the fusion thereof to the base member can be effected by the use of die means similar in function to that illustrated in FIGURE 2. Provided for cooperating with the emitter **20** is a heating element **23**. Upon ener-

gization of the heating element **23** the base **21** and the coating **22** are heated, whereby the reducing agent in the coating **22** is effective for reducing chemically the barium orthosilicate or barium orthotitanate in the mixture for producing barium for migration to the outer surface of the coating **22**. In this embodiment also, by controlling the operating temperatures of the system, the amount of barium produced is controllable, whereby the device is adapted for relatively low evaporation of the activator. Alternatively, the emitter **20** can be in a tubular form instead of the planar form illustrated.

Illustrated in FIGURE 4 is another modified form of my invention. In this embodiment an emitter generally designated **25** is tubular in form and comprises a unitary compressed fused and self-sustaining cylinder of the mixture employed in manufacturing the plug-like emitter **10** in FIGURE 1 and the emissive coating **22** in FIGURE 3. In this embodiment the member **26** contains a heating element **27** adapted when energized for heating the member **26** thereby to provide the desired reaction between the reducing agent and the activator compound in the member **26** for producing elemental barium to enable diffusion thereof through the member **26** and migration to the outer surface thereof. In this embodiment also the evaporation rate of the barium is controlled by the amount of reaction occurring between the activator compound and the reducing agent contained in the matrix and, thus, the amount of barium produced and which can be vaporized is controllable.

While I have shown and described specific embodiments of my invention, I do not desire my invention to be limited to the particular forms shown and described, and I intend by the appended claims to cover all modifications within the spirit and scope of my invention.

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

1. A thermionic emitter comprising a porous refractory matrix and a mixture consisting of an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate and a discrete reducing agent for said activator compound dispersed in said matrix.

2. A thermionic emitter comprising a densely packed fused mixture of powders consisting of a refractory matrix material, an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate, and a reducing agent for said activator compound and which is in addition to and not a constituent of said matrix material.

3. A thermionic emitter according to claim 2, wherein said mixture is positioned in one end of a tubular refractory metal support member and said support member contains heating means adapted when energized to effect a reaction between said activator compound and reducing agent, thereby to produce elemental barium for migration to the surface of said mixture.

4. A thermionic emitter according to claim 2, wherein said mixture comprises a coating fused to a refractory metal base member associated with heating means adapted when energized to effect a reaction between said activator compound and reducing agent, thereby to produce elemental barium for migration to the surface of said mixture.

5. A thermionic emitter according to claim 2, wherein said mixture is in an integral self-sustaining form and contains heating means adapted when energized to effect a reaction between said activator compound and reducing agent, thereby to produce elemental barium for migration to the surface of said mixture.

6. A thermionic emitter, comprising a body of compressed fused powdered constituents consisting essentially of: (1) a refractory matrix material selected from the group consisting of tungsten, tantalum and molybdenum, and the silicides, borides and carbides of tungstens, tantalum and molybdenum; (2) an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate; and (3) a discrete reducing agent selected from the group consisting of aluminum, zirconium and titanium.

7. A thermionic emitter according to claim 6, wherein the activator compound constitutes approximately 9.5% and said reducing agent comprises approximately 0.5% by weight of said mixture.

8. The method of manufacturing a thermionic emitter comprising the steps of providing a powdered mixture consisting essentially of a refractory material, an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate and a discrete reducing agent, and compressing said mixture at a pressure of between about 70 tons to 80 tons per square inch into a densely packed coherent body until the particles of the constituents are fused together, thereby to provide a porous matrix formed of said refractory material and having said activator compound and reducing agent dispersed in the pores of said matrix.

9. The method of manufacturing a thermionic emitter comprising the steps of providing a powdered mixture consisting essentially of (1) a refractory matrix material selected from the group consisting of tungsten, tantalum and molybdenum, and the silicides, borides and carbides of tungsten, tantalum and molybdenum; (2) an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate; and (3) a discrete reducing agent selected from the group consisting of aluminum, zirconium and titanium and combinations thereof, and compressing said mixture at a pressure of between approximately 70 and 80 tons per square inch for effecting a densely packed body wherein the particles of the constituents are fused, thereby to provide a porous matrix formed of said refractory material and having said reducing agent dispersed in the pores of said matrix.

10. A thermionic emitter comprising a densely packed fused mixture of powders consisting of a refractory metal selected from the group consisting of tungsten, tantalum and molybdenum, an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate, and aluminum.

11. A thermionic emitter comprising a densely packed fused mixture of powders consisting of materials selected from the group consisting of tantalum, tungsten and molybdenum; an activator compound selected from the group consisting of barium orthosilicate and barium orthotitanate; and aluminum, and said activator compound and aluminum comprising approximately 9.5% and approximately 0.5%, respectively, by weight of said mixture.

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