Dec. 13, 1949 R. W. SEARS 2,491,284

ELECTRODE FOR ELECTRON DISCHARGE DEVICES
AND METHOD OF MAKING THE SAME
Filed Dec. 13, 1946

FIG. 1

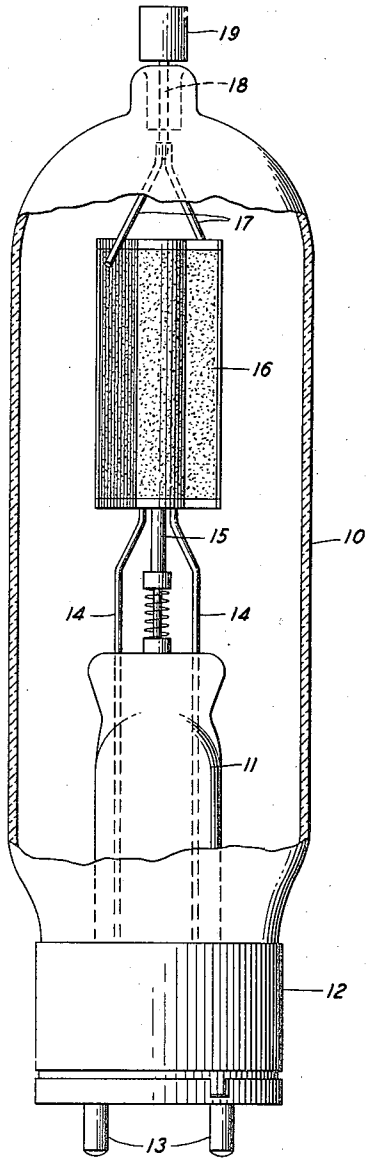
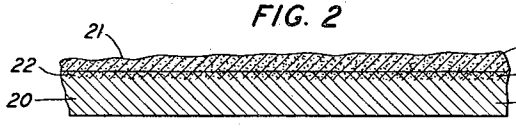


FIG. 2



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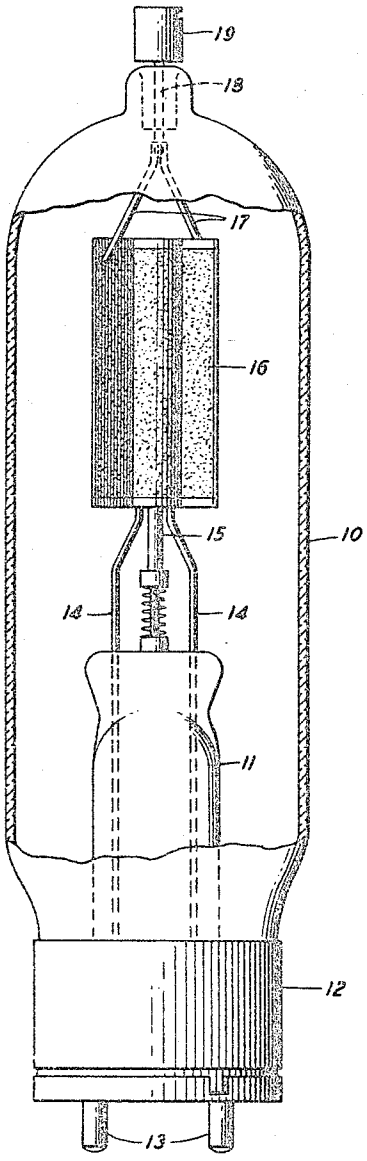
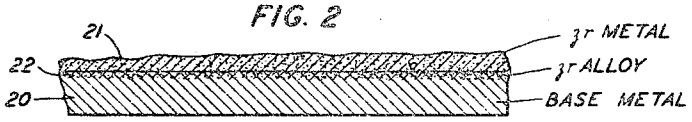


FIG. 2



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ELECTRODE FOR ELECTRON DISCHARGE DEVICES AND METHOD OF MAKING THE SAME

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14 Claims. (Cl. 250—27.5)

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This invention relates to electronic discharge devices and more particularly to such devices capable of supplying a high power output.

This is a continuation in part of my application, Serial No. 497,330, filed August 4, 1943, now abandoned.

