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**Continuation-in-part of application Ser. No.
666,802, Sept. 11, 1967, now abandoned.**

3,212,169 10/1965 Glaser et al. 313/107 X
3,329,601 7/1967 Mattox 204/298
3,386,909 6/1968 Hough 204/312

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[54] **NONELECTRON EMISSIVE ELECTRODE
STRUCTURE UTILIZING ION-PLATED
NONEMISSIVE COATINGS**
1 Claim, 6 Drawing Figs.

[52] U.S. Cl. **313/107,
313/106, 313/355, 117/216, 204/298, 204/312**

[51] Int. Cl. **H01j 43/00**

[50] Field of Search. **313/106,
107, 355; 29/155.5; 204/298, 312; 117/216, 217,
218**

[56] **References Cited**
UNITED STATES PATENTS
3,177,094 4/1965 Dijksterhuis et al. 313/107 X

ABSTRACT: A nonemissive electrode structure is disclosed together with a method for fabricating same. The nonelectron emissive electrode structure includes a core member which may be made of any one of a number of different metals such as molybdenum, copper, tantalum or tungsten. A nonelectron emissive material is deposited over the core metal. The nonemissive deposited layer may be any one of a number of different materials which will provide electron emission inhibiting characteristics in the presence of surface contamination by barium and/or strontium. Examples of such electron emission inhibiting materials include titanium, chromium, zirconium, or silicon. An outer coating of carbon is formed over the emission inhibiting layer to further enhance the nonelectron emissive characteristics of the electrode. Alternatively, the nonemissive deposited layer and carbon coating may be codeposited into a single covering layer deposited over the core material. The electrode structure is especially suitable as a grid structure in an electron discharge device employing either an oxide coated cathode or a dispenser cathode of the type containing barium and/or strontium.

