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H. D. MILLER ET AL

2,497,090

ELECTRODE AND METHOD OF MAKING THE SAME

Filed Dec. 13, 1947

2 Sheets-Sheet 1

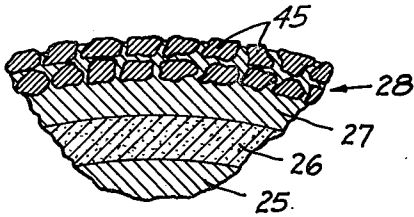


Fig. 7

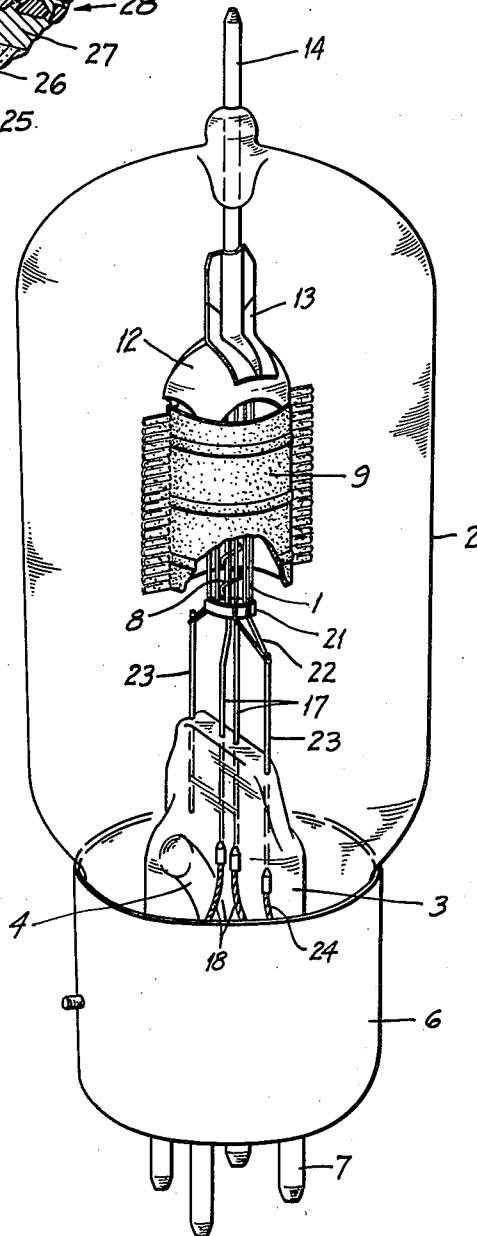


Fig. 1

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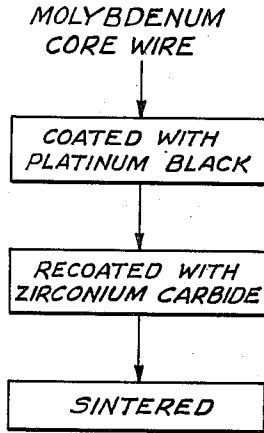