In the usual power rectifier or amplifier device, the output electrode or anode is formed of a highly refractory metal, such as tungsten, molybdenum or tantalum which can sustain the high efficiency output of the device without appreciable buckling or distortion due to the intense heat energy dissipated in the anode. In order to facilitate the dissipation of heat energy, it is common practice to apply a black body material to the anode surface in the form of a heat radiating coating. Carbon, a desirable coating substance at low energy levels, is unsatisfactory for operating temperatures above 1000° C. In the high energy range it is more practical to employ high melting point materials as the coating substance, such as zirconium, titanium and tantalum. However, the problem of adherence of the coating material to the highly refractory base metal, heretofore, has greatly handicapped the manufacture of such devices and the longevity of operation of power rectifiers and similar devices, since peeling and chipping of the coating rendered the device unsuitable after a short period due to localized burning of the anode at the unprotected spots. Furthermore, the binder material, usually of a low melting point substance, exposed by the chipping, readily vaporized and retarded the efficiency of the device by diffusing deleterious gases or vapors not absorbed by the getter properties of the coating and which reduced the high vacuum in the device.

Another disadvantage of employing these materials as coatings on a highly refractory base metal is the readiness of the material, particularly zirconium, when heated in the presence of oxygen to change the character of the black body heat radiating material to a white insulating oxide which is not a satisfactory heat radiator. A further characteristic of the coating material employed as a high temperature heat radiation layer on the electrode develops during manufacture when the electrode is outgassed in pumping procedure. If the coating attains a temperature of 1500° C. under high vacuum conditions, zirconium sinters to a hard brittle and compact matrix which destroys the good heat radiating and gas absorbing properties of the coating on the electrode. Similar effects occur in the cases of coatings of tantalum or titanium.

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An object of this invention is to overcome these difficulties in high power discharge devices.

Another object of the invention is to materially enhance the operating life of discharge devices by eliminating low melting point metals or binders from the coating of the electrode.

A further object of the invention is to facilitate the efficient application of the coating substance to the base metal electrode to insure constant adherence.

Another object of the invention is to provide a method of the application whereby an alloy interface is formed to produce a more stable bond between the coating and the base metal.

A further object is to provide a heat treatment for the electrode and coating which insures positive adherence of the coating without endangering the properties of the coating by high sintering temperatures.

These objects are obtained in accordance with this invention by introducing an agent in the nature of a catalyst in the processing of the coating on the base metal, the agent being a metal of the iron group, such as nickel, cobalt and iron, which is vaporized during the heat treatment of the coating and promotes the formation of an alloy interface of the coating and base metals which firmly bonds the porous coating to the base metal.

In a preferred aspect of the invention, the coating material is applied to the base metal and the electrode is heated in nickel vapor in a low pressure environment to facilitate the alloying of the coating metal to the base metal at the interface and provide a permanent bond between the coating and the base metal. The temperature of treatment is sufficient to completely eliminate all binder material from the coating and produce alloying on the surface of the base metal through the catalyst-like action of the nickel vapor. The nickel does not combine with the base and coating metals since it is continually in the vapor phase so that no low melting point metal enters into the constituents of the composite electrode. The iron group metal agent may be introduced as a part of the coating substance and during the heat treatment is reduced to the vapor state to perform its function in partially alloying the coating to the base metal. Any desired degree of interfacial alloy thickness may be obtained by varying the temperature and time of treatment in the vapor or the amount of metal agent incorporated in the coating material.

These and other aspects of the invention will be more clearly understood from the following

detailed description when considered in connection with the accompanying drawing. In the drawing:

Fig. 1 illustrates a rectifier device with an anode treated in accordance with this invention; and

Fig. 2 is a grossly enlarged but proportional illustration of a portion of the anode shown in cross-section to more clearly disclose the bonding of the coating resulting from the technique of this invention.

Referring to Fig. 1 of the drawing, a high power electron discharge device is disclosed and comprises an enclosing vessel 10 having an inwardly projecting stem 11 at one end which is secured to a shell or base 12 carrying terminals 13 which are secured to conductors 14 extending through the stem and supporting an electron emitting cathode (not shown) which is also supported by a central tensioned standard 15 within a cylindrical flanged metallic anode 16 supported by a pair of arms 17 extending upwardly to a lead-in wire 19 sealed in the top of the vessel and connected to a terminal 19.

The temperatures encountered in the processing and operation of a high power rectifier device, such as disclosed, require the anode to be formed of a highly refractory base metal, such as tungsten, molybdenum or tantalum, and the outer surface thereof is coated with a porous black body material having high heat radiating properties, to more readily dissipate the heat energy generated in the output electrode or anode. Due to the high operating voltages applied between the electrodes of the rectifier device and the consequent electron bombardment of the anode, it is necessary to readily dissipate the heat energy generated in the anode whereby the anode is maintained at a minimum temperature to avoid distortion or buckling as a result of the inherent heat energy of the electrode. The ability of the output electrode or anode to readily dissipate the heat energy is enhanced by providing an outer coating thereon of a black body material which will be influential in the transfer of heat energy from the base metal to the surrounding discharge space where it may be conveyed away from the anode and dissipated.