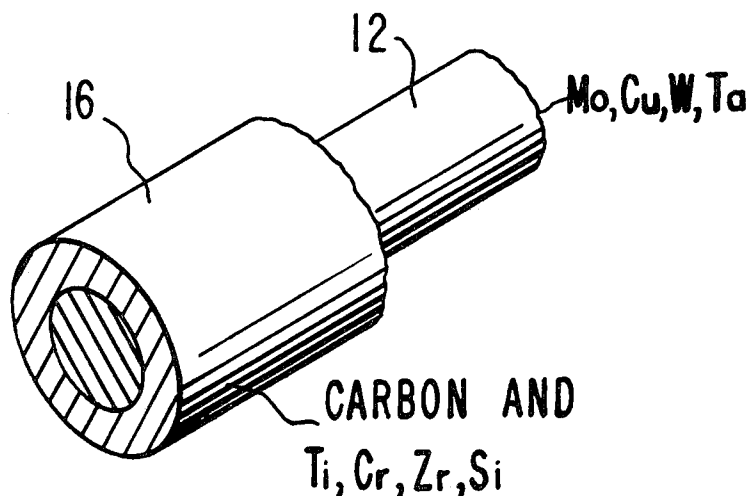


FIG. 1

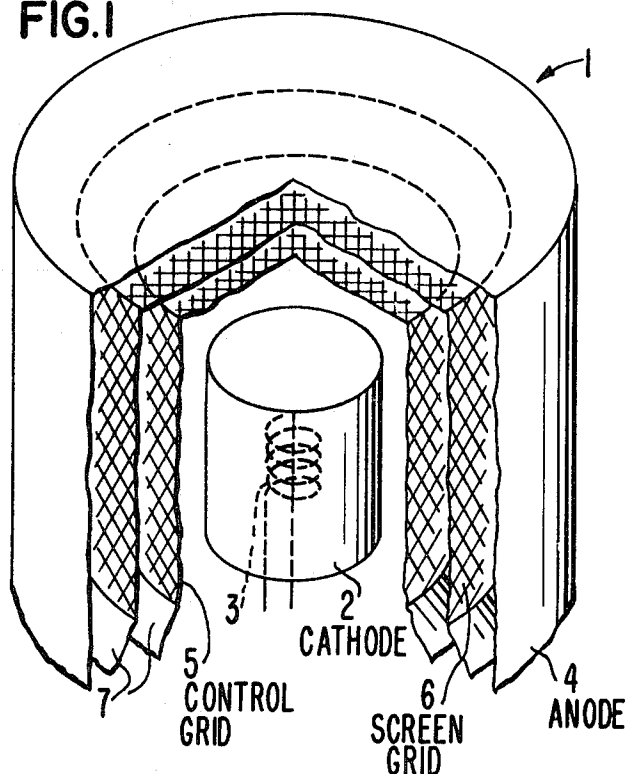


FIG. 2

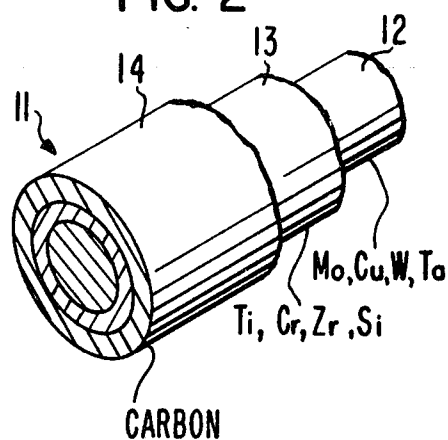


FIG. 3

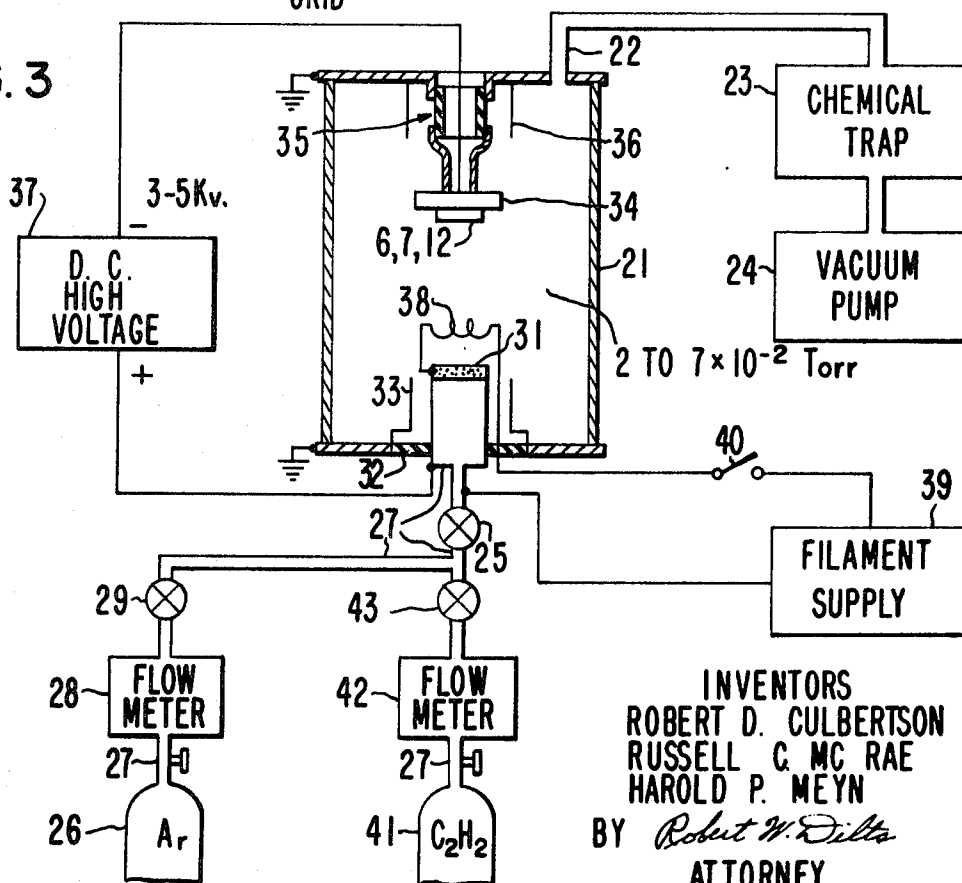
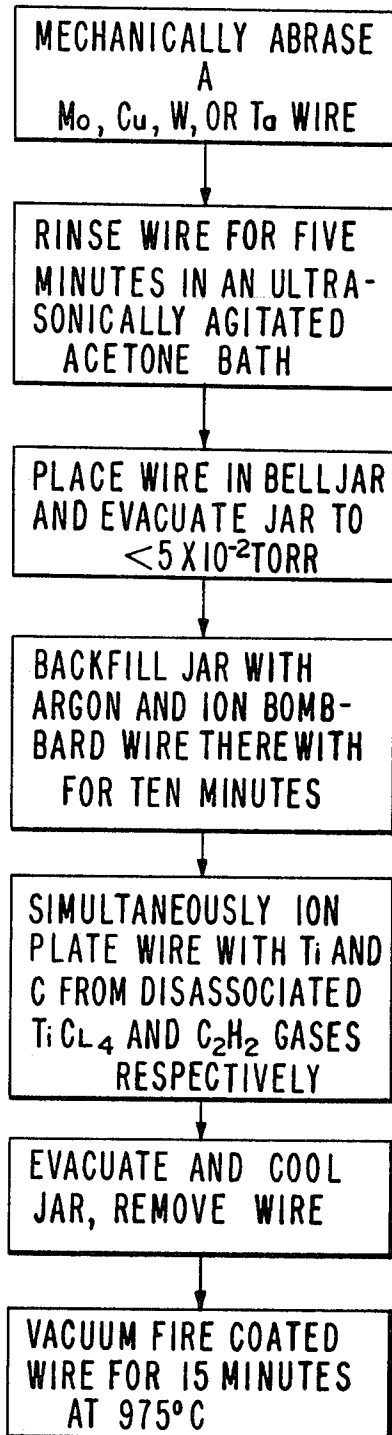