Fig. 3

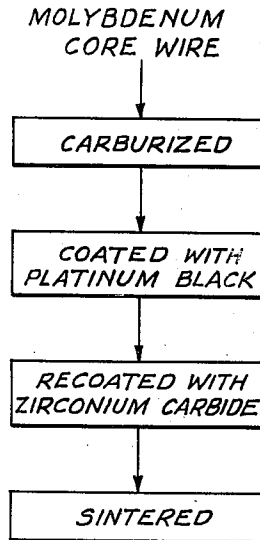


Fig. 4

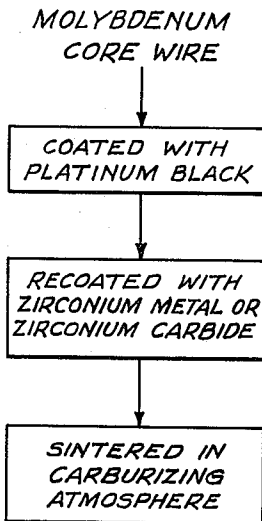


Fig. 5

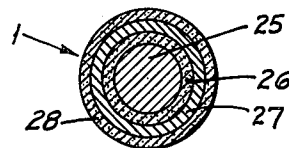
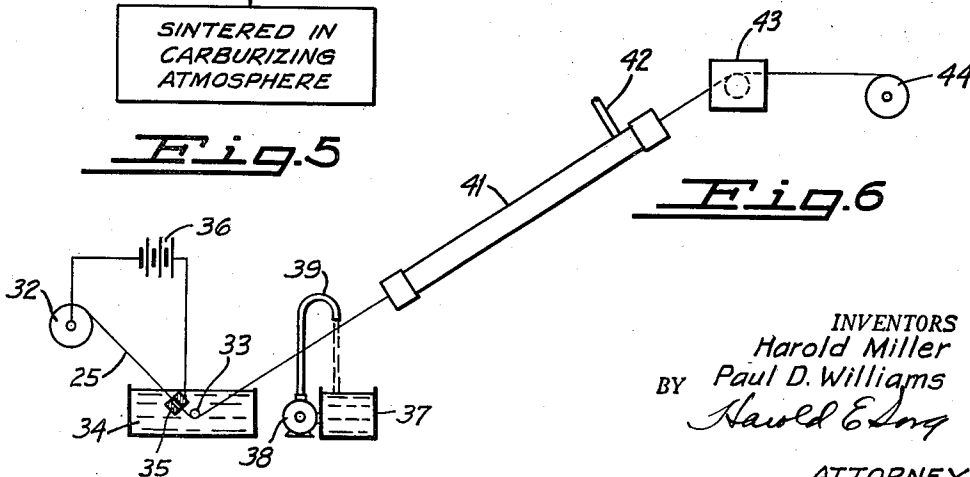


Fig. 2



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2,497,090

ELECTRODE AND METHOD OF MAKING
THE SAME

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Application December 13, 1947, Serial No. 791,524

6 Claims. (Cl. 250—27.5)

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Our invention relates to electrodes for electron tubes, and more particularly to improvements in electrodes such as grids involving combinations of metals and metallic carbides such as disclosed in the copending applications of Paul D. Williams, Serial Nos. 645,443 and 727,409.

In recent years considerable attention has been given to the problem of electron emission from electrodes, such as grids, whose function is best performed in the absence or suppression of such emission. As to a control grid, for example, it is desirable to substantially eliminate the emission of primary electrons and to limit the emission of secondary electrons to a predetermined value. Our present invention constitutes further improvements in such grids and particularly to those adapted for use in tubes having thoriated type cathodes such as thoriated tungsten filaments.

It is among the objects of our invention to provide an electrode such as a grid, having improved properties with respect to primary and secondary electron emission.

Another object is to provide a special processed material such as grid wire for an electrode of the character described which is capable of being preprocessed in the wire form prior to fabricating the grid.

A further object is to provide a method of processing the wire continuously.

The invention possesses other objects and features of advantage, some of which, with the foregoing, will be set forth in the following description of our invention. It is to be understood that we do not limit ourselves to this disclosure of species of our invention, as we may adopt variant embodiments thereof within the scope of the claims.

Referring to the drawing:

Figure 1 is an elevational view of an electron tube having a grid electrode embodying the improvements of our invention; and

Figure 2 is an enlarged sectional view of the grid wire.

Figures 3, 4 and 5 are flow diagrams of our process; and

Figure 6 is a diagrammatic view showing apparatus for carrying out the process.

Figure 7 is a further enlarged fragmentary sectional view of the grid wire showing the nature of the surface layer in the final grid material.

In terms of broad inclusion, our improved electrode such as a grid or the like comprises a metallic core, an intermediate layer comprising a metal in group 8 of the periodic table, and a surface layer comprising the carbide of a metal selected from the group consisting of zirconium, tantalum, molybdenum and tungsten. In our preferred electrode an inner layer of metallic carbide is also provided, which carbide is preferably

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similar to that used in the surface layer. Thus, in the preferred electrode, the intermediate layer of platinum or the like is interposed between two carbide layers. An important feature of the invention is a method of continuously processing the electrode material prior to fabricating the electrode. This method, as applied to a grid wire, comprises feeding the metallic core wire along a path, and forming the several layers on the core wire as it moves along the path.

