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DISPENSER CATHODE. MATERIAL AND METHOD OF MANUFACTURE

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Fig. 1.

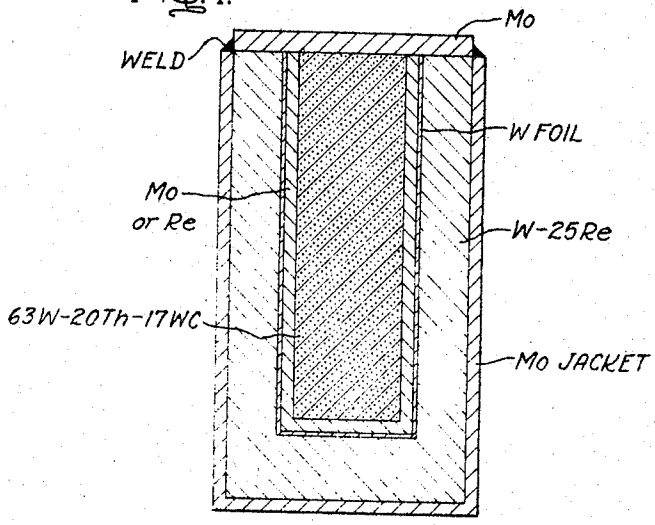
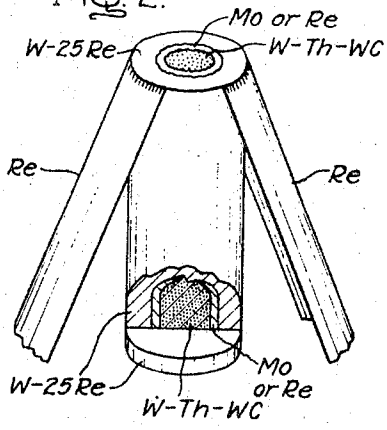


Fig. 2.



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DISPENSER CATHODE MATERIAL AND METHOD OF MANUFACTURE

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ABSTRACT OF THE DISCLOSURE

Dispenser cathode material is provided in the form of wire with thorium-bearing emission material at the center and a sheath of tungsten or tungsten-base alloys, particularly tungsten-25% by weight rhenium, and with a barrier of molybdenum or rhenium between the tungsten alloy sheath and the emission material. The barrier prevents contamination of the sheath by thorium and may prolong life of the cathode by preventing or impeding thorium attack of the tungsten. A process is provided for producing such dispenser cathode material by mechanically deforming and elongating a billet which comprises a tungsten-rhenium sheath in cylindrical form with one end closed, inside the sheath a molybdenum or rhenium tube of substantial thickness, and the tube filled with the emission material. By preventing thorium grain boundary corrosion of the sheath, the barrier keeps the sheath intact and permits deformation of the billet. Processes of canning the billet in molybdenum, and extruding, swaging, and continuously drawing it down to the desired wire size are quite economical in producing dispenser cathode material which can be cut into short lengths and one end of which can be capped.

The cathode material of the invention is particularly useful in producing nearly circular cathodes of uniform and reproducible high quality. Such cathodes are capable of emitting electron beams of very small diameter, such as might be used in producing diffraction gratings on deformable light-valve media employed for the production of three-color television pictures.

BACKGROUND OF THE INVENTION

This invention relates to dispenser cathode material and a method for making the same. More particularly, it relates to such material in wire form and individual dispenser cathodes cut from said wire.

Dispenser cathodes for vacuum tubes and the like containing a quantity of electropositive material have the advantage of long life and high electron emission density. In the usual dispenser cathode, applied heat causes the electropositive material to be dispensed from the cathode interior through a porous barrier, forming a monatomic layer upon the cathode surface at a rate substantially equal to the evaporation of such material from the surface. Cathodes of this type are employed in high power transmitting tubes and the like, wherein they present a relatively large emitting surface area and produce a relatively broad and somewhat scattered electron beam. This emission usually takes place not only from the designated

emitting area, but also as edge or side emission from the cathode body around the emitting area, the breadth of the emitted beam frequently depending upon the cathode size. For producing a smaller concentrated electron beam, a small cathode would be desirable; however, dispenser cathodes conventionally require bulky heating coils for elevating the cathode to the proper emitting temperature, placing a lower limit on the size of the cathode.