FIG. 6



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FIG. 4

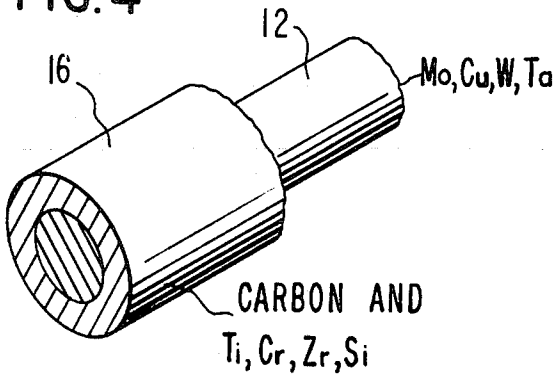
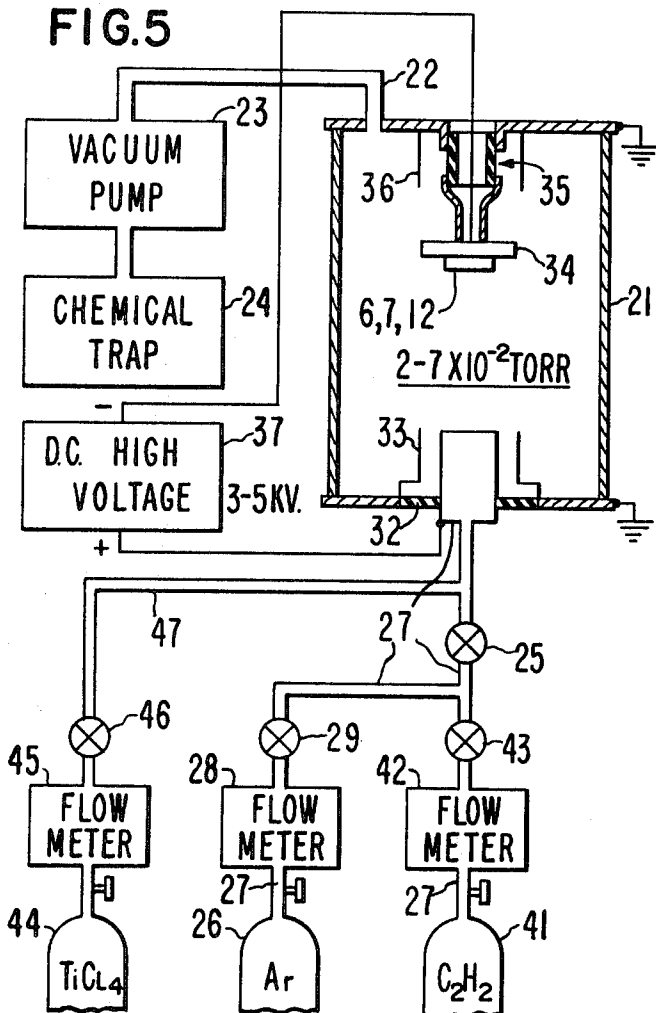