In greater detail, and referring to Figures 1 and 2 of the drawings, our improved electrode is shown as a grid 1 in a triode type of electron tube having an evacuated envelope 2 with a stem 3 carrying an exhaust tubulation 4 and provided with a base 6 having terminal prongs 7. The glass envelope encloses a filamentary cathode 8, tubular metal anode 9 and the cage type wire grid 1. Anode 9 has a cap 12 supported by bracket 13 on lead 14 sealed to the upper end of the envelope.

Cathode 8 comprises a helix of thoriated tungsten wire welded to a pair of leads 17 sealed to stem 3, these leads being connected to a pair of the base prongs 7 by conductors 18. Structurally speaking, grid 1 is of the cage type comprising vertical wire bars terminating at a base ring 21 supported by brackets 22 on a pair of rods 23 sealed to stem 3. One of these rods functions as a grid lead and is connected by a conductor 24 to a base prong.

This tube structure is merely for purposes of illustration and may be varied widely, it being understood that the improvements may be incorporated in many other tube designs.

The composition of improved grid electrode 1, as shown in Figure 2, comprises a core wire 25 of a metal having a high melting point and low vapor pressure such as molybdenum, tantalum, zirconium or tungsten, these metals being generally classified in the art as refractory metals. Molybdenum is well suited for the core material and is preferred.

The core wire is surrounded by a sheath made up of three layers comprising an inner layer 26, an intermediate layer 27 and a surface layer 28. The intermediate layer 27 comprises one or more metals in group 8 of the periodic table such as platinum, rhodium or iridium, platinum being preferred. Surface layer 28 comprises the carbide of one or more metals selected from the group consisting of zirconium, tantalum, molybdenum and tungsten. A surface layer of zirconium carbide is preferred. The inner layer 26 also comprises a metallic carbide, such as the carbide of one or more of the metals specified for the surface layer. An inner layer of molybdenum carbide is preferred.

With reference to Figure 2 our preferred grid material therefore comprises a core wire 25 of

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molybdenum, an inner layer 26 of molybdenum carbide, an intermediate layer 27 of platinum, and a surface layer 28 comprising zirconium carbide, the intermediate platinum layer being interposed between the two layers of metallic carbide. The inner carbide layer 26 functions as a barrier layer to prevent alloying of the core metal into the platinum layer, and the surface layer containing metallic carbide functions in combination with the platinum layer to control electron emission. It is understood that Figure 2 is an exaggerated view for purposes of showing the layer structure more clearly. Actually, the layers 26, 27 and 28 are quite thin compared to the wire diameter.

As hereinbefore stated an important feature of our invention resides in a process whereby a grid wire is preprocessed in the wire form prior to fabricating the grid. Figure 3 is a flow diagram of a simplified process indicating the steps of coating a molybdenum core wire with platinum black, then recoating it with zirconium carbide, and then sintering the coated wire in an oxygen free atmosphere at a temperature of about 1350° C. to 1400° C. This results in a two layer wire without the inner layer 26. Figure 4 is a flow diagram of the preferred process which includes formation of the inner carbide layer. In this diagram the core wire is carburized in a separate step ahead of the platinum coating step. Carburization of the molybdenum core wire may be simply accomplished by heating it to say 1350° C. in a carburizing atmosphere such as natural gas. Figure 5 is a flow diagram of the most desirable embodiment of the preferred process in which the inner carbide layer is formed simultaneously with the final sintering step. This is done by sintering the coated wire in a carburizing atmosphere.