Small-dimension electron beams are ordinarily produced with the more common type of directly heated or indirectly heated cathode. The conventional cathode ray tube, for example, includes an indirectly heated cathode at the rearward extremity of the electron gun for producing a narrow stream of electrons. The beam produced in this type of cathode ray tube is suitable for wave-form portrayal, television reproduction and the like. However, in many applications an electron beam of yet smaller dimension is required. A small electron beam is required, for example, for "writing" finely detailed charge patterns on a charge receiving surface. The charge pattern may comprise, for example, the lines of a three-color diffraction grating on a deformable light-valve medium employed for the production of three-color television pictures. An apparatus employing such charge pattern is illustrated and claimed in Patent 2,813,146 to William E. Glenn, Jr., issued Nov. 12, 1957, and assigned to the assignee of the present invention.

Suitable dispenser cathodes for producing such fine electron beams are described and claimed along with a method for their manufacture in Patent 3,263,115—Glascock et al., issued July 26, 1966, and assigned to the assignee of the present invention. That patent describes a process wherein individual cathodes are manufactured by plugging one end of fine diameter tantalum tubing with pressed tantalum powder and sintering to strengthen the powder, filling the tube with emission material such as thorium metal or barium-aluminum alloy, and sealing the other end. The patent states that tungsten sheaths are preferable for such cathodes which are to be used at higher temperatures, although their emission is not as good at lower temperatures as cathodes made with tantalum sheaths. Due to the unavailability of small tungsten tubing, when tungsten has been used it has been necessary to use expensive techniques to produce a cup and fill it with emission mix. The cathodes were produced by starting with an 0.050 inch length of 0.030 inch diameter tungsten wire and machining a hole 0.040 inch deep by 0.017 inch diameter into the center of the wire from one end. Electrical discharge machining involving costly equipment and expensive set-up operations seems necessary for this machining. The emission powder mixture was then added a mil at a time and pressed down into the hole by a plunger.

It would be desirable to have a process available for producing tungsten- and tungsten alloy-sheathed small diameter dispenser cathodes suitable for forming fine electron beams by techniques that would not require the major expenses of individual handling, machining, filling and compacting of the tungsten cathodes of the prior art.

Previous attempts to produce such cathode materials in continuous form by compacting a core of thorium-

containing emission materials in a tungsten or tungsten-base alloy sheath to make a billet and deforming the billet to produce a wire, have been unsuccessful. This is primarily because of attack by the thorium metal on the tungsten sheath material during sintering and deformation and accompanying anneals, and probably continuing during operation of the resultant cathodes.

SUMMARY OF THE INVENTION

Thus, it is an object of the invention to provide tungsten-sheathed, thorium-containing, small diameter dispenser cathode wire material in continuous form at low expense and in a reliable form which can be used readily. A further object is to provide a process suitable for the production of such cathode materials. Additionally, another object of the invention is to provide such cathode materials and processes for their manufacture in which the thorium will not diffuse destructively into the tungsten sheath.

Briefly stated, the present invention in certain of its embodiments provides dispenser cathode material in wire form having an outer sheath of tungsten or alloys of tungsten, preferably tungsten containing 5 to 35% rhenium, or more preferably tungsten with about 25% rhenium, with a core of emission material including thorium, and preferably containing, in powder form, thorium and tungsten carbide, or tungsten, thorium, and tungsten carbide, with optimum proportions being about 63% W, 20% Th, and 17% WC. Percentages herein are by weight. A tungsten-base alloy is herein defined as an alloy containing at least 50% tungsten. A barrier of molybdenum or rhenium of substantial thickness, provided between the emission material and the tungsten sheath, acts as a diffusion sink or barrier for thorium and prevents further deleterious grain boundary diffusion of the thorium out into the tungsten which could lead to destruction of the cathode body, or emission from the side of the cathode which would impair the desired small diameter electron beam produced by the cathode. Although pure molybdenum or rhenium is generally preferred, essentially equivalent molybdenum-base or rhenium-base alloys can be used. Individual cathodes can be cut from such material and preferably have one end sealed and a length not more than a few times the wire diameter.