The high temperature of operation and the highly refractory nature of the electrode material necessitate the utilization of a black body material having heat radiating characteristics having relatively high thermal conductivity to facilitate the transfer of heat energy from the electrode. Such materials are zirconium, titanium and tantalum which are amorphous and highly porous and may be applied to the surface of the anode with suitable binder material by painting or spraying. As shown in Fig. 2, the composite anode is formed of a base metal 20, such as tungsten, molybdenum or tantalum, and the porous heat radiating coating applied thereto is indicated at 21, which may be zirconium, titanium or tantalum, or combinations thereof.

The high temperature of operation of the device and the refractory character of the base metal and coating impose adverse conditions on the coating material due to its nature which seriously affect the coherence of the coating to the base metal. Heretofore, various binders have been employed to enhance the adherence of the coating to the surface of the metal but such binders have been unsatisfactory from the standpoint of introducing deleterious matter which is evolved during the operating life of the device or residual substances remaining in the coating affecting the gas absorbing properties thereof. Another disadvantage is that superficial adherence is obtained for a short period after which the coating peels or chips off thereby decreasing the efficiency of the device for its intended operation. Attempts have been made to secure adherence by sintering treatment of the coating to attain a satisfactory bond to the base metal. However, such treatment depreciates the characteristics of the coating in heat radiation and the ability to absorb gases which is an inherent and desirable characteristic of these coating materials.

In accordance with a feature of this invention, constant adherence of the coating is obtained without endangering the characteristic properties of the coating substance by a heat treatment which is considerably below the sintering temperature of the coating and the base metal. This is accomplished by coating the base metal electrode 20 in the usual manner by spraying or painting a mixture of the coating metal held in a fluid viscous binder, such as cellulose nitrate and amyl acetate, to form a uniform coating 21 on the surface of the electrode. After suitable drying, as by baking, to set the coating, the anode is subjected to a heat treatment in a low pressure environment, for example, a vacuum chamber evacuated to a high degree wherein a heating temperature from 1100° C. to 1300° C. is employed to completely remove the constitutents of the binder material and produce coalescence in the coating. During this treatment a small quantity of a metal of the iron group, such as nickel, cobalt and iron, is introduced into the heating chamber and completely reduced to the vapor phase, due to the high heating temperature and low pressure, the vapor having a catalytic-like action in converting the particles of the coating material in interfacial relation to the base metal electrode to an alloy 22 of the coating and base metals. Since the alloy is homogeneously formed on the surface of the base metal, a coherent bond is secured for the flocculent or porous coating layer superimposed thereon and constant adherence of the coating is secured throughout the operating life of the device. If desired, the coating metal may be applied in the form of a decomposable compound, such as a hydride. The temperature of heat treatment is considerably below the sintering temperature of the coating material and, therefore, the character of the porous coating is unchanged except for the interfacial layer or stratum 22 which is alloyed with the base metal. Furthermore, the iron group metal agent is continually in the vapor phase so that it does not combine with the coating or base metal and consequently no low melting point metals are included in the constitutents of the electrodes. The alloy bonding of the coating has a particular advantage in high voltage rectifiers in which operating voltages of 10,000 volts or more create electric fields which attract particles of the coating material away from the anode unless sufficiently bonded to the base metal of the electrode.

An illustrative example of the procedure of heat treatment is as follows: After the electrode, for instance a molybdenum electrode for a power tube of 50 watt capacity having an area of 100 square centimeters, is coated with the porous zirconium layer in an amunt approximately 4 milligrams per square centimeter or 400 milligrams total coating, the electrode is placed in a closed receptacle, such as a glass bottle, having a tubulation sealed to an evacuating pump system. A

molybdenum cylindrical container or boat surrounds the electrode as a heating chamber or oven and a small piece of sheet metal, for example nickel, approximately 2 milligrams weight, is welded to the inner surface of the boat. The bottle is evacuated by the pumps to a low pressure, of the order of 1×10^{-6} millimeters of mercury, to secure a high vacuum in the system. The molybdenum container is heated by high frequency induction by surrounding the bottle in the vicinity of the boat with an external high frequency coil supplied with high voltage current to inductively heat the container to a temperature sufficient to radiate heat to the coated electrode so that the temperature of the electrode is raised to 1100° C. to 1300° C., these temperatures being below the sintering temperature 1500° C., of the zirconium coating. The temperature of the electrode may be observed by the use of an optical pyrometer.