FIG. 5



NONELECTRON EMISSIVE ELECTRODE STRUCTURE UTILIZING ION-PLATED NONEMISSIVE COATINGS

DESCRIPTION OF THE PRIOR ART

This is a continuation-in-part of our copending application Ser. No. 666,802, filed Sept. 11, 1967 and now abandoned.

Heretofore, nonemissive grid structure for electron discharge tubes have been proposed wherein the grid structure was made of a wire material having a core of a refractory metal such as molybdenum, tungsten or tantalum which was carburized on its outside surface and then plated with a metal of group 8 of the periodic table such as platinum, rhodium, or iridium which serves to produce an electron emission inhibiting layer which in turn was covered by a carbide of a metal selected from a class of zirconium, tantalum, molybdenum and tungsten. Such an electron nonemissive electrode structure is described and claimed in U.S. Pat. No. 2,497,090 issued Feb. 14, 1950 and assigned to the same assignee as the present invention. The problem with this prior art electrode structure is that the coating layers are carburized in a furnace at about 1,350° C. to 1,400° C. in order to form the various carbide layers. This heat treatment of the electrode produces embrittlement which makes the wire difficult to work into a grid structure or, if the grid structure is formed before carburizing, tends to make the resultant grid electrode structure relatively brittle and, therefore, relatively easy to fracture in use.

Other prior art nonemissive electrode structures for electron tubes have been made of a molybdenum wire coated with a nickel coating which in turn was coated with carbon. One of the problems with this electrode structure was the same as that previously mentioned with regard to the first electrode structure, namely, that the carbon coating had to be carburized to the electrode structure in order to form a tightly adherent layer to prevent flaking and the like and that the carburization of the electrode was obtained at relatively high temperatures such that the resultant electrode structure was relatively brittle and therefore prone to fracture in use.

Still other prior art nonemissive electrode structures have included a core wire of molybdenum or other refractory metal coated with an electron emission inhibiting material such as platinum, iron, cobalt, iridium or osmium with an outer coating of carbon which is then heated to a relatively high temperature in a hydrogen atmosphere until the surface is shiny and clean. In the case of a platinum emission inhibiting layer, this indicates that the carbon has diffused through the platinum to form a carbide layer with the core material such that the shiny platinum is left on the outside surface. Such a nonelectron emissive grid structure is described in U.S. Pat. No. 2,282,097 issued May 5, 1942. Such a grid structure may be utilized to advantage in electron discharge devices employing a thoriated tungsten cathode but the electrode structure does not exhibit the desired nonelectron emissive characteristics when employed with oxide cathodes or with dispenser cathodes incorporating barium or strontium and operating at relatively low temperatures, as of less than 1,000° C.