The method of production of the dispenser cathode material according to this invention comprises providing the tungsten sheath in the form of a cylinder with one end closed of tungsten or tungsten alloys, preferably with 25% rhenium, fitting into this sheath a molybdenum or rhenium tube having substantial thickness, and filling the tube with compacted emission material. The open end of the sheath preferably is sealed over, such as by welding a sheet of molybdenum onto the end, to form a billet. The billet is then mechanically deformed to produce the wire. Preferable processes include canning the billet in molybdenum for oxidation protection and lubrication, and extruding it at elevated temperatures at a sufficient ratio of reduction in cross section to permit further working as by swaging, generally at least 3:1 or 4:1, preferably 10:1, dissolving the can, and then swaging and drawing down to the desired wire size. Recrystallization anneals after about every 40% of reduction in area are quite desirable if not necessary for producing the dispenser cathode with a sheath of the preferred tungsten-25% rhenium alloy. Fewer anneals would be necessary if the sheath were pure tungsten. In certain embodiments of the invention, it is desirable to insert one or more layers of tungsten or molybdenum or rhenium foil such as of about 0.015 inch thickness inside the tungsten-rhenium cylinder before fitting the molybdenum or rhenium tube into the cylinder. This foil serves as an additional impediment to diffusion by creating an extra interface which can persist during sintering and annealing processes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional schematic elevation of a billet for producing certain dispenser cathode materials by processes of the invention.

FIG. 2 is an elevation view partly in section of a dispenser cathode of the invention ready for use.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Dispenser cathode wire material has been fabricated according to the invention to small wire 0.030 inch in diameter with an essentially concentric core of emission material, and it can readily be produced in smaller sizes if desired. Cathode guns have been produced with lengths of this wire 0.030 inch in diameter by 0.05 inch long and their emission characteristics and lifetimes evaluated at high voltages under simulated actual use conditions.

This cathode material was produced by a process described below, exemplary of the invention.

A powder mixture of W-25% Re was pressed into a billet 1.25 inches in diameter by 2.5 inches long. The billet was presintered at 1200° C. for two hours to increase its strength. A hole 0.430 inch in diameter by 2 inches deep was then easily drilled in the billet. Sintering of the alloy was done at 2750° C. for two hours in order to get density over 90% of theoretical. Then, the inside walls of the cylinder were lined with 0.015 inch thick tungsten foil, and a molybdenum tube with 0.075 inch thick walls was fitted into the cavity. It is preferable but not necessary to use a molybdenum tube that has one end closed. The molybdenum tube was then filled with powder consisting of 63% tungsten, 20% thorium, and 17% tungsten carbide, and this powder was densely packed in the tube by tapping the billet. Final sintering was accomplished at 1550° C. for two hours in vacuum at a pressure lower than 10^{-6} atmospheres with some reaction of the thorium reducing the tungsten carbide to produce thorium carbide. The rate of heating was very slow in order to insure purification, particularly of the emission mix powder. The heating schedule was as follows:

1 hour to 1100° C.,
1½ hours at 1100° C.,
1 hour at 1550° C., and
2 hours at 1550° C.

The sintered billet was jacketed in molybdenum, which acted as a lubricant and gave some oxidation protection during extrusion. This gave a jacketed billet in accordance with FIG. 1. Extrusion was accomplished on a Dynapack machine with the billet at 2050° C. and using a 10.4:1 reduction ratio. The firing pressure for extrusion was 1200 pounds per square inch, equivalent to 312,000 inch-pounds of energy. The extrusion rod was 0.35 inch in diameter by 12 inches long.