Figure 6 is a diagrammatic view of the preferred apparatus for carrying out the method illustrated in Figure 5. The molybdenum core wire 25 is peeled from a supply spool 32 and is directed under a guide roll 33 through a bath 34 of the first treating station. At this station the intermediate layer 27 of platinum is applied. The platinum is preferably deposited as a coating of minute platinum particles of a degree of fineness known as platinum black. Such a coating is readily obtained by electrodepositing the particles from a chlorplatinic acid bath 34, a source of direct electrical potential 36 being connected with its negative terminal to the supply spool 32 and its positive terminal to a hollow electrode 35 surrounding the wire in the bath. By this arrangement the platinum black is continuously deposited as the core wire 25 moves along its path. With a given bath composition the thickness of coating deposited will depend upon the electrical current and upon the speed of wire travel through the bath, as will be readily understood. The thickness of the platinum layer 27 is not critical in the final wire providing complete coverage over the core wire is obtained. As the wire leaves the bath 34 the platinum particles exist on the wire as discreet minute particles in a fluffy layer having a sooty appearance. Platinum particles so deposited are very small in size, say of the order of a few tenths of a micron. While the platinum exists as discreet particles in this stage, the particles are nevertheless sufficiently adherent to be retained as a distinct layer on the wire.

The wire is then recoated with finely divided metallic zirconium particles to make up the sur-

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face layer 28. The coating device at this second station comprises a tank 37 containing a mixture of zirconium metal particles of about 300 mesh size in a liquid vehicle such as lacquer. A recirculating pump 38 discharges through a spout 39 over the wire so that a coating of the zirconium particles is deposited over the platinum particles. Here again the thickness of coating deposited, using a given coating composition, will depend upon the speed of the wire travel. The thickness of this surface coating is also not critical providing complete coverage over the intermediate layer 27 is obtained. Since the underlying layer of platinum particles is of a fluffy or flocculent nature the somewhat larger zirconium particles are at least partially embedded in the platinum layer.

The coated wire is then carburized and sintered. This done in a tube furnace 41 at a third station, which furnace preferably has an electrical resistance coil for heating purposes. The sintering is done in a carburizing atmosphere free of oxygen, a hydrocarbon gas such as natural gas being satisfactory. This gas may be admitted into the furnace through an inlet duct 42. The furnace is preferably maintained at an operating temperature of about 1350° C. to 1400° C., and the wire travel is preferably such that the wire is subjected to this temperature for about one minute. During this heating step the particles of zirconium in layer 28 are converted to zirconium carbide. Also, a certain amount of carbon from the atmosphere penetrates through the platinum layer and combines with the core metal to form the inner layer 26 of molybdenum carbide. It is unlikely that any of the platinum in layer 27 is converted to a platinum carbide under the conditions involved in our process. Heating the wire in furnace 41 also functions to sinter the coated wire so that the particles of platinum in layer 27 and the particles of zirconium carbide in layer 28 are fused or sintered together and to the core wire 23. Because of the minute size of the platinum particles these particles fuse together into a relatively dense mass as indicated by the layer 27 in Figure 7. The zirconium carbide exists in the form of particles 45 in the surface layer 28 (Figure 7), which particles are embedded either wholly or partially in the platinum layer. As was the case with Figure 2, the view in Figure 7 is also exaggerated to illustrate the structure more clearly.

Instead of relying wholly upon carbon present in the furnace atmosphere to carburize the coated wire, we find it desirable to mix some carbon powder with the zirconium powder when the surface coating is applied. For example, carbon particles may be added to the mixture in tank 37 in the ratio of about 33 parts by weight of carbon to 500 parts of zirconium, the carbon particles being preferably of about 600 mesh size. An ample amount of carbon, particularly for carburizing the zirconium in surface layer 28, is thus assured.

When zirconium is employed in the outer layer, and when applied in the metallic form as in our preferred process, a small amount of the zirconium may be alloyed into the platinum layer 27 under certain conditions. Likewise, when carbon particles are added with the zirconium as suggested in the preceding paragraph, there may be some free carbon admixed with the zirconium carbide in layer 28. In any event, the composition of layer 28 is predominantly zir-

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conium carbide and that of layer 27 is predominantly platinum.

Instead of applying the zirconium as a metal and then converting it to a carbide, we have found it convenient in some cases to apply particles of preformed zirconium carbide. If tantalum, molybdenum or tungsten are used in the surface layer these are preferably applied in the form of the carbides. A carburizing atmosphere is preferred in the furnace 41, even though preformed carbides are applied to the wire, in order to accomplish formation of the inner carbide layer 26. Of course, if the inner carbide layer is formed in a separate prior step (as suggested in Figure 4), the surface layer of preformed carbide particles may be sintered in any suitable oxygen free atmosphere.

