

May 15, 1951

V. J. DE SANTIS ET AL
ELECTRON DISCHARGE DEVICE ELECTRODE

2,552,535

Filed Jan. 24, 1949

Fig. 1.

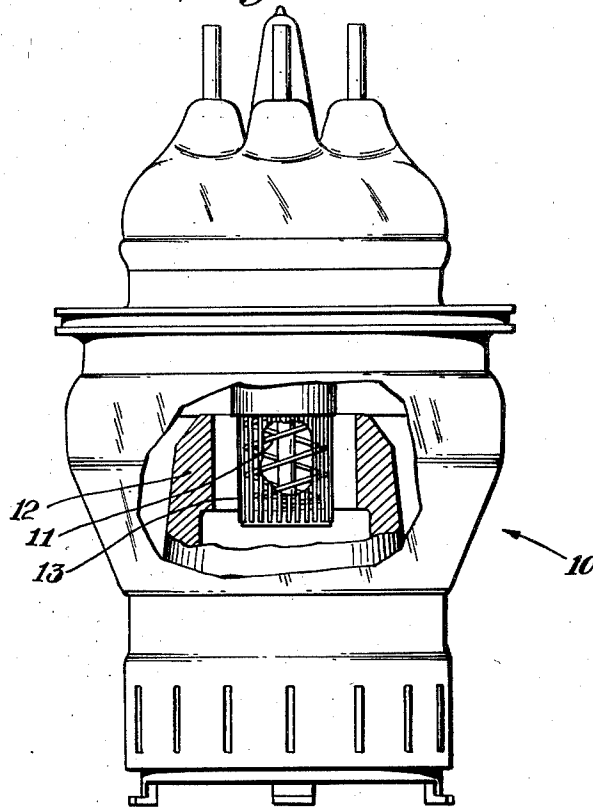
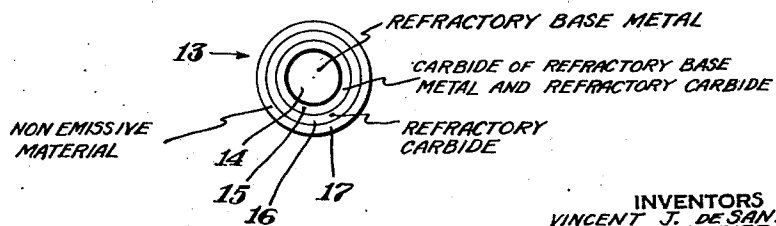


Fig. 2.



INVENTORS
VINCENT J. DE SANTIS
FRED L. HUNTER
BY CHARLES P. MATKZAK
Thomas F. Hayden
ATTORNEY

UNITED STATES PATENT OFFICE

2,552,535

ELECTRON DISCHARGE DEVICE ELECTRODE

Vincent J. De Santis, Chatham, N. J., Fred L. Hunter, Lake Bluff, Ill., and Charles P. Majkrzak, South Orange, N. J., assignors to International Standard Electric Corporation, New York, N. Y., a corporation of Delaware

Application January 24, 1949, Serial No. 72,404

21 Claims. (Cl. 250—27.5)

1

This invention relates generally to electron discharge devices, particularly improved electrodes for such devices and especially electrodes which, under conditions of use are non-emitters of electrons.

In a general sense, every electron discharge device comprises a cathode or source of electrons, an anode or collector to which the electrons move from the cathode, and, in the majority of types, one or more other electrodes so located with relation to the electron stream that the stream may be controlled, for example, by variation of the potential of the electrode relative to the anode or cathode. Hereinafter, for convenience in describing the subject matter of this invention, reference will be made to grid electrodes which function as control electrodes in devices of this type, but it is clearly to be understood that the principles of the invention are applicable to the fabrication of other types of electrodes for use in electron-discharge devices in which the electrode is to be substantially non-emissive. By the term non-emissive as herein employed is meant substantial freedom from primary electron emission such as may be produced by mere heating of the electrode.