During the heating cycle the nickel, attached to the inner surface of the container, will be completely converted to the vapor phase under the low pressures within the bottle and necessarily increases the pressure within the bottle slightly to 1×10^{-3} to 2×10^{-5} millimeters of mercury depending on the temperature. In the nickel vapor atmosphere at a temperature of 1300° C., and a pressure of 1×10^{-3}, the interfacial film of zirconium at the surface of the molybdenum electrode is alloyed therewith to form a bonding linkage between the base metal and the outer porous coating. The nickel is continually in the vapor phase so that it does not combine with the interfacial alloy and, therefore, does not introduce low melting point metal in the alloy. The nickel vapor acts in the nature of a catalyst in promoting alloyage between molybdenum and zirconium at temperatures below the sintering temperature of zirconium and molybdenum. After a period of five to seven minutes at the above temperature and pressure the desired interfacial alloy is formed and the nickel vapor condenses on the cooler portions of the glass bottle. The nickel may be vaporized at a lower temperature of 1100° C. at which point the vapor pressure of the nickel vapor is 2×10^{-5} millimeters of mercury, and heating for the same period of five minutes. Of course, any desired degree of alloyage of the interface material may be accomplished by varying the pressure, amount of nickel or the time of treatment during the heating process. Furthermore, the iron group vapor treating method achieves complete bonding of the porous coating to the base metal electrode at temperatures 200 to 400° C. below the sintering temperature of the coating material so that the porous surface of the matrix is unimpaired during this heat treating method.

An alternative method may be practiced, in accordance with this invention, which secures the same results wherein the iron group metal agent is incorporated in the coating metal or compound as a powdered material mixed with the coating metal and binder. The amount of the powdered metal agent incorporated in the coating material is substantially the same as used in the example heretofore described, being about ½ per cent by volume of the coating material, i. e., 2 milligrams for the case of the specific tube heretofore noted, and the degree of alloyage at the interface being secured by determination of the amount of the iron group metal incorporated in the process, the time of treatment, temperature of the electrode and the pressure extant within the system. During the heating step of the process at the temperatures heretofore mentioned, the binder is vaporized and completely removed from the coating and the iron group metal agent is reduced to the vapor state by diffusion from the coating whereupon alloying of the coating and base is secured at the interface after a short period of heating, approximately five to ten minutes.

During the above-mentioned treatment the iron group metal agent in the vapor state is completely evaporated from the coating and condenses on the cool wall of the treating chamber.

Either of the methods above described may be used in producing coatings of tantalum or titanium. The quantity of iron group metal, the temperature, pressure and time of treatment are of the same order of magnitude as in the specific illustrations given for the forming of the zirconium coating.

While the invention has been disclosed in connection with an output electrode or anode it is, of course, understood that the invention may be applied to other electrodes, such as a grid or control electrode, in which the porous coating is applied thereto for the purpose of inhibiting primary and secondary emission of electrons and to render the electrode relatively cool by heat radiation. Therefore, the invention should be limited only within the scope of the appended claims.

What is claimed is:

1. The method of heat treating an electrode for an electron discharge device which comprises heating an electrode of metal of the group consisting of molybdenum and tungsten having a coating thereon of a metal of the group consisting of titanium and zirconium in vacuum in the presence of a metal of the iron group in the vapor phase, and alloying an interfacial layer of said coating metal with the surface of said electrode.

2. The method of heat treating a refractory metal electrode for an electron discharge device, said electrode being of the group consisting of tungsten and molybdenum and having a porous refractory metal coating thereon of the group consisting of zirconium and titanium, which comprises heating said electrode and coating in a low pressure atmosphere at high temperature, introducing nickel vapor during the heating, and forming an alloy between said coating metal and electrode at the interfacial surface of said electrode at a temperature below the sintering temperature of said coating.

3. The method of heat treating a refractory metal electrode for electron discharge devices having a porous refractory metal coating thereon, said electrode being of the group consisting of tungsten and molybdenum and said coating being of the group consisting of zirconium and titanium which comprises, heating said electrode and coating in a highly evacuated vessel at a temperature between 1100° C. to 1300° C., introducing a vaporized metal of the iron group during the heating period, and alloying said coating metal to the surface of said electrode to form an intermediate bonding film between said electrode and said coating metal.

