Oct. 31, 1950

M. ARDITI ET AL

NONEMISSIVE ELECTRODE FOR USE
IN ELECTRON DISCHARGE DEVICES

Filed Aug. 19, 1947

2,527,514

Fig. 1.

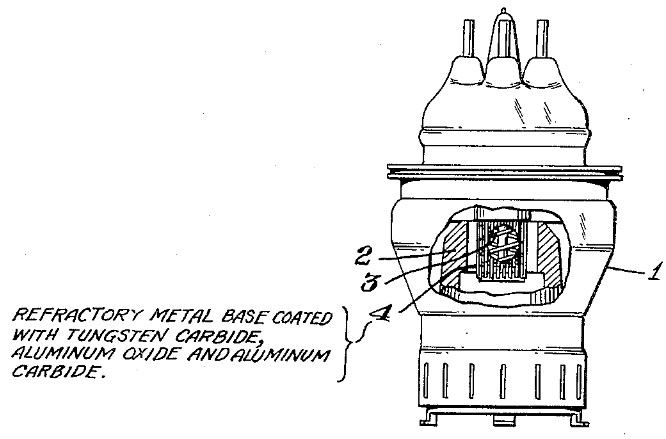
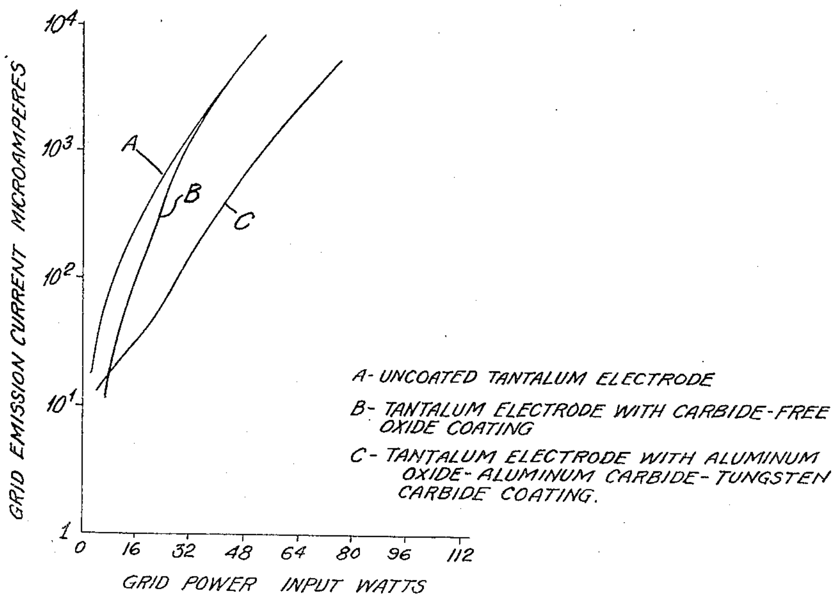


Fig. 2.



INVENTORS
MAURICE ARDITI
VINCENT J. DESANTIS

BY Thomas G. Heyden

ATTORNEY

Patented Oct. 31, 1950 2,527,514

UNITED STATES PATENT OFFICE

2,527,514

NONEMISSIVE ELECTRODE FOR USE IN ELECTRON DISCHARGE DEVICES

Maurice Arditi, New York, N. Y., and Vincent J. De Santis, Chatham, N. J., assignors to International Standard Electric Corporation, New York, N. Y., a corporation of Delaware

Application August 19, 1947, Serial No. 769,330

11 Claims. (Cl. 250—177)

1

This invention relates to improvements in electron tubes, particularly in electrodes suitable for use in electron discharge devices, and especially is concerned with an improved type of electrode characterized by low primary and secondary electron emission.

In electron discharge devices a stream of electrons passes from the cathode or emitter electrode to the anode or receiver electrode, and characteristics of the stream are effected or controlled by one or more grid electrodes interposed in the stream or placed adjacent thereto. The grid electrodes usually are biased at potential levels above the cathode but below the anode potentials with the result that inevitably during the course of operation of the device certain electrons from the electron stream bombard and are retained by the grid electrodes. When thus bombarded many types of grid electrodes emit electrons, the ratio between the number of electrons bombarding the surface and the number of electrons emitted being determinative of the coefficient of secondary emission of the substance from which the surface is formed. Inasmuch as secondary emission is generally an undesirable phenomenon in the operation of an electron discharge device, various expedients have been utilized from time to time in an effort to minimize this secondary emission.

Present day electronic research has resulted in the development of devices functioning at ever increasingly high frequencies ranging upward into thousands of megacycles per second. In electron discharge devices used at these high frequencies the electrodes are exceedingly minute and inter-electrode spaces are very small. Inasmuch as the primary or thermionic electron emissivity of metallic surfaces is enhanced by increase in the temperature of the surfaces, it is obvious that the control of the primary and secondary emission of electrodes in electron discharge devices operated at high frequencies presents unique design problems because the grid electrodes are disposed in such close proximity to the cathode electrodes that they are thereby heated resulting normally in primary emission and the bombardment by electrons from the cathode additionally causes high secondary emission at the grid electrodes unless extraordinary measures are taken to prevent the same.