It is well recognized that, inasmuch as efficient operation of such devices is dependent upon control of the electron stream, any conditions which introduce a spurious electron stream, such as may be caused by emission from an intended non-emitter, are undesirable. Accordingly, it is of primary importance that the control electrodes and the anode of the device be substantially non-emissive. This desirable condition is achieved only with great difficulty. In many types of electron discharge devices, because of the close spacing required between electrodes where electron transit time is important, the non-emissive electrodes of the device are heated to extremely high temperatures, a condition which greatly favors thermal emission.

The problems presented in the design of electron-discharge devices include those of providing electrodes which, although physically small, are sufficiently rugged to maintain the closely-spaced relationship which will not change under operating conditions.

The high temperatures encountered, especially in high power tubes, soften or melt most metals. The magnitude of this problem is obvious from the fact that, in typical tubes for use at a frequency of about 600 megacycles, the cathode-grid spacing is of the order of .015 inch, for 1000 megacycle operation, about .006 to .007 inch, and

2

even less for tubes to be used at higher frequencies. Inasmuch as the cathodes of high power tubes frequently operate at temperatures of 1000° C. or above, it is clear that the materials, from which the grids for these types of tubes are fabricated, must be extremely resistant to high temperatures.

Another special consideration which introduces a further problem in the design of electron-discharge devices for use at high power and high radio frequencies is the fact that, for high-power output, it clearly is desirable to have the emissivity of the cathode at as high a level as possible and to this end it is customary to provide either in or on the cathode a substantial quantity of highly-emissive material such as thorium. At operating temperatures this highly-emissive material, especially if it is metallic thorium, is vaporized to a substantial degree, migrates from the cathode and condenses upon the grid, with the result that the grid thereby becomes an emitter due to this condensed material. If an attempt is made to destroy the material deposited on the grid by having present on the grid a substance which will render it non-emissive, the danger exists that this material may become transferred to the cathode, thereby destroying its emissivity unless, of course, the substance is non-volatile and thus incapable of such transfer.

Various expedients have been utilized in an effort to solve the above-mentioned problems. For example, the making of grids of carbon, either directly from graphite or by carbonizing preshaped organic materials, has been investigated but the grids so produced were found to be extremely fragile and easily damaged during transportation and under conditions of ordinary use of the tubes in which they were incorporated. Furthermore, very-considerable manufacturing difficulties were presented in fabricating carbon because of its extreme brittleness and because of the problem presented in uniting carbon to the supporting metal standards. Thus, despite the fact that carbon has negligible vapor pressure even at very-high temperatures, it is an excellent heat radiator, is substantially non-emissive, even at very high temperatures, does not poison activated thermionic cathodes, has low radio frequency resistance and is capable of destroying the emissivity of thorium which might migrate from the cathode to the grid, despite these many and important advantages, carbon has been found unsatisfactory on a purely-practical basis as a material for use in making grids.

Refractory metals have also been investigated

as materials for grids and, of these metals, tungsten (m. p. 3370° C.), the platinum series of elements including platinum (m. p. 1755° C.), iridium (m. p. 2350° C.), palladium (m. p. 1555° C.), rhodium (m. p. 1995° C.), and osmium (m. p. 2700° C.), tantalum (m. p. 2770° C.), molybdenum (m. p. 2620° C.), columbium (m. p. 1950° C.), and members of the iron group, particularly nickel (m. p. 1452° C.), cobalt (m. p. 1480° C.), and iron itself (m. p. 1535° C.) have received the most attention from investigators. It was found that for the purposes of making grids tungsten was much too tough and springy; tantalum and columbium were too emissive because of their tenacious powers of gas absorption; the platinum metals were prohibitively expensive and became soft when heated to even ordinary operating temperatures; the metals of the iron group, being of relatively low melting points, softened even at ordinary operating temperatures; and all of these metals, in addition to having appreciable inherent thermionic emissivity, particularly molybdenum, were found to be excellent bases upon which the highly-emissive material, distilled from the cathodes, could condense and thus make the grid structures themselves emissive.

