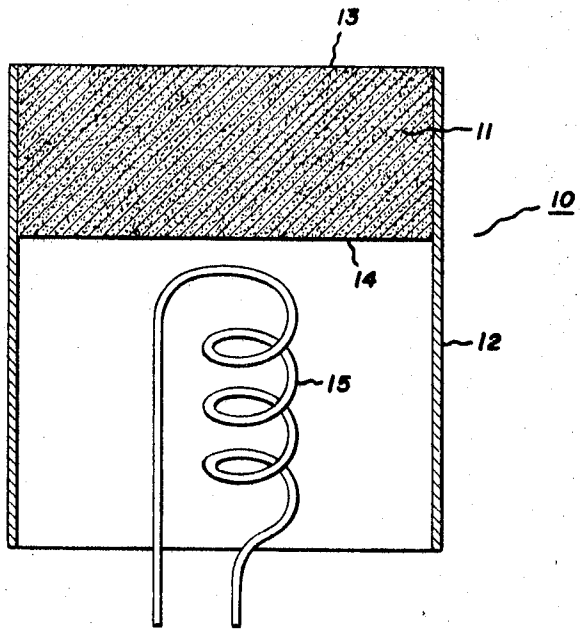
Aug. 25, 1970 R. J. BONDLEY 3,525,135

THERMIONIC CATHODE

Original Filed Sept. 8, 1966



INVENTOR:
RALPH J. BONDLEY,
BY Henry T. Olsen
HIS ATTORNEY.

United States Patent Office 3,525,135 Patented Aug. 25, 1970

3,525,135

THERMIONIC CATHODE

Ralph J. Bondley, Scotia, N.Y., assignor to General Electric Company, a corporation of New York

Original application Sept. 8, 1966, Ser. No. 578,060, now Patent No. 3,434,812. Divided and this application Dec. 20, 1967, Ser. No. 692,030

Int. Cl. H01j 9/16, 9/44

U.S. Cl. 29—25.18 7 Claims

ABSTRACT OF THE DISCLOSURE

Method of producing a long-life high-emission-density thermionic dispenser cathode comprising mixing predetermined proportions of barium strontium and a refractory metal and compressing and firing the resultant mixture into coherent dispenser cathode pellets containing a 50 atomic weight percent solid solution of Ba_2SrWO_6 and Ba_3WO_6.

This application is a divisional application of copending application Ser. No. 578,060, filed Sept. 8, 1966, now U.S. Pat. 3,434,812 and assigned to the same assignee as the present invention.

This invention relates to improved dispenser cathodes and more particularly to an improved high emission density thermionic cathode and a prescribed process of combining and activating certain specifically prescribed ingredients to obtain increased high emission density characteristics.

In various electronic applications generally, and particularly with respect to high power output beam devices operative in the ultra high frequency and microwave frequency ranges, a dispenser cathode plays an extremely important if not limiting part for increased power output. Increased power output in many of the frequency generation devices may be obtained by means of thermionic cathodes capable of emitting a stable D-C current of high density over a long period of time with comparatively small heater power consumption. There is an ever increasing need, for example, for hot cathode devices which are capable of operating over many hundreds of hours of continuous operation in the temperature ranges of 900° to 1200° C. and which will, under these conditions, provide an emission current density of in excess of at least 5 amperes per square centimeter. Such a dispenser cathode as described, when employed in a high frequency generator depending upon a high power electron beam, will provide a substantial increase in the power output of the generator in addition to the overall increase of efficiency thereof.

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 process to yield an increased emission density cathode.

It is yet another object of this invention to provide a continuous high emission density from a barium tungstate cathode.

It is a further object of this invention to provide an improved process to provide barium tungstate dispenser cathodes of increased emission densities at lower temperatures under continuous use.

It is another object of this invention to provide an improved thermionic dispenser type cathode comprising a sintered mixture of a refractory metal having interspersed therein a solid solution of a pair of barium compounds, and operative for high emission density at lower temperatures.

It is a further object of this invention to provide an

improved sintering and shaping process in the manufacture of barium strontium tungstate dispenser cathodes.

It is a further objcet of this invention to provide a barium strontium tungstate dispenser type cathode for general usage which will have an emission density of in excess of at least about 5 amperes per square centimeter emission density at temperatures below about 1000° C. over extended periods of time.