Upon leaving the furnace 41 the processed wire passes through a suitable speed controlling device 43 and thence to a rewind spool 44.

If the inner carbide layer 26 is to be formed in a separate step, as indicated in Figure 4, a second tube furnace similar to the furnace 41 is provided ahead of the bath 34 so as to carburize the wire 25 immediately after it comes off the supply spool 32. In this event the following furnace 41 may have either a carburizing atmosphere or an ordinary oxygen free sintering atmosphere depending upon whether the surface coating is applied as a metal or as a preformed metal carbide.

Our improved grid wire is quite ductile and can be readily fabricated on a mandrel into grid shape. We have also found that the processed wire spot welds together quite easily and is superior to ordinary molybdenum wire in that respect.

The fabricated grid is sealed into the envelope along with other electrodes including the thoriated tungsten cathode, and the envelope is then exhausted in accordance with usual practice. Heating the electrodes during the exhaust for outgassing purposes is done in the conventional manner, the grid temperature for this purpose with our improved material being preferably held under 1400° C. During this grid heating in the tube the only change, if any, taking place in the grid material is a further embedding of the carbide particles 45 into the platinum. Such further embedding of the carbide particles, however, does not detract from the primary electron emission suppression properties of the grid.

The final grid embodying our improvements has the desired properties with respect to electron emission. This is due to the metallic carbide surface layer in combination with the adjacent layer of platinum-like metal. The carbides of the metals specified in the surface layer 28 coact in a special way with the base metal of the intermediate layer 27 to inhibit primary electron emission and to limit secondary electron emission. The amount of secondary emission exhibited in the final grid is somewhat dependent upon the particular metallic carbide used. For example, grids surfaced with tantalum or tungsten carbides exhibit less secondary emission compared to grids surfaced with zirconium carbide. While the theory involved in this mechanism is not fully understood, we have proven by extensive life testing of tubes under operating conditions that the improved grids exhibit the desired properties. As already pointed out, the inner carbide layer 26 contributes to the de-

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sired result by providing a barrier layer between the platinum and the core metal.

Our improvements are not to be confused with platinum coated grids heretofore used. For example, the patent to Hansell, No. 2,226,720 discloses a coating of platinum metal over a wire core. Also, a patent to Taylor, No. 2,282,097 discloses a platinum covered grid similar to Hansell but with the outer surface of the platinum coated with carbon (carbonized). Our improvements differ in the use of a metallic carbide in the surface layer, and in the fact that the platinum in our grid is interposed between carbide layers.

We claim:

1. An electrode for an electron tube comprising a layer of platinum interposed between two layers of metallic carbide.
2. A grid material for an electron tube comprising a molybdenum core, an intermediate layer of a metal selected from the group rhodium, iridium, and platinum, and a surface layer comprising a metallic carbide, the metal of said carbide being selected from the group consisting of zirconium, tantalum, molybdenum and tungsten.
3. A grid material for an electron tube comprising a core of molybdenum, an intermediate layer of platinum, and a surface layer comprising zirconium carbide.
4. A grid material for an electron tube comprising a core of molybdenum, an inner layer of molybdenum carbide, an intermediate layer of platinum, and a surface layer comprising zirconium carbide.
5. The method of processing a grid material for an electron tube, which comprises electrodepositing platinum black on a molybdenum core wire, applying over the platinum black a coating comprising a mixture of powdered carbon and finely divided particles of a metal selected from the group consisting of zirconium, tantalum, molybdenum and tungsten, and then sintering the coated wire.
6. The method of continuously processing a grid material for an electron tube, which comprises feeding a molybdenum core wire along a path, and, while the wire is fed along said path, electrodepositing platinum black on the core wire, applying over the platinum black a coating comprising a mixture of powdered carbon and finely divided particles of a metal selected from the group consisting of zirconium, tantalum, molybdenum and tungsten, and then sintering the coated wire.

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