The possibility of applying a non-emissive material as a coating to refractory metal bases which would render the base metal non-emissive under operating conditions has also been investigated. Because of the obviously desirable properties of carbon, it was early considered that carbon, per se, might be applied to a base of refractory metal so that the composite structure would have the desirable non-emissivity and other electrical properties of carbon, together with the ruggedness and ease of fabrication characteristic of metal electrodes. For example, an attempt was made to fabricate non-emissive grids using a base of nickel, or the like, bearing a coating of carbon, but it was found that the nickel was inherently incapable of resisting high temperatures due to its low melting point, thus the composite grids were unsatisfactory.

It was then considered that the use of tantalum, columbium, tungsten, zirconium, or molybdenum as the base metal with a carbon or platinum coating would be satisfactory, but then it was found that grids of this type, although initially non-emissive and rugged, soon lost their non-emissivity and ruggedness due to migration of carbon into the interior portions of the metal base with resultant embrittlement of the base metal and/or exposure of uncoated base metal surface upon which highly-emissive material from the cathode could deposit with the disadvantages attendant on this event as above mentioned.

It was then proposed to apply a metallic barrier layer, by electrodeposition or spraying, on the molybdenum or tungsten base before the carbon coating, which would prevent migration of carbon and embrittlement of the base. For this purpose, a metal of the iron group, particularly nickel, cobalt or iron, was applied to the tungsten or molybdenum base, then the applied metal was successively oxidized and reduced, the last in a carbonaceous atmosphere, to produce the carbon-coated finished article. This type of grid structure was found unsatisfactory because it soon became emissive at high operating temperatures, due perhaps to thermal decomposition and migration of the barrier layer into the interior parts of the base metal, followed by a similar migration of the carbonaceous outer layer, thus re-

sulting in eventual breakdown of the grid structure by progressive embrittlement after a comparatively limited useful life.

In view of these discouraging results obtained with refractory metal bases bearing carbonaceous coatings, investigators in this field turned to electrode structures coated with non-emissive refractory oxides, particularly the oxides, singly or mixed, of tantalum, tungsten, columbium, vanadium, chromium, molybdenum, titanium and beryllium. For many purposes, particularly in tubes of medium power rating, this type of coated grid has been found quite satisfactory for not only is the surface coating of low, though appreciable, emissivity, but thorium or other highly emissive material deposited upon the coating loses its emissivity. The disadvantages of this type of coated grid are, primarily, that the coating is not strongly adherent to the base metal and, as it differs in its coefficient of thermal expansion from that of the base metal, it tends to loosen from its base or crack as a result of temperature changes of the coated electrodes, thus the fragility of the electrode and likelihood of damaging the continuity of the coating are materially increased after substantial use of the tube in which it is incorporated. It is, of course, obvious that, if the continuity of the coating upon which non-emissivity depends is interrupted, the base metal will be exposed and thus the emissivity of that base metal surface will become a factor limiting the tube efficiency. Further disadvantage of this type of coated grid is that very high temperatures result in more or less decomposition of the oxide coating with inevitable increase in the gas content of the tube which, of course, is undesirable and with increase in the emissivity of the coating. For these reasons oxide-coated grids, though satisfactory for use in low or medium power tubes, are unsuited for use in tubes of high power rating to be operated at abnormally high temperatures, e. g. above 1000° C.