Briefly described, this invention in one of its preferred forms includes the combination of specific proportions of certain powdered ingredients, for example barium carbonate ($BaCO_3$), strontium carbonate ($SrCO_3$), and tungsten trioxide (WO_3), which are intimately mixed, wet milled, dried, and fired in pellet form to provide a solid solution of barium compounds such as Ba_3WO_6 and Ba_2SrWO_6 in generally equal amounts. The pellets are then crushed and sieved, and about 9% by weight thereof is mixed with about 1% by weight zirconium hydride and about 90% by weight tungsten metal powder. The resulting mixture is dry milled, compacted under high pressure, and then subjected to high temperatures in a reducing atmosphere to fuse or melt one of the barium compounds and provide an integral cohesive body which is formed as a high current density thermionic dispenser type cathode.

This invention will be more fully understood when taken in connection with the following description and the drawing in which:

The drawing is an exemplary illustration of an assembly utilizing a dispenser cathode of this invention.

In the dispenser cathode prior art there exists a vast number of different processes potentially employing the same materials, which in turn provide different dispenser cathodes. By the same token the dispenser cathode prior art indicates a great number of various ingredients and various proportions and mixings thereof which in turn provide different dispenser cathode characteristics. In many of these instances, the intermediate reaction and combinations which take place in the production of a dispenser cathode are not known, and at the same time, in a great number of instances those ingredients originally employed to provide the cathode do not appear in the final cathode in the same form or in the same amount. Therefore, it is not readily apparent by examination just what specific material, or combinations of materials, or process steps give rise to a preferred cathode, or which parameters may provide a greatly increased emission density.

The prior art of dispenser cathodes is indicative of barium tungstate cathodes representing a potential area from which dispenser cathodes of substantially increased continuous emission densities at low temperatures might be obtained. It has been discovered that a barium tungstate thermionic cathode having the constituents above described, and in the proportions given, provides a very high emission density disproportionate to the known reaction or contributions of the constituent elements. In addition, this very high emission density takes place at lower temperatures and is continuous for long life operation. Such cathodes may be produced repetitively in large numbers by following certain prescribed proportions and process steps.

It has also been discovered in this invention that critical items with respect to a high emission density cathode are related as well as to those ingredients appearing in the final item as to the beginning ingredients. In addition, certain final processing may change or alter the original ingredients to provide the final ingredients in a more desired form sometimes irrespective of the particular amount of particular material available in the original form.

The basic dispenser cathode of this invention includes a porous matrix metal body having therein a tungstate activator material and a reducing agent. The matrix body

is a refractory metal, for example one or more of those metals taken from Groups IV, V and VI of the Periodic Table of Elements such as tungsten, molybdenum, rhenium, tantalum, etc., and in a preferred form of this invention is tungsten. The matrix body is further defined as composed of a starting material which is finely divided or powdered high purity tungsten preferably having an average particle size in the range of about 2–5 microns. Particle sizes in excess of this range provide less than optimum results in the final product as based upon a series of exemplary cathodes of varying tungsten matrix particle sizes. Powdered refractory metals, particularly tungsten, have been employed in this invention in a general range of from about 80 weight percent to about 94 weight percent. A preferred range is from about 88 weight percent to about 92 weight percent with best results from about 90 weight percent to about 92 weight percent.

The activator material which is included in the matrix material is a barium tungstate compound, which, under operative conditions of the cathode, will be reduced and dispense barium to an active surface of the cathode. One or more barium compounds may be so employed. It has been discovered that best results are obtained in the practice of this invention when the activator starting material includes a single phase solid solution of equimolecular amounts of Ba_3WO_6 and Ba_2SrWO_6 having cubic symmetry. Peak emission density at lower temperatures is obtained when the noted barium-strontium compounds are provided in substantially stoichiometric proportions. The strontium containing tungstate has been found superior to other alkaline metal tungstates. Other barium compounds which may be employed as activator materials are BaO, Ba_2CaWO_6, etc., which may provide tailored cathodes for specific usage where maximum density proportionate to lower temperature and longer life is not the major circumstance. The activator material has been employed in this invention in the general range of from about 5 weight percent to about 11 weight percent with from about 7 weight percent to about 9 weight percent being a preferred range.