Recently methods have been developed for ion plating carbon and other materials from a glow discharge onto structures to be coated. Such coatings are relatively adherent and are produced at essentially room temperature. Such methods for depositing carbon and other materials are disclosed and claimed in copending U.S. application Ser. No. 632,361 filed Apr. 20, 1967 and now abandoned and assigned to the same assignee as the present invention.

SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is the provision of an improved nonelectron emissive electrode structure and of improved methods for fabricating same.

One feature of the present invention is the provision of a nonelectron emissive electrode structure for use in environments subject to surface contamination by barium and/or

strontium and comprising a core material having a covering layer comprising carbon and one or more materials selected from the class consisting of titanium, chromium, zirconium, and silicon, whereby the electrode structure has improved nonelectron emissive properties.

Another feature of the present invention is the provision of a nonelectron emissive electrode structure for use in the just-stated environments and comprising a core material having an outer layer of carbon and an intermediate layer made of a material selected from the class consisting of titanium, chromium, zirconium, and silicon, whereby the electrode structure has improved nonelectron emissive properties.

Another feature of the present invention is the method for fabricating a nonelectron emissive electrode structure comprising the step of simultaneously ion plating carbon and an electron emissive inhibiting material selected from the class consisting of titanium, chromium, zirconium, and silicon from a glow discharge onto the electrode core. The coated wire may then be heated to a temperature between 750° C., and 1,000° C.

Yet another feature of the present invention is the method for fabricating a nonelectron emissive electrode structure comprising the steps of coating a core metal of the electrode structure with an electron emissive inhibiting material and ion plating carbon from a glow discharge over the layer of nonelectron emissive material to form the composite nonelectron emissive electrode structure, whereby the carbon coating forms a tightly adherent coating and is produced at a relatively low temperature which will not adversely affect the ductility of the electrode structure.

Another feature of the present invention is the same as the preceding feature wherein the electron emissive inhibiting layer is ion plated from a glow discharge onto the core material to provide a uniform tightly adherent intermediate layer.

Other features and advantages of the present invention will become apparent upon a perusal of the following specification taken in connection with the accompanying drawings wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary perspective view, partly broken away, of an electron tube incorporating an electrode structure of the present invention,

FIG. 2 is an enlarged fragmentary perspective view of a wire electrode structure incorporating features of the present invention,

FIG. 3 is a schematic diagram of an apparatus for performing the ion plating method of the present invention,

FIG. 4 is an enlarged fragmentary perspective view of another wire electrode structure incorporating features of the present invention,

FIG. 5 is a schematic diagram of an alternative apparatus for performing the ion plating method of the present invention; and

FIG. 6 is a flow diagram in block form of a series of specific steps which may be taken in fabricating the wire electrode structure shown in FIG. 4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, there is shown a typical electron tube employing nonelectron emissive electrode structures of the present invention. More specifically, the electron tube 1 includes a hollow cylindrical cathode electrode structure 2 which is heated to thermionic emission temperature by means of a filamentary heater 3 contained within the cylindrical emitter 2. A hollow cylindrical anode structure 4 is disposed surrounding the cathode emitter 2 for collecting the electrons emitted from the emitter 2. A control grid structure 5 is disposed surrounding the cathode 2 between the cathode 2 and the anode 4 for controlling the beam current passed through the control grid 5 from the emitter 2 to the anode 4. A screen grid structure 6 is disposed surrounding the control grid 5 between the control grid 5 and the anode 4 for reducing

the control grid to anode capacity. The screen grid structure 6 operates near the anode potential and will intercept some of the beam current. It is desirable that the screen grid should be as nonelectron emissive as possible. The screen and control grids 6 and 5 are typically cylindrical cage-like structures supported at their bases from conical support structures 7, as of nickel.