As a result of this experience investigators, seeking improved properties, have modified the simple oxide coating above-mentioned by incorporating in it a substantial amount of substantially non-emissive metal capable of integrating the film and making a permanently-adherent bond between the coating and the base metal. One such procedure according to the prior art involves initially producing a mixed oxide coating as a superficial layer upon the base metal and thereafter partially reducing the mixed oxide layer in situ so that the resultant coating comprises a mixture of unreduced oxide with the most easily reduced metal moiety in the mixture. Refractory metal carbides have also been used, mixed with refractory metal, as non-emissive coatings for electrodes. However, these modified types of coating in addition to being temperature limited and deleteriously affecting the cathode, have not been found altogether satisfactory for the further reason that, the emissivity of even relatively non-emissive metals after contamination with highly emissive material, is quite substantial at the operating temperatures encountered in tubes of high power rating. Thus, a solution to the problem of providing a satisfactory non-emissive grid for tubes of this type, which can be used at such temperatures while retaining its non-emissivity throughout its useful life, has still been sought. The principal object of the present invention is to provide a solution to this problem.

In accordance with the present invention, a permanently non-emissive, rugged electrode is provided having the desirable characteristics of the refractory metal electrode and of carbon electrodes, but free of the disadvantages above mentioned which heretofore have precluded use of either of these types of electrodes in commercial practice. Regarded in certain of its broader aspects, the novel electrode according to this invention comprises a refractory metal base, bearing a coating of high-temperature-resistant, non-emissive material that normally deleteriously affects said refractory metal by migrating at elevated temperatures into said refractory metal, and a barrier layer between said coating and the base metal that prevents said migration, said barrier layer comprising refractory carbides. Viewed in another aspect, this novel electrode structure comprises a base of refractory metal, such as a metal or mixture of metals of the group consisting of molybdenum, tantalum, columbium and tungsten bearing a layer predominantly comprised of the carbide or carbides of said metal or metals mixed or alloyed with a refractory carbide of the class consisting of zirconium carbide, titanium carbide and silicon carbide, said layer being adherent and formed in situ upon the metal base, an overlying layer comprised of said refractory carbide likewise formed in situ, and an outside layer predominantly comprised of a non-emissive, high-temperature-resistant material such as carbon or platinum. The invention also embraces an electron discharge tube including a non-emissive electrode of this type and processes for making the same.

In accordance with the process of this invention, this novel electrode structure is produced by selecting a base of refractory metal, applying thereto a coating of oxide of zirconium, of titanium or of silicon, by spraying, dipping, electrophoresis or any other suitable method for applying such a coating, drying the oxide coating and heating it so that it is sintered into a porous layer partially dissolved into and adhering to the base metal, applying a coating of carbon onto said sintered layer in quantity such that there is more than the stoichiometric amount of carbon present to effect conversion of the oxide in the oxide layer to the corresponding carbide, heating the coated article under reduced pressure at a temperature of at least 1700° C. whereby the oxide is converted to the corresponding refractory carbide and, at the interface of the carbide layer and the base metal, some of the excess carbon combines with the base metal to produce a thin layer of the carbide of the base metal mixed or alloyed with the refractory carbide, underlying the layer of refractory carbide, and then applying an outermost layer of high-temperature-resistant, non-emissive material, such as carbon or platinum, by any convenient or desirable coating technique.

In order to facilitate a better understanding of the matter of this invention and of how the invention may be practiced most advantageously, a specific embodiment thereof will hereinafter be described in which reference is made to the accompanying drawings wherein:

Fig. 1 is a side elevational view of a typical electron-discharge device including a grid element pursuant to this invention, parts of the tube envelope, anode and grid being broken away for clearness of illustration of underlying parts; and;

Fig. 2 is a transverse enlarged sectional view of

one of the grid wires of the tube in Fig. 1 illustrating the relationship of the several coatings on the non-emissive grid embodying the principles of this invention.

Referring now to the drawings and particularly Fig. 1 thereof, it will be noticed that the vacuum tube generally indicated by the reference numeral 10, comprises a cathode 11, an anode 12, and a grid 13 interposed between the anode and the cathode. The cathode is activated in the usual manner by having coated thereon or incorporated therein a highly emissive material such as thorium. The grid of this tube is provided with multiple coatings as are illustrated in detail in Fig. 2 in which the numeral 14 designated the base metal wire, preferably tantalum, bearing a first layer 15 of the carbide of the base metal, mixed or alloyed with refractory carbide, a second layer 16 of refractory carbide and an outermost layer 17 of non-emissive material such as carbon or platinum. The manner in which the successive layers are produced in situ upon the base metal wires will now be described.