Before commencing swaging, the molybdenum jacket was removed by etching or dissolving it in a solution of one part HNO_3, one part H_2SO_4 and three parts H_2O by volume. Swaging started at 1650° C. with a gradual lowering of the temperature to 1300° C. on further swaging. Because W-25% Re alloy is known for its rapid work hardening, it was considered necessary not to exceed about 40% reduction in area between anneals. Initial recrystallization anneals were accomplished at 2000° C. for five minutes. Upon further swaging, the recrystallization temperature was lowered to 1600° C. for fifteen minutes.

Wire drawing was carried on at a much lower temperature. Because of the high ductility of W-25% Re, it was feasible to draw the wire at sizes below 0.044 inch diameter at room temperature. A summary of the swaging and drawing reductions and temperatures and the recrystallization anneals (Rexl.) appears in the table below.

TABLE.—SWAGING AND DRAWING SCHEDULE OF CATHODE EMISSION MATERIAL

	Temp., ° C.	From, inches	To, inches	Percent R.A.
Swaging:				
Initial	1,650	0.330	0.285	27
Rexl	2,020, 5 minutes			
Intermediate	1,550	0.285	0.243	27
Rexl	2,020, 5 minutes			
	1,550	0.243	0.200	32
Rexl	2,200, 5 minutes			
Final	1,300±50	0.200	0.163	31
Rexl	2,020, 5 minutes			
	1,300±50	0.163	0.134	31
Rexl	1,600, 15 minutes			
	1,300±50	0.134	0.105	38
Rexl	1,600, 15 minutes			
	1,300±50	0.105	0.082	40
Rexl	1,600, 15 minutes			
	1,300±50	0.082	0.064	40
Rexl	1,600, 15 minutes			
Drawing:				
	1,100±100	0.064	0.050	39
Rexl	1,600, 15 minutes			
	900±100	0.050	0.044	22
Rexl	1,600, 15 minutes			
	900 to Rm. Temp. (25)	0.044	0.030	46

To make the composite wire product more ductile and easier to handle in subsequent fabrication, a final anneal at the finished size, in this case 0.030 inch diameter, is desirable. The wire was treated in a hydrogen atmosphere at temperatures between 1200 and 1600° C. for 15 minutes. Anneals at temperatures between 1200 and 1500° C. resulted in substantial decreases in the hardness of the material from the initial hardness of 640 DPH down to the range of 560–600 DPH and the treatment at 1600° C. resulted in a major decrease in hardness down to about 450 DPH. Based on these heat treatments, the optimum temperature to ductilize the wire is around 1500 to 1600° C.

Wire produced according to this procedure is continuous with a substantially concentric core of emission material. The thorium did not diffuse out into the sheath and cause intergranular corrosion as did occur in previous experiments in which the wire was produced without using the molybdenum barrier layer. Diffusion of the thorium seems to have been arrested by the molybdenum acting as a diffusion sink. The tungsten foil with its additional interface between the molybdenum and the tungsten sheath likely contributed to minimizing diffusion.

When rhenium is used instead of molybdenum as the barrier material, more frequent anneals will be required as is known in the art due to work hardening of the rhenium. The mechanism of reaction of thorium with tungsten and its alloys seems to be different than with molybdenum and rhenium. Harmful grain boundary attack of thorium on tungsten-25% rhenium has been noted. There is limited general solubility of thorium in molybdenum, and grain boundary attack has not been observed. This mechanism appears to prevent destruction of the molybdenum barrier cathode by thorium corrosion. Rhenium does not seem to be attacked by thorium either along its grain boundaries or by general dissolution, but provides a good barrier to any thorium penetration.

Cathode wire material with a molybdenum barrier is less expensive due to lower material and working costs, and is satisfactory for certain applications. The material made with a rhenium barrier is more expensive but can have a longer life in vacuum applications, since the thorium and molybdenum may tend to evaporate together over a period of time.