While the object of the present invention, viewed in its broader aspects is to provide an electron discharge device including means for controlling and inhibiting both primary and secondary emission from the electrodes of the de-

2

vice, the principles of the invention are particularly applicable to the control of primary emission in electron discharge devices of the type used in generating high-power very-high-frequency radiation.

Another object of the present invention is to provide an electrode structure which is characterized by substantially no primary or secondary emission even when operated at very high temperatures.

The further object of the present invention is to provide an electrode structure which can be utilized in controlling an electron stream emanating from a thoriated tungsten emitter without either primary or secondary emission from the control electrode and which does not develop undesirable primary or secondary emissive properties, not even as a result of deposit thereof of thorium from the emitter.

In the accompanying drawings Fig. 1 is an illustration of an electron discharge device including a non-emissive electrode in accordance with the present invention; and

Fig. 2 is a graphic illustration of certain electrical characteristics of electrodes according to this invention contrasted with other types of electrodes.

Regarding certain of its broader aspects, the novel non-emissive electrode structure according to this invention comprises a refractory metal base element carrying a tenaciously adherent continuous coating that comprises an essentially homogenous mixture of tungsten carbide, aluminum oxide and aluminum carbide. When operated in conjunction with a thoriated tungsten cathode and at temperatures within the range of 1000° C. to 1200° C., this electrode is substantially free of secondary emission thus making it ideally suited for use in moderately high-power high-frequency electron discharge devices.

Viewed in a more particular sense, the electrode according to this invention comprises a base element, preferably formed from tantalum, columbium, tungsten or, less desirably, from molybdenum, provided with a substantially continuous coating consisting of tungsten carbide in the proportion of 40% to 60% based on total weight of the mixture, the remainder being a mixture of aluminum oxide and aluminum carbide. The coating is composed of these substances homogenously mixed and in finely divided state with particles having a size of about 4 microns or less, and the coating being approximately 12 microns thick. It has been found by experience that coatings produced by using particles exceeding about 4 microns in size are not wholly satisfactory for the purposes of this invention because such coatings are usually porous and in some instances discontinuous.

A novel non-emitting electrode embodying the principles of this invention can be produced by forming an essentially homogenous suspension of tungsten carbide, aluminum carbide and aluminum oxide, in the proportions and the particle size above mentioned, in an organic or inorganic binding agent of the type commonly used in the manufacture of coated electrodes, applying this suspension to a refractory metal electrode element and consolidating the coating upon the element by drying either at atmospheric or elevated temperatures, the latter being preferable. Pyroxylin solution is an example of the type of organic binder which can be used in the practice of this invention and when this binding agent is used, the coated electrode is fired in vacuo at a temperature of about 800° C. or higher. Silicate binders are examples of the type of inorganic binding agent that can be used satisfactorily in practicing this invention and of these binders the alkyl silicates e. g. tetraethylorthosilicate, are particularly preferred. When silicate binders are used the coated electrodes are fired at temperatures in the vicinity of 1000° C. for about 4 to 5 minutes.

In Fig. 1 of the drawings there is illustrated an electron discharge device that comprises a gas tight envelope 1 within which are mounted an anode 2 and cathode 3 between which is interposed a control electrode 4 bearing a non-emissive coating in accordance with the present invention. The properties of this control electrode are graphically represented in Fig. 2 of the drawings wherein certain electrical characteristics of electrodes according to this invention are depicted in contrast with corresponding properties of other electrodes not according to this invention. It will be noted that in this graph grid emission is plotted against grid input power, and the temperature of operation of the grid is proportional to the electrical energy or power dissipated in that electrode. The curve A reflects data obtained by testing an uncoated electrode formed from tantalum. Curve B relates data obtained by testing a typical so-called "non-emissive" electrode according to the prior art. In this instance the electrode consisted of tantalum bearing a coating of metallic oxides free from metallic carbides. Curve C depicts correlated data obtained by testing an electrode embodying the principles of this invention, namely, a tantalum electrode bearing an adherent continuous coating comprising tungsten carbide and a mixture of aluminum oxide and aluminum carbide. It is to be understood that these data are based on tests conducted subsequent to the usual ageing of the electrodes by operation for a short period under the conditions of intended use.

In order to facilitate a better understanding of the matter of the present invention and how the same may be practiced, certain specific examples herewith follow, which, it is to be understood, are provided by way of illustration and not by way of limitation of the invention.