In practicing this invention, the refractory oxide coating can be applied by any conventional method utilized for producing coatings of divided material such as a refractory oxide, upon a metal surface. For example, the coating may be applied by dipping or spraying a mixture of the refractory oxide with an organic or inorganic binder upon the metal surface and for this purpose a binder containing ethyl silicate may be used quite satisfactorily. Alternatively, an organic solution of pyroxylin may be used as a vehicle for application of the oxide and to provide a residue of organic matter after evaporation of the solvent which will serve to hold the particles of oxide as an integral layer on the metal until the oxide is sintered. It will, of course, be obvious that the binder must be so chosen that it will not be itself emissive nor render the refractory oxide or carbide layer emissive during subsequent use.

Although these above-mentioned methods of coating are satisfactory, it is preferred to produce the refractory oxide coating by electrophoresis of a bath containing finely divided particles of the oxide because of the uniformity, purity and easy reproducibility of the coating so obtained. A suitable procedure for so depositing an oxide film using zirconium oxide for example is as follows: about .5 gram of magnesium nitrate, about .5 gram of zirconium nitrate and about 1.5 grams of tannic acid are dissolved in approximately 25 c. c. of distilled water. This solution is then added, portionwise with agitation, to about 20 grams of divided zirconium oxide to produce a paste which then is added slowly with agitation to about 475 c. c. of methanol. This mixture is ball-milled for about 24 hours using flint pebbles in the grind. The article to be coated is cleaned by vacuum firing, for example at 1500° C. for two minutes, and then is immersed in the zirconium oxide suspensoid prepared as above described and one or more aluminum electrodes are arranged in relationship to the tantalum article so that a uniform potential gradient during the electrophoresis may be obtained. The aluminum electrodes are connected to the positive output terminal of a D. C. potential source and the article to be coated is connected to the negative terminal of that potential source. Using a current density of about 15 ma/cm² for a period sufficient to produce a coating of the desired thickness. After the period mentioned, the potential source

is disconnected, the coated tantalum electrode is withdrawn from the bath and is immediately immersed in acetone. It is slowly withdrawn from the acetone, excess acetone is shaken off, the article is allowed to dry in air and then the coating procedure is repeated twice so that, after drying, the zirconium oxide layer on the tantalum base is about .002 inch thick. The coated article then is fired at a temperature sufficient to cause sintering and partial solution of the zirconium oxide particles, into the surface of the tantalum electrode say a temperature of about 1500° C. to about 1700° C. and at a pressure of about 10⁻⁵ mm. of mercury. It of course will be understood that silica or titanium dioxide may be substituted for the zirconium oxide in the foregoing process if desired.

The coating of carbon, like the zirconium oxide coating, may be applied by dipping, spraying or by electrophoresis, the last mentioned method being preferred. This preferred method for applying the carbon coating is substantially as follows: to about 185 volumes of tetraethylorthosilicate, 60 volumes of Synasol are added. Synasol is a trade name designating a mixture of about 100 parts denatured ethanol, 5 parts ethyl acetate and 1 part aviation gasoline (or methyl isobutyl ketone). Approximately 5 volumes of .3% aqueous hydrochloric acid are added with stirring to the ethyl silicate-Synasol mixture which is then allowed to stand for a period of at least 12 hours after which 7 volumes of distilled water per hundred volumes of original solution are added with agitation, followed by shaking, until the solution is apparently substantially homogeneous. This hydrolyzed ethyl-silicate suspensoid may be stored for at least one month without substantial change in its viscosity or deposition of silica. The available silica content of the solution is approximately 20.5%, based on weight.