The cathode emitter 2 need not be of the indirectly heated type as shown but may also be made of a directly heated configuration wherein the emitter is formed by a thoriated tungsten wire through which the heating current is passed for heating same to its operating temperature of approximately 1,500° C. Emitter 2, as shown in FIG. 1, is of the oxide coated variety wherein a nickel base material is coated by carbonates of barium and strontium and has an operating temperature of 850° C.

Referring now to FIG. 2, there is shown a section of nonelectron emissive wire 11 incorporating features of the present invention and which may be employed for fabricating the grid structures 5 and 6 as described with regard to FIG. 1. The grid wire 11 includes a cylindrical central core member 12 as of molybdenum, tungsten, tantalum or copper, as of 0.010 inch in diameter. The core 12 is coated with a layer of material, which will inhibit electron emission in the presence of surface contamination by barium or strontium at temperatures less than 1,000° C., such as titanium, chromium, zirconium or silicon to a thickness as of 0.003 inch to form an intermediate layer 13 of the wire 11. An outer coating of carbon 14 is formed over the intermediate layer 13 to provide a dark coating for the electrode and to further inhibit electron emission. The carbon layer 14 is preferably on the order of 2 microns thick. FIG. 4 illustrates an alternative configuration in which core 12 of nonelectron emissive wire 15 is coated with but a single covering layer of material 16. Layer 16 consists of both one of the just-listed emission-inhibiting materials and carbon.

Referring now to FIG. 3, there is shown an apparatus for fabricating the electrode structures of the present invention. More specifically, the preformed electrode structures of core material may be plated with layers 13 and 14 or the core wire 12 may be coated with layers 13 and 14 and then fabricated with the control electrode configuration. Briefly, the method for fabricating the nonelectron emissive electrode structures comprises the steps of ion plating the emission-inhibiting layer 13 onto the core material 12 from a glow discharge and then ion plating the carbon layer 14 from the glow discharge to produce the composite electrode structure. The structure may finally be heated in an inert gas or a vacuum.

The ion plating apparatus includes an evacuable glow discharge chamber 21, such as a bell jar, which is evacuated to a relatively low pressure of 10^{16} torr via exhaust tubulation 22, chemical trap 23 and vacuum pump 24 in order to remove undesired gases and substances from the chamber 21. The chamber 21 is then backfilled with a glow discharge gas, preferably a noble gas such as argon, through a variable leak 25 to a pressure of 1 to 5×10^{12} torr. The glow discharge gas is supplied from a source 26 and fed into the chamber 21 via inlet tubulation 27 containing a glow meter 28 and a metering valve 29. Within the chamber 21 the gas inlet tubulation includes a porous tungsten plug 31 through which the gas enters the chamber 21 and which also serves as the positive electrode for producing the glow discharge. The inlet tubulation 27 is insulated from the bottom wall of the bell jar 21 via insulator 32. A sputter shield 33 shields the insulator 32 from material sputtered within the chamber 21.

A second glow-discharge-forming electrode 34 projects toward the first electrode 31 from the top wall of the chamber 21. A feedthrough insulator 35 supports the second electrode 34 from the top wall. A sputter shield 36 surrounds the feedthrough insulator 35 to prevent the insulator 35 from being shorted out due to condensation of conductive materials over the insulator 35. A high-voltage DC power supply 37 provides a potential as of 1 to 5 kv. between the glow discharge electrodes 31 and 34 with a negative potential being applied to the upper electrode 34.

An evaporator element 38 such as a resistive filament coated with one of the aforementioned electron emission inhibiting materials is disposed in the vicinity of the glow discharge electrodes 31 and 34 for evaporating the electron emissive inhibiting material into the glow discharge. In one form, the evaporator 38 comprises a filamentary element having one terminal connected to the porous tungsten block 31 and having the other terminal connected to a filament supply 39 via a switch 40. The filament supply 39 has one terminal connected to the porous tungsten block and supplies heating current through switch 40 to the evaporating element 38 for evaporating the emission inhibiting material into the glow discharge.