Example one

About 17 grams of aluminum oxide, about 17 grams of aluminum carbide and about 17 grams of tungsten carbide are ground in a ball mill until a homogenous mixture having an average particle size of 4 microns or less is obtained. A solution of 25 cc. tetraethylorthosilicate is formed in about 15 cc. of alcohol (denatured alcohol may be used satisfactorily for this purpose) and about 0.5 cc. of $\frac{3}{10}$% hydrochloric acid aqueous solution is added to the mixture to produce the binding agent. A homogenous mixture is formed of about 60 cc. of this binding agent and about 5 grams of the mixed aluminum oxide, aluminum carbide, tungsten carbide powder to be used as a coating composition. A grid electrode element is formed of tantalum and the above described coating composition is applied to this element by spraying, dipping or other operations conventional in the art of applying coating compositions to articles. After coating the coated electrode is fired in vacuo at about 1000° C. for approximately 4 to 5 minutes. Under these conditions volatile components of the coating composition are volatilized and a tenaciously adherent coating of the consolidated aluminum oxide-carbide tungsten carbide mixture is produced upon the electrode element. This electrode exhibits substantially no emission when operated at a temperature in the range of 1000° C. to 1200° C. and this characteristic of non-emissivity remains essentially unaltered over a substantial period of time even when the electrode is used in conjunction with a thoriated tungsten cathode.

Example two

The operations described in Example 1 are repeated except that 40 parts by weight of a mixture of equal parts aluminum oxide and aluminum carbide are milled with 60 parts by weight of tungsten carbide. The coated electrode so produced possesses substantially some electrical characteristics as the electrode obtained in accordance with Example 1.

Example three

The operations described in Example 1 are repeated with the modification that about 40 parts by weight of tungsten carbide are mixed with about 60 parts by weight of a mixture of equal parts aluminum oxide and aluminum carbide, instead of mixing these substances in the proportions in Example 1. The electrode so produced has electrical properties comparable to those of the electrodes produced as described in Example 1.

Example four

The operations described in Example 1 are repeated except that instead of the binder therein described the following binding composition is used:

	cc.
Pyroxylin solution	30
Amylacetate	200

The mixture of pulverized aluminum oxide, aluminum carbide and tungsten carbide are homogenously incorporated in this binder in substantially the manner described in Example 1 in conjunction with the silicate binder, and the coating composition so obtained is applied to a refractory metal base element as described in Example 1. The coated electrode so produced possesses electrical properties similar to those of the electrode obtained as described in Example 1. In like manner the operations according to Examples 2 and 3 can be repeated using the pyroxyline binder instead of the silicate binder and produce electrodes having electrical properties similar to those obtained according to Examples 2 and 3.

The coated electrodes produced in accordance with the principles of this invention can be incorporated in any desired type of electron discharge device. It will be found that during operation of the device under conditions such that the coated electrode is at a temperature in the range of 1000° C. to 1200° C. the coated electrode is substantially free of primary and secondary electron emission. It will be understood that although this invention has been described with particular reference to the fabrication of grid electrodes, these principles are equally applicable to the manufacture of other types of electrodes which are desired to be free of primary and secondary electron emission.

In the following claims the terms "non-emissive electrode" mean an electrode that is substantially free of primary and secondary electron emission when operated at a temperature within the range of 1000° C. to 1200° C. subsequent to ageing by operation for a brief period of time under conditions of intended use. This substantial absence of secondary emission which is characteristic of electrodes according to this invention is observed with grid electrodes at potentials of 20 volts or even higher voltages.

What is claimed is:

1. A non-emissive electrode for use in an electron discharge device that comprises a refractory metal element carrying an adherent coating comprising tungsten carbide and a mixture of aluminum oxide and aluminum carbide.

2. An electrode as defined in claim 1 wherein the tungsten carbide constitutes 40% to 60% of the coating based on weight.

3. A non-emissive electrode for use in an electron discharge device that comprises a refractory metal element carrying an adherent coating comprising the following substances in the proportions by weight indicated:

Tungsten carbide	⅓
Aluminum oxide and aluminum carbide	⅔

4. A non-emissive electrode for use in an electron discharge device that comprises a refractory metal element carrying an adherent coating comprising the following substances in the proportions by weight indicated:

Tungsten carbide	⅓
Aluminum oxide	⅓
Aluminum carbide	⅓

5. A non-emissive electrode for use in an electron discharge device that comprises a base element formed from a metal selected from the class consisting of tantalum, columbium, tungsten and molybdenum, carrying an adherent coating comprising tungsten carbide and a mixture of aluminum oxide and aluminum carbide.

6. An electrode as defined in claim 5 wherein the tungsten carbide constitutes 40% to 60% of the coating based on weight.

7. A non-emissive electrode for use in an electron discharge device that comprises a tantalum base element carrying an adherent coating comprising tungsten carbide and mixture of aluminum oxide and aluminum carbide.

8. An electrode as defined in claim 7 wherein the coating comprises the following substances in the proportions by weight indicated:

Tungsten carbide	⅓
Aluminum oxide	⅓
Aluminum carbide	⅓

9. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide, aluminum oxide and aluminum carbide.

10. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide, aluminum oxide and aluminum carbide, the tungsten carbide being present in said composition in the proportion of forty per cent to sixty per cent based on total weight.

11. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide, aluminum oxide and aluminum carbide, said substances being present in the coating in substantially equal proportions based on weight.

MAURICE ARDITI.
VINCENT J. DE SANTIS.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,722,121	Wilson	July 23, 1929
2,035,003	Thompson	Mar. 24, 1936
2,232,083	Strohfeldt	Feb. 18, 1941
2,417,461	Becker	Mar. 18, 1947