A bath is prepared by dissolving about 3 grams of tannic acid and about .7 gram of magnesium nitrate in approximately 100 c. c. of Synasol and then adding about 40 grams of micronized graphite to this solution to produce a paste which is added slowly and with stirring to about 465 c. c. of the hydrolyzed ethyl-silicate suspensoid prepared as above described. This mixture is then ball-milled for about 24 hours using flint pebbles in the grind. After ball-milling, the graphite suspensoid bath is placed in a suitable container and the zirconium oxide coated tantalum electrode, together with graphite electrodes, are immersed in the bath. It is to be understood that the graphite electrodes are disposed relative to the zirconium oxide coated electrode so that a substantially uniform potential gradient may be maintained around the zirconium oxide-coated electrode. The graphite electrodes are then connected to the positive terminal of a direct-current potential source and the zirconium oxide coated electrode is connected to the negative terminal of that source. There is then applied a potential of 25 to 120 volts, preferably about 70 volts at a current density of about 10 milliamperes per square centimeter for about 5 seconds after which the potential source is disconnected from the electrodes, the tantalum electrode is removed, excess solution is shaken off, it is then dipped in Synasol, slowly withdrawn at a uniform rate and dried in air, after which the coating procedure is repeated until a coating of the desired thickness is obtained. The coated article then is baked for 15 minutes at about 110° C. followed by vacuum firing at

about 2000° C., the degree of vacuum used being preferably at least 10⁻⁵ mm. of mercury.

As a result of the foregoing processing, there is produced upon the base metal a layer of zirconium carbide mixed with the base-metal carbide, and a surface layer of zirconium carbide upon the mixed carbide layer. The preparation of the electrode according to this invention is then completed by applying a final refractory coating of carbon, platinum or a refractory metal of the platinum group of elements.

The platinum coating can be produced by the following procedure which, although constituting the preferred process of this invention, is merely illustrative of how this final coating may be applied. The coated article is dipped in a solution comprising an organic platinum compound or chloroplatinic acid, withdrawn from the solution and heated, say at about 375° C. for 5 minutes or so, to cause decomposition of the platinum compound and deposition of metallic platinum. This procedure is then repeated at least 10 times to provide a coating of platinum having the desired thickness, after which further coating of platinum may be applied by plating in a conventional platinum plating bath using a potential of 4 volts for about 45 minutes and thereafter a potential of about 1.5 volts for one hour. It will be understood that the foregoing procedure may be suitably modified to produce coatings of other metals of the platinum group as will be obvious to those versed in this art. The article then is fired at a temperature of about 1500° C. and at a pressure of about 10⁻⁵ mm. of mercury. When this is done, the electrode is ready for use.

If the final coating upon the non-emissive electrode according to this invention is to be carbon, the coating is applied by repeating the above-described procedure for producing the initial carbon coating upon the oxide layer.

The remarkable improvement in non-emissive electrodes according to this invention over types of non-emissive electrodes previously used is obvious from the following data: using electrodes of identical physical dimensions, each having a surface area of about 10 square centimeters and operating them under a load of 9 watts per square centimeter at a temperature of 1300 to 1400° C., a platinum-clad molybdenum electrode became emissive to the extent of 4.5 milliamperes after exhaust and a tantalum electrode became emissive to the extent of 6.2 milliamperes after 300 hours of operation, whereas a non-emissive electrode embodying the principles of this invention emitted to the extent of .0001 milliampere after more than 4,000 hours of operation.

While the principles of the invention have been described above in connection with specific apparatus, it is to be clearly understood that this description is made only by way of example and not as a limitation to the scope of the invention.

We claim:

1. An electron discharge device electrode that comprises a base of refractory metal chosen from the group consisting of tantalum, columbium, molybdenum and tungsten, bearing a refractory non-emissive coating and a barrier layer between said coating and the base that prevents migration of said coating into the base at elevated temperatures, said barrier layer comprising the base metal carbide and a carbide chosen from the class consisting of silicon carbide, titanium carbide and zirconium carbide.

2. An electron discharge device electrode as de-

finished in claim 1, characterized in that the base is tantalum.