4. The method of coating an electron discharge device electrode having a highly refractory metal core of the group consisting of molybdenum and tungsten with a heat radiating highly porous metal of the group consisting of zirconium and titanium, which comprises, mixing a viscous binder carrier with said low vapor pressure metal, adding a powdered metal of the iron group, applying the mixture to said metal core, and heat-

; said electrode and coating in a low pressure vironment to remove the binder carrier and porize said powdered metal whereby a portion said porous metal lying on the interfacial sur-ce of said core is converted to an alloy film for nding the porous metal to said core.

5. The method of coating an electron discharge vice electrode having a highly refractory metal re of the group consisting of molybdenum and ngsten with a heat radiating highly porous etal of the group consisting of zirconium and anium, which comprises, mixing a viscous bind- carrier with said low vapor pressure metal, ding a small amount of a powdered metal of the on group, applying the mixture to said metal re, heating said electrode and coating to a tem-rature of the order of 1300° C. in a high vacu-n of the order of 1 x 10^{-3} millimeters of mer-ry to evaporate the binder carrier and vapor-e said powdered metal, and alloying the con-cting particles of said porous metal in inter-cial relation on said core.

6. An electrode for an electron discharge de-ce comprising a highly refractory core metal, a owdered black body metallic coating thereon aving gas absorbing and heat radiating prop-ties, and an intermediate alloy stratum formed said core metal and said powdered coating etal to form a contiguous base between said core nd said coating.

7. An electrode for an electron discharge de-ce comprising a molybdenum core, a powdered etallic coating thereon having gas-absorbing nd black body properties, and an intermediate lloy stratum formed of said core metal and coat-ng metal.

8. The method of fabricating an electrode for n electron discharge device, the electrode com-rising a core and a coating of a black body ma-erial thereon which comprises coating a core of a efractory metal of the group consisting of mo-ybdenum and tungsten with a porous black body naterial of the group consisting of zirconium and itanium. heating the core with the coating ma-erial thereon in a sealed chamber at low pres-ure at a temperature several hundred degrees elow the sintering temperature of said black ody material, and maintaining in said vessel dur-ng the heating a vapor of the metal included in he group consisting of nickel, cobalt and iron.

9. The method of fabricating an electrode for n electron discharge device, the electrode com-rising a core and a coating of powdered zir-onium, which comprises applying to a core of efractory metal of the group consisting of mo-ybdenum and tungsten, a coating of powdered irconium, placing the core with the coating hereon in a low pressure chamber, producing ickel vapor in said chamber, and heating said ore with the coating thereon in said chamber and in the presence of said nickel vapor to a temperature between 1100° C. to 1300° C. to form an interfacial layer of refractory metal zirconium alloy coherently bonding the zirconium coating to said core.

10. The method of alloying a metal of the group consisting of zirconium and titanium with a metal of the group consisting of tungsten and molybdenum which comprises applying a coating of said first metal to a body of said second metal, positioning the body with the coating thereon in a vacuum of the order of 1 x 10^{-6} millimeters of mercury, producing a vapor of an iron group metal in said vacuum, and heating said body with the coating thereon, in the presence of said vapor, to a temperature of the order of 1000° C. to 1300° C.

11. The method of producing a zirconium coating upon a molybdenum base, which comprises applying a layer of powdered zirconium upon said base, and heating said base with said layer thereon for a period of the order of five minutes at a temperature between about 1100° C. and about 1300° C. and in the presence of nickel vapor at a pressure of between about 1 x 10^{-3} and 2 x 10^{-5} millimeters of mercury.

12. The method of producing a zirconium coating upon a molybdenum base, which comprises applying to said base a layer of a mixture of zirconium and nickel in which the nickel constitutes of the order of ½ per cent by volume of the mixture, and heating the base with said layer thereon in a high vacuum of the order of 1 x 10^{-3} millimeters of mercury and at a temperature between about 1100° C. and about 1300° C. for a period of five to ten minutes.

13. An electrode for an electron discharge device, comprising a refractory metal core, a porous coating thereon of a black body metal easily oxidizable under high temperature conditions in air, and an interfacial binder layer contiguous with said core metal and coating metal, said binder layer being alloyed black body metal.

14. An electrode for an electron discharge device, comprising a molybdenum core, a porous coating of zirconium thereon, and an interfacial layer of an alloy of molybdenum and zirconium between said core and said coating.

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