The reducer material employed in the dispenser cathode of this invention performs the function of reducing the barium compound so that barium may migrate through the porous tungsten body to provide an active low work function surface. While there are various materials, elecments or compounds which may be added to the cathode to provide this function, it has been discovered that only a limited number of refractory metals provide optimum results. Zirconium is one preferred reducer metal in the practice of this invention. Zirconium should be added by way of a zirconium compound such as a hydride, zirconate or oxide. Zirconium hydride, ZrH_2, as a preferred compound provides distinguishable results by emission density tests over the other reduced compounds. Zirconium hydride has been employed in this invention in the general range of at least a significant amount, i.e., an amount which will provide measurable reduction to about 2.5 weight percent with a preferred range being from about .25 weight percent to about 1.0 weight percent. Incremental additions of ZrH_2 to standardized mixes of matrix metal and activator compound indicate, by emission tests, that negligible improvement is obtained by greater amounts, and particularly, diminishing results are noted in many instances.

It has also been discovered that hafnium may be employed as a reducer metal in this invention. Hafnium may be added by way of such compounds as oxides and hydrides, hafnium hydride HfH_2 being preferred in proportions which may include up ot about 2 weight percent. The amount of hafnium to be added should also be maintained in the same general range as expressed for ZrH_2, taking into consideration the different atomic weight involved. Other refractory metals, particularly titanium, may be employed but with distinguishable diminishing and non-equivalent results.

In the preparation of the initial materials, very great importance is attached to proportions, particle sizes, mixing time, compression pressures, firing or sintering temperatures and other related parameters, with respect to the final emission properties and life of a cathode. It is a common occurrence to seriously alter an otherwise optimum cathode by an inadvertent or mistaken or incorrect change of materials or processes or by assuming an equivalency not borne out by experimentation.

It has been discovered that one outstanding and preferred cathode of this invention, i.e., one having a long life with a substantially continuous emission density of about 10 amperes/cm.^{2} at a temperature below about 1000° C., is provided in the specific controlled proportions of ingredients. For example, these ingredients may comprise a general range of 88% to 92% by weight of refractory metal, about 7% to 9% by weight barium compound and the balance, usually about 0.25 to 2.5% by weight of a reducer material. For a high emission density cathode approaching 10 or more amperes per square centimeter at 1000° C. or less, a more preferred range, and materials, are about 90% to 92% by weight tungsten, 7% to 9% by weight of a single phase solid solution corresponding to the general formula $Ba_5Sr(WO_6)_2$ obtained by a reaction of constituents such as for example Ba_3WO_6 and Ba_2SrWO_6, and from about 0.5% to 1.0% zirconium halide. Outstanding examples include

(a) about 92% by weight tungsten, about 7½% by weight of the described solid solution activator compound and about 0.5% by weight zirconium hydride, and

(b) about 90.2% by weight tungsten, about 9.2% by weight activator compound as described, and the balance zirconium hydride, about 0.6% by weight.

The proportions so indicated may be further described by a major percent by weight of refractory metal, i.e., 50 weight percent or more, a minor percent by weight of an activator material, i.e., less than 50% by weight, and an additive but significant amount of a reducer material which is substantially less than the amount of activator material.

The process requirements of cathodes made in accordance with the proportions above indicated are critical to the emission density characteristics of the final dispenser cathode. Best results are obtained when considerable care is exercised to maintain cleanliness in conjunction with the use of high purity materials. In a preferred form of this invention, the activator material is provided by wet milling in methanol a combination of barium carbonate ($BaCO_3$), strontium carbonate ($SrCO_3$), and tungsten trioxide (WO_3) in substantially stoichiometric proportions. After milling sufficiently to provide a very intimate mixture, the methanol is decanted and the powder material is dried and compressed into pellets in a hydraulic press. These pellets are thereafter fired in an air or oxygen atmosphere at a temperature above 1400° C. for several hours.

X-ray analysis of these pellets indicates a solid solution of $BaWO_3$ and Ba_2SrWO_6 at a composition of 50 atomic percent. Best results have been obtained with this composition. However, variations are tolerable for a number of specific applications where criteria other than or in addition to high emission rate is required. The 50 atomic percent composition depends on the ratio of starting materials particularly for example a ratio in stoichiometric proportion such as 18.525 grams $BaCO_3$ barium carbonate, 2.770 grams $SrCO_3$ strontium carbonate and 8.705 grams WO_3 tungsten oxide. The reaction product is $Ba_5Sr(WO_6)_2$ or alternately $5BaO.SrO.2WO_3$.