Although the cathodes described above were produced with emission mixes containing W, Th, and WC in the stated proportions, it is also feasible to use emission mixes of about 50% Th, 50 WC, which possess a larger thorium supply, but this fill material is less structurally strong than the one also containing WC.

Thermal life tests on emitters produced in the configuration of FIG. 2 from dispenser cathode elongated wire material of the invention by closing one end of a short length of the wire produced as described in detail above with a tungsten weld have shown satisfactory results. These tests involve holding the emitter at a temperature around 1600° C. for an extended length of time, and periodically measuring emission pulses to determine the electron emission efficiency. Some such tests with emitters of the invention have demonstrated a useful pulse life in excess of 6000 hours.

The foregoing is a description of illustrative embodiments of the invention, and it is applicant's intention in the appended claims to cover all forms which fall within the scope of the invention.

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

1. Dispenser cathode material in wire form comprising thorium-bearing emission material at the center of the wire laterally enclosed by a sheath of metal selected from the group consisting of tungsten and tungsten-base alloys, said emission material and said sheath being separated by a continuous layer of a metal selected from the group consisting of molybdenum and rhenium.

2. Dispenser cathode material according to claim 1 in which said emission material contains thorium, tungsten, and carbon.

3. Dispenser cathode material according to claim 2 in which said emission material consists essentially of tungsten, thorium, and tungsten carbide, in which sufficient tungsten carbide is present to convert substantially all of said thorium to thorium carbide.

4. Dispenser cathode material according to claim 3 in which said thorium has been converted to thorium carbide.

5. Dispenser cathode material according to claim 1 in which said sheath is a tungsten-base alloy containing rhenium.

6. Dispenser cathode material according to claim 5 in which said alloy consists essentially of tungsten with about 25% by weight of rhenium.

7. Dispenser cathode material according to claim 1 which has been cut into short lengths, with their lengths being not more than a few times the wire diameter, and one end of each of said lengths having been sealed with a metal selected from the group consisting of tungsten and tungsten-based alloys.

8. A process for producing dispenser cathode material of claim 1 in which

a billet is produced comprising a cylindrical sheath with one end closed, said sheath being composed of a metal selected from the group consisting of tungsten and tungsten-based alloys, a tube of material selected from the group consisting of molybdenum

and rhenium of substantial thickness fitted into said sheath, and thorium-containing emission material in said molybdenum tube, the open end of said billet being sealed, and

said billet is mechanically deformed to lengthen it and reduce its diameter to produce said elongated dispenser cathode in wire form.

9. A process of claim **8** in which a layer of tungsten foil is provided between said sheath and said bolybdenum tube.

10. A process according to claim **8** in which

said sheath is composed of a tungsten-based alloy containing rhenium.

11. A process according to claim **8** in which the sheath is composed of an alloy consisting essentially of tungsten with about 25% by weight rhenium.

12. A process according to claim **8** in which the emission material contains thorium, tungsten and carbon.

13. A process according to claim **8** in which the emission material consists essentially of thorium, tungsten and tungsten carbide in which sufficient tungsten carbide is present to convert substantially all of said thorium to thorium carbide.

14. A process according to claim **8** in which said emission material consists essentially by weight of about 63% tungsten, 20% thorium, and 17% tungsten carbide, all mixed together in the form of a powder.

15. A process according to claim **14** in which said emission material is exposed to elevated temperatures for a time sufficient to convert essentially all the thorium to thorium carbide.

16. A process according to claim **8** in which

the sheath consists essentially of an alloy of tungsten with about 25% by weight rhenium,

the emission material is a mixture of powders of tungsten, thorium, and tungsten carbide,

the billet is enclosed in a molybdenum jacket,

the jacketed billet is extruded for a substantial reduction in cross-sectional area and said jacket is then removed from said billet, and

the extruded billet is then further deformed by swaging followed by drawing to the ultimate desired size, with said extruded billet being recrystallized by heat treatments after reduction in area of not more than about 40% before further deformation.

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U.S. Cl. X.R.

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