3. An electron discharge device electrode as defined in claim 1, characterized in that the base is molybdenum.

4. An electron discharge device electrode as defined in claim 1, characterized in that the base is tungsten.

5. An electron discharge device as defined in claim 1, characterized in that the refractory non-emissive material is carbon.

6. An electron discharge device as defined in claim 1, characterized in that the refractory non-emissive material is chosen from the metals of the platinum group.

7. An electron discharge device electrode as defined in claim 1, characterized in that the base is columbium.

8. Process for the manufacture of an electrode for an electron-discharge device that comprises selecting a base of a refractory metal, applying thereto a coating of an oxide chosen from the class consisting of silicon oxide, titanium oxide and zirconium oxide, sintering said coating, applying a coating of carbon on to the oxide coating, firing the coated article at a temperature of at least 1700° C. under reduced pressure whereby the oxide is changed to the corresponding carbide, and then applying a coating of refractory, non-emissive material onto said carbide coating.

9. The process as defined in claim 8, characterized in that the refractory non-emissive material is carbon.

10. The process as defined in claim 8, characterized in that the refractory non-emissive material is chosen from the metals of the platinum group.

11. The process as defined in claim 8 further characterized in that the base is tantalum and the refractory non-emissive material is platinum.

12. The process as defined in claim 8 further characterized in that the base is molybdenum and the refractory non-emissive material is platinum.

13. The process as defined in claim 8 further characterized in that the base is tungsten and the refractory non-emissive material is platinum.

14. The process as defined in claim 8 further characterized in that the base is molybdenum and the refractory non-emissive material is carbon.

15. The process as defined in claim 8 further characterized in that the base is tungsten and the refractory non-emissive material is carbon.

16. Process for the manufacture of an electrode for an electron discharge device that comprises applying a coating of zirconium oxide on a base of tantalum, heating said coating to cause sintering and partial solution of the oxide into the surface of the base, applying a coating of carbon

on to the oxide coating sufficient in amount to exceed the stoichiometric amount of carbon for reducing the oxide and converting it to zirconium carbide, firing the coated article at a temperature of at least 2,000° C. under reduced pressure whereby the oxide is changed to the corresponding carbide and then applying a coating of platinum on to the carbide coating.

17. Process for the manufacture of an electrode for an electron discharge device that comprises applying a coating of zirconium oxide on a base of tantalum, heating said coating to cause sintering and partial solution of the oxide into the surface of the base, applying a coating of carbon onto the oxide coating sufficient in amount to exceed the stoichiometric amount of carbon for reducing the oxide and converting it to zirconium carbide, firing the coated article at a temperature of at least 2,000° C. under reduced pressure whereby the oxide is changed to the corresponding carbide and then applying a coating of carbon on to the carbide coating.

18. In an electrode having a base of refractory metal and a refractory non-emissive coating; characterized in that a barrier layer is interposed between said base metal and said coating which comprises a carbide of a metal chosen from the group consisting of tantalum, columbium, molybdenum and tungsten and a carbide chosen from the class consisting of silicon carbide, titanium carbide and zirconium carbide.

19. In an electrode according to claim 18, characterized in that the refractory base metal is chosen from the group consisting of tantalum, columbium, molybdenum and tungsten.

20. In an electrode according to claim 18, characterized in that the refractory non-emissive coating is carbon.

21. In an electrode according to claim 18, characterized in that the refractory non-emissive coating is chosen from the metals of the platinum group.

VINCENT J. DE SANTIS.

FRED L. HUNTER.

CHARLES P. MAJKRZAK.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,180,614	Simpson	Apr. 26, 1916
1,862,138	Else	June 7, 1932
2,051,828	Dester	Aug. 25, 1936
2,226,720	Hansell	Dec. 31, 1940
2,232,083	Strohfeldt	Feb. 18, 1941
2,263,164	Dailey	Nov. 18, 1941
2,417,461	Becker	Mar. 18, 1947