After firing the pellets are crushed and sieved through a 325 mesh screen. This material is then mixed with tungsten which is provided in finely divided or powder form with an average particle size of 2–5 microns. The proportions are in the ranges previously described, par-

ticularly specific examples (a) and (b). To this mixture there is added a reducer such as zirconium hydride or hafnium hydride also of about 325 mesh or finer particle sizes, also in the preferred range given, specific examples being by weight ½% and 0.6% respectively. This mixture is then placed in a mixing apparatus, in this instance a small molybdenum ball mill, and milled for several hours. The milling time for optimum emission is a function of the mill size, speed and charge for one particular mill.

In operative practices of this invention, ball milling was performed in an all molybdenum ball mill. The mill chamber was in the form of a molybdenum cup measuring about 2¾ inches diameter and 2¾ inches depth. The milling or grinding members were molybdenum slugs of about ¼ inch diameter and ¼ inch length. Fifty of these milling members were employed for each milling session or operation. A molybdenum cover plate was secured to the open end of the mill chamber during a milling operation. During operation the mill revolved at the rate of 120 r.p.m.

Operative curves, i.e., emission density vs. milling time, of a representative number of these milling operations indicated a peak condition of emission in the 2 to 6 hour milling operation range. Unexpectedly it was discovered that in extended milling operations a second emission peak occurred in the 12 to 18 hour range. Best emission results were obtained in cathodes of this invention when the second peak condition was utilized, i.e., where ball milling of the constituents was continued for 12 to 18 hours.

After milling, the powder mixture is then placed in a die and compacted in a hydraulic press into pellets of the general desired size. Compacting pressures contribute to the final characteristics because they predetermine to some extent the pore size of the finished product. In the practice of this invention compacting pressures were employed in the range of about 40 to 90 tons/in.^{2}. Between about 80 to 90 tons/in.^{2} provided best results.

The pressed powder pellets were sintered by heating in a predetermined atmosphere at about 1900° C. for a period of a few minutes to about 5 or 6 minutes. Sintering is carried out under a relatively high purity reducing atmosphere. For example, a high purity hydrogen atmosphere which was carefully deoxygenated and dried was employed in the preferred practice of this invention. It was noted that the presence of contaminants in the hydrogen, for example water vapor and other gases, markedly affected the emission characteristics of the final cathode by reducing obtainable emission densities. The hydrogen employed had a dew point below about −100° F. It was further noted that the final product from hydrogen sintering was superior to those cathodes sintered under other atmospheres, such as inert gas atmospheres, or other atmospheres consisting of a mixture of hydrogen and an inert gas. Additionally, comparative emission density results indicate that the sintering process should be carried out at temperatures in excess of about 1800° C. with optimum results falling between 1850° and 1900° C., which is at or above the melting point of $BaWO_3$, higher temperatures not indicating any further favorable results.

After sintering, the cathode bodies are prepared by having the emitting surface suitably formed or shaped to provide a fresh active surface, generally by a clean removal of a thin layer of the cathode. Best results were achieved when a cathode surface was carefully lathe machined with the use of a very sharp Carboloy cutting tool similar to a facing tool. A high head stock speed, thin and slow cross feed cut is employed. It is believed that this type of cutting process exposes and/or prepares an optimum surface with excellent communication into the porous body. The pore openings of the surface are not deformed or closed by this process. Other similar processes include sputtering or electron machining. Comparative results indicate a markedly superior cathode is provided by the machining or cutting process as compared to, for example, an uncut surface or one obtained by grinding by different abrasive wheels, i.e., diamond or Alumdum wheels.

A great number of dispenser cathodes have been produced by the described process. These dispenser cathodes provided greatly increased emission densities at low temperatures for continuous operation, unexpected in view of the prior art knowledge of dispenser cathode technology. Emission density measurements were carried out in a manner to substantially preclude any errors in the test equipment and to provide a measurement more reliable and precise than those indicated in ASTM standardization test diodes for cathode evaluation. In this connection a vacuum system was constructed from 347 stainless steel and bakable to the extent of freeing the system from water vapor or absorbed gases. All openings were made through metal ceramic seals and compression flanges. The system is initially pumped by mercury diffusion pump because mercury is a well defined substance that does not break down or decompose with heat and is not deleterious to cathode emission. For the higher evacuation conditions an ion pump was utilized to bring the pressure of the system to about 10^{-7} torr. A cathode diameter of one centimeter was chosen as being representative of sizes encountered in microwave tubes. Since cathodes of this size and made in accordance with this invention are capable of delivering large currents, a six-phase variable voltage rectifier of 20 amperes capacity at 500 volts was constructed and used for all measurements. The ripple encountered in six-phase rectification is low enough to permit the RMS values to be equivalent to straight D-C measurements. Anode dissipation is one of the first problems encountered in high current measurements. To keep anode dissipation to a minimum, diodes with 0.010 inch anode-to-cathode spacing were chosen as being a well defined compromise of electrical and mechanical considerations. Even with these close spacings, power densities of about four to six kilowatts per square centimeter are encountered at current levels approaching 10 amperes. These are near maximum power concentrations that can be dissipated with water-cooled anodes.