The electrode structure made of the core material to be coated such as, for example, performed grid structure 5 or 6 to core wire 12 is mechanically abraded, rinsed and dried, and placed on the negative electrode 34. The glow discharge is started by applying the operating potentials, as of 1 to 5 kv., to the electrodes 31 and 34 and maintaining the glow discharge gas pressure at about 1 to 7×10^{12} torr with a glow discharge current as of 10 to 80 ma. Gas is continuously pumped by pump 24 and new gas is continuously leaked into the chamber 21 via inlet tubulation 27. The glow discharge ionizes the argon gas and drives the argon ions into the surface of the electrode structure 5, 6 or 12 to be coated, thereby cleaning the surface of the electrode structure at a relatively low temperature as of 50° C. The cleaning glow discharge is maintained for 5 to 45 minutes in order to thoroughly clean the surface to be coated.

After the cleaning step, and while the glow discharge is maintained, switch 40 is closed to energize the evaporator 38 and the electron emission inhibiting material is evaporated from the evaporator 38 into the glow discharge to ionize the electron emission inhibiting material. Suitable electron emission inhibiting materials for use where subjected to barium or strontium contamination of less than 1,000° C. include titanium, chromium, gold, platinum, zirconium and silicon. Platinum is a useful electron emission inhibiting material for thoriated emitters. Ions of the electron emission inhibiting material are electrodeposited (ion plated) onto the surfaces of the electrode structure to be coated, thereby forming the intermediate electron emission inhibiting layer 13. The intermediate layer is deposited to a suitable thickness preferably less than a few microns thick. When the intermediate layer has reached a sufficient thickness switch 40 is opened and the evaporation ceases.

After depositing the intermediate layer 13, a suitable hydrocarbon such as acetylene, C_2H_2 , is introduced into the glow discharge. Other suitable hydrocarbon gases include methane and ethane. The hydrocarbon gas is leaked into the glow discharge from a source 41 via flow meter 42 and metering valve 43 in the inlet tubulation 27.

The acetylene is dissociated by the glow discharge and most of the carbon atoms are ionized to form positive carbon ions. Positive carbon ions are electrodeposited (ion plated) by the electric field between the electrodes 31 and 34 onto the surface of the electrode structure 5, 6 or 12 to be coated, thereby plating same. The acetylene gas will sustain the glow discharge. Thus, as the acetylene is introduced, the argon is slowly valved off such that within 5 minutes the discharge is operating on pure acetylene. The glow discharge is maintained for 5 to 45 minutes to produce a carbon coating of suitable thickness after which the leak 25 is closed to extinguish the discharge and the high potential removed from the electrodes 31 and 34. The system is then allowed to cool, opened to air, and the coated articles removed. The coated articles are then placed in a vacuum furnace and fired at 975° C. for 15 minutes to drive off any hydrogen which may not have dissociated from the acetylene during the ion plating step, and any plated material from the evaporator other than the electron emission inhibiting matter.

FIG. 6 illustrates the preferred sequential steps to be taken in producing the electron-emissive inhibited structure shown in FIG. 4. In performing these steps the apparatus of FIG. 5 is

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preferably used. This apparatus is the same as that shown in FIG. 3 with the exclusion of porous block 31, evaporator 38 and filament supply 39. Instead titanium is introduced to chamber 21 through inlet tubulation 47, containing a flow meter 45 and a metering valve 46, which communicates with a volatile supply of titanium tetrachloride 44. If desired, this alternate means for supplying titanium to chamber 21 may also be used in forming the three layer electrode structure shown in FIG. 2.