A substantial number of cathodes in accordance with the practice of this invention were produced to better determine and define optimum materials, material proportions, process step times and other parameters. For example, in representative numbers of cathodes with all other parameters being maintained equal, both the kind and the proportion of given materials were varied, as well as process steps. For each change emission density measurements were taken to indicate the effect of the change. Among these changes are included proportional change of materials, the use of other refractory metals such as molybdenum and combinations thereof, the use of other additive materials and other alkaline earth activator compounds, the use of other sintering atmospheres, and the use of other active surface preparation means. The results of these investigations reveal that preferred cathodes are those containing

(a) about 92 weight percent tungsten, about 7½ weight percent barium compound which includes a solid solution of Ba_3WO_6 and $Ba_5Sr_2WO_6$ and about ½ weight percent ZrH_2 and

(b) 90.2 weight percent tungsten, 9.2 weight percent solid solution and the balance zirconium or hafnium hydride.

Furthermore, using the standard optimum proportions above described, process steps were varied over a wide range and emission densities of the resulting cathodes compared. The results reveal that the most preferred cathode includes the solid solution of Ba_3WO_6 and Ba_2SrWO_6 in the activator material, sintering in a high purity reducing (hydrogen) atmosphere and very sharp clean cutting preparation of an emitting surface.

Repetitive cathodes are accordingly produced by this invention having continuous emission densities in excess of 7 to 10 amperes per square centimeter at operating temperatures from about 850 to 1000° C. when the preferred compositions and production parameters as described are followed.

The dispenser cathodes of this invention may be utilized in a number of different assemblies and configurations. A common example **10** is illustrated in FIG. 1. In FIG. 1 a generally cylindrical button or pill **11** of the dispenser cathode of this invention is concentrically fixed or contained within the end of a support cylinder **12**. Button **11** is provided with an exposed emitting face surface **13** and an opposite surface **14** which is adjacent a filamentary type electrical heater **15**. Button **11** may be a separate assembly which is joined to cylinder **12** or may be formed therein in position. Cylinder **12** is preferably a refractory material for example molybdenum, tungsten, etc.

While this invention has been described with reference to particular and exemplary embodiments thereof, it is to be understood that numerous changes can be made by those skilled in the art without actually departing from the invention as disclosed, and it is intended that the appended claims include all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A process of producing an improved dispenser cathode which consists essentially of

(a) intimately combining a powdered refractory metal with a finely divided single phase solid solution of about 50 atomic weight percent Ba_3WO_6 and Ba_2SrWO_6 to form a combination,

(b) adding to said combination a refractory metal reducing material which is effective to reduce Ba_3WO_6 and Ba_2SrWO_6 at operating cathode temperatures,

(c) sintering said combination into a cohesive body at elevated temperatures above the melting point of a constituent of said solid solution and in a reducing atmosphere, and

(d) removing a surface layer of material from said body to expose an emitting face thereof without adversely affecting porosity of said body through the surface exposed by said removal.

2. The invention as recited in claim **1** wherein said metal reducing material contains zirconium.

3. The invention as recited in claim **1** wherein said metal reducing material contains hafnium.

4. A process of producing a long life high emission density thermionic dispenser cathode having a continuous emission density in excess of about 5 amperes per square centimeter at temperatures less than about 1000° C. which consists essentially of

(a) intimately combining and reacting stoichiometric proportions of predetermined materials containing barium, a refractory metal and oxygen,

(b) compressing the said combination into pellet form,

(c) firing the said pellet at an elevated temperature to provide a solid solution of Ba_3WO_6 and Ba_2SrWO_6,

(d) reducing the said pellet to fine particle form,

(e) mixing the reduced pellets with finely divided tungsten, and a refractory metal hydride as a reducer compound in a ratio of at least about 88% by weight tungsten, at least about 6% by weight of said pellets in fine particle form, and less than about 1% by weight refractory metal hydride,

(f) pressing the mixture in an integral cohesive form,

(g) firing the cohesive form in a reducing atmosphere at a temperature substantially above about 1800° C. and above the melting temperature of one of the constituents of said solid solution for several minutes, and

(h) removing a layer of said cohesive form to expose a low work function emitting face surface without adversely affecting the underlying porosity of the cathode.