In forming the two layer electrode structure shown in FIG. 4, the specific steps shown in FIG. 6 are preferably taken. Following the abrading and argon bombardment steps as hereinbefore explained in fabricating the structure of FIG. 2, valve 29 is closed and valves 43 and 46 are opened while the flow discharge is maintained. This allows gaseous acetylene, C_2H_2 , and titanium tetrachloride, $TiCl_4$, to be introduced into the glow discharge within chamber 21. Here the titanium is dissociated from the chlorine, and the carbon is dissociated from the hydrogen. The chlorine and hydrogen gases are pumped out of the chamber to chemical traps 23 while the particulate carbon and titanium ions are drawn by cathode 34 to structures 6, 7 and 12 mounted thereon. This step is maintained for 10 minutes following which period high-voltage source 37 is disconnected and valves 43 and 46 are closed. After this the chamber is evacuated and cooled and the coated wire removed. The wire electrode is then vacuum-fired for 5 to 45 minutes at between $750^\circ C.$ and $1,000^\circ C.$, preferable for 15 minutes at $975^\circ C.$

The exact character of the ion plated coatings is not precisely known. For example, an electron nonemissive electrode structure fabricated by the aforescribed method and comprising a molybdenum core with a carbon outer coating and a titanium intermediate layer was subjected to both X-ray diffraction and emission spectroscopy analysis. The X-ray diffraction showed no carbon, titanium or carbides of titanium or molybdenum. Emission spectroscopy showed titanium as a major constituent. The conclusion is that the coatings and interface compounds, if any, are amorphous or extremely small crystallites in structure or they are very thin.

Referring now to the table below, there is shown a comparison between the primary electron emission characteristics of the prior art grid structures compared to grid structures of the present invention.

More specifically, the grid structures were tested in a tetrode-type tube similar to that shown in FIG. 1 which employs an oxide coated nickel base cathode 2 and commercially available as the Eimac 4X150A tube type. A series of these tubes was constructed wherein the screen grid 6 was made of wire having the configuration as indicated in column 1 of the table. The primary electron screen grid emission current was measured for the screen grid as a function of the power dissipated by the screen grid under two conditions. Namely, an

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initial condition just after tube processing when the screen grid is uncontaminated and a second condition 500 hours later after substantial contamination of the screen grid by barium and/or strontium evaporated from the nickel oxide cathode 2.

As seen from the table, screen grid electrodes employing ion plated carbon were initially much superior to the electrodes employing gold-plated molybdenum, carburized molybdenum and bare molybdenum wire. More specifically, the latter three screen grid materials could collect only 30, 18 and 16.5 watts, respectively, before they emitted 100 microamperes of screen grid current. On the other hand, the screen grids employing ion plated carbon on gold and ion plated carbon on ion plated titanium could dissipate 55 watts while producing only 18 microamperes and between 12 and 40 microamperes, respectively, of primary screen grid current. These grid structures were employed in a tube having an oxide coated cathode on a nickel base material wherein the operating temperature of the cathode is about $850^\circ C.$ The grids become contaminated after many hours of use by barium and/or strontium evaporated from the oxide cathode and which condense upon the screen grid structure. This barium and/or strontium coating reduces the work function of the surface of the screen grid electrode structure causing it to become more electron emissive substantially counteracting the nonelectron emissive layer and carbon coating placed upon the electrode structure.

The screen grid electrode structure No. 5 having ion-plated carbon on ion-plated titanium on molybdenum core material has substantial advantage over the gold plated molybdenum wire, identified as sample No. 1, and the ion plated carbon on gold plated molybdenum grid identified as sample No. 4, in that the titanium is less expensive than the gold and, in addition, permits grids to have a much higher power-handling capability because the titanium has a lower vapor pressure than the gold. Thus, grid No. 5 utilizing the ion plated carbon on ion plated titanium on a molybdenum core permits the screen grid electrode to dissipate much higher power than would be possible with a gold plated screen grid electrode structure. Evaporated gold will also poison the cathode causing the tube to become inoperative.

Since many changes may be made in the above construction and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An electrode for an electron tube comprising a metallic core and an emission-inhibiting outer layer on said core, said layer comprising carbon and a material selected from the group consisting of titanium, chromium, zirconium and silicon, said material being intimately commingled with said carbon.

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