5. A process of producing a long life high emission density thermionic dispenser cathode having a continuous emission density in excess of about 5 amperes per square centimeter at temperatures less than about 1000° C. which consists essentially of

(a) intimately combining and reacting stoichiometric proportions of predetermined materials composed of barium, strontium, a refractory matrix metal selected from the group consisting essentially of molybdenum and tungsten, and oxygen,

(b) compressing the combination into pellet form,

(c) firing the pellets at an elevated temperature to provide an integral cohesive structure consisting of a solid solution of Ba_3WO_6 and Ba_2SrWO_6,

(d) reducing the said pellet to fine particle form,

(e) mixing the reduced pellets with finely divided tungsten, and zirconium hydride in a ratio of at least 90% by weight tungsten, at least 6% by weight of said pellets in fine particle form, and less than about 1% by weight of a hydride selected from the class consisting essentially of zirconium and hafnium,

(f) pressing the mixture in an integral cohesive form,

(g) firing the said cohesive form in a reducing atmosphere at a temperature substantially above about 1800° C. and above the melting temperature of one of the constituents of said solid solution for several minutes, and

(h) removing a layer of said cohesive form by a cutting operation to expose a low work function emitting face surface without adversely affecting the underlying porosity of the cathode.

6. A method of producing a barium tungstate dispenser cathode having a continuous emission density in excess of about 7.5 amperes per square centimeter at an operating temperature of about 1000° C. consisting essentially of

(a) intimately combining $BaCO_3$, $SrCO_3$ and (WO_3) in substantially stoichiometric proportions,

(b) pressing the combination in pellet form,

(c) firing the said pellets in excess of about 1400° C. to provide a solid solution of 50 atomic percent of Ba_3WO_6 and Ba_2SrWO_6,

(d) reducing said pellets to fine particle form,

(e) mixing the fine particle form of said reduced pellets with finely divided tungsten of 2 to 5 micron average particle size in a ratio of at least about 90% tungsten, at least about 7½% of said reduced pellets, and the balance zirconium hydride,

(f) compressing the said mixture into cathode form,

(g) firing said cathode form in a high purity hydrogen atmosphere in excess of about 1850° C. and the melting point of one of the constituents of said solid solution for several minutes, and

(h) machining one surface of said cathode form to provide a low work function face surface.

7. A process of providing a dispenser cathode which consists essentially of

(a) wet milling in methanol the proper proportions of barium carbonate, strontium carbonate, and tungsten trioxide, to provide a combination of Ba_2SrWO_6 and Ba_3WO_6, after evolution of CO_2,

(b) compressing the said combination into pellets,

(c) firing the said pellets in an air atmosphere at a temperature in excess of about 1400° C. for several hours to provide a single phase solid solution of Ba_2SrWO_6 and Ba_3WO_6 of about 50 atomic weight,

(d) crushing the said pellets into fine particle size sufficient to pass through a 325 mesh screen,

(e) mixing the fine particle crushed pellets with tungsten powder of about 2 micron average particle size and zirconium hydride in the weight percent proportions of 90 to 92% tungsten powder, 7 to 9% of the

fine particle crushed pellets, and the balance zirconium hydride,

(f) dry milling said mixture in a refractory metal ball mill for a period of 12 to 18 hours which corresponds to the second maximum of a curve of emission density versus milling time,

(g) compacting the resultant powder into a cathode body of a desired size,

(h) heating the cathode body in a high purity hydrogen atmosphere at a temperature of about 1900° C. and above the melting point of one of the constituents of said solid solution for several minutes, and

(i) machining the resultant cathode body to remove at least a part of a layer of material from a surface comprising the emitting surface of said cathode body.

References Cited

UNITED STATES PATENTS

2,722,626	11/1955	Coppola et al.	29—25.17 XR
2,753,615	7/1956	Claude et al.	29—25.17 XR
2,848,644	8/1958	Koppius	313—346
2,881,512	4/1959	Huber et al.	75—207
3,265,495	8/1966	Freytag et al.	29—25.18
3,269,804	8/1966	Affleck et al.	29—182.5

JOHN F. CAMPBELL, Primary Examiner

R. B. LAZARUS, Assistant Examiner

U.S. Cl. X.R.

29—25.17