

Dec. 1, 1964

D. MacNAIR
THERMIONIC CATHODE

3,159,461

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3 Sheets-Sheet 1

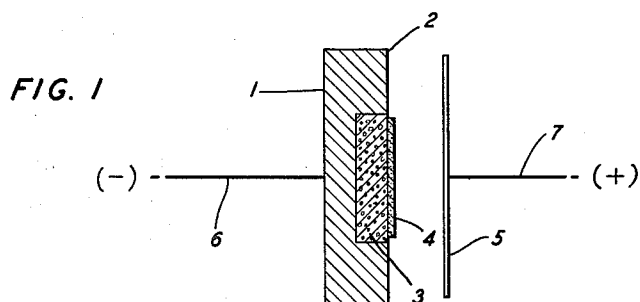


FIG. 2A

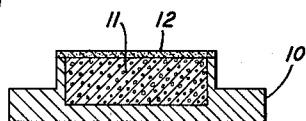


FIG. 3A

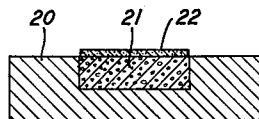


FIG. 2B

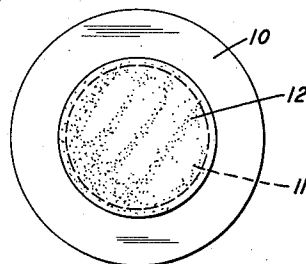


FIG. 3B

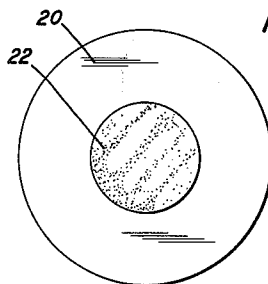


FIG. 4A

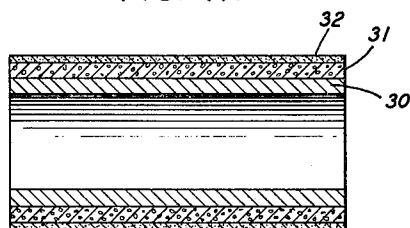
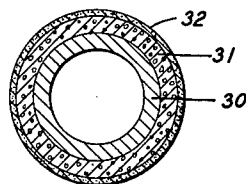


FIG. 4B



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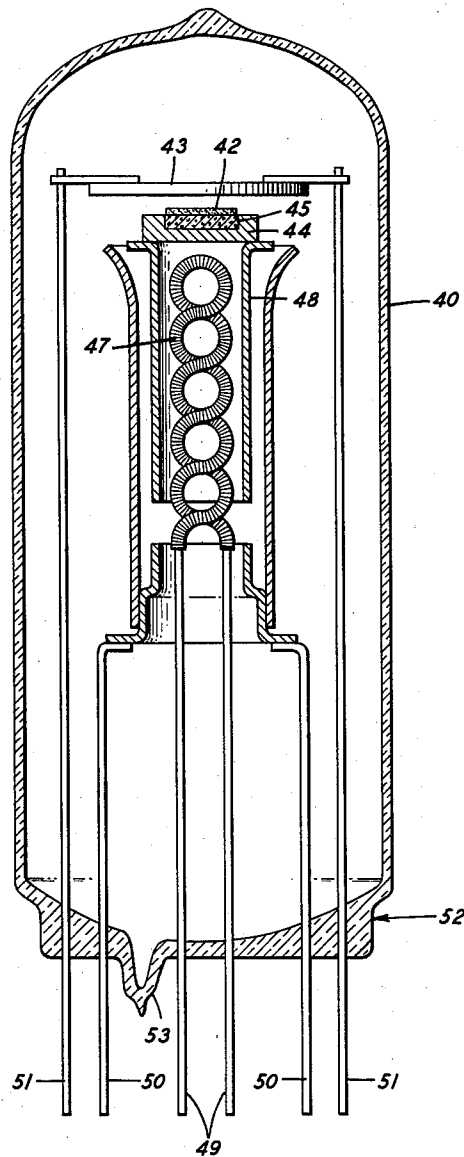
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FIG. 5



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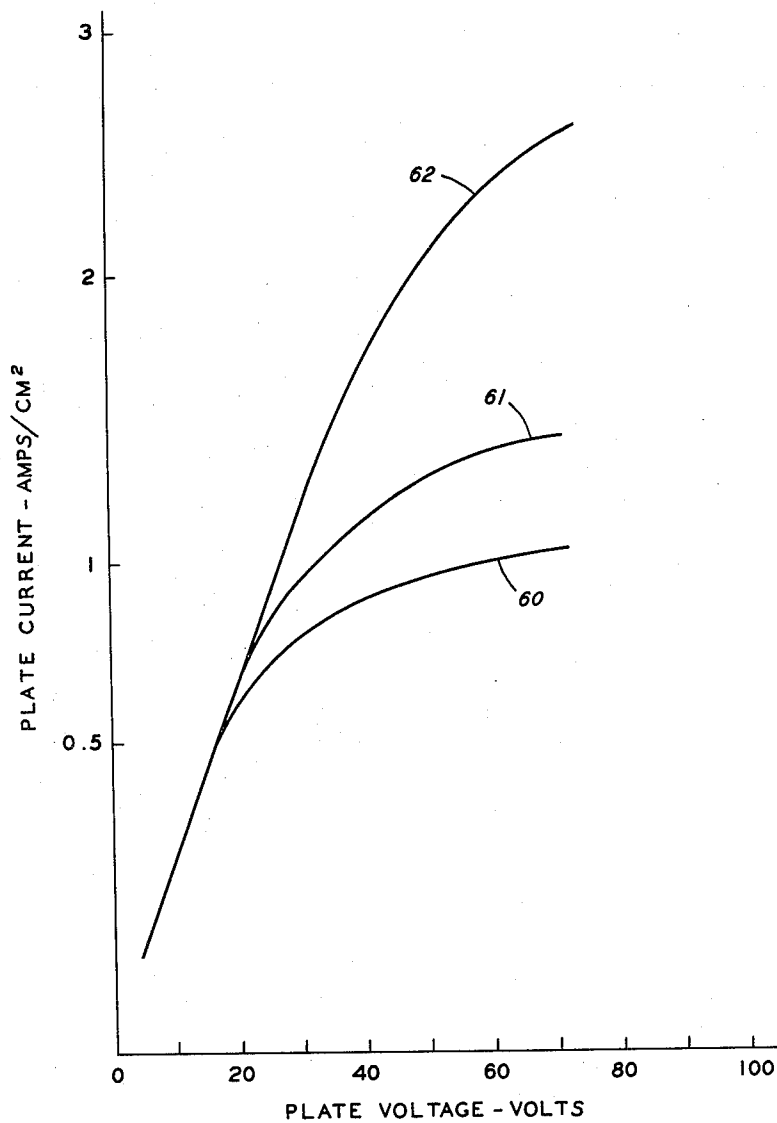
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FIG. 6



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3,159,461

THERMIONIC CATHODE

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5 Claims. (Cl. 29—195)

This invention relates to cathode elements for use in electron tubes and to methods of manufacturing the same.

There are two fundamental types of cathode structures in commercial use at this time. The first of these, and the most conventional, consists of a nickel base having a coating of an alkali earth metal oxide generally including barium oxide. A second type of structure, described in United States Patent 2,543,439, includes a molded element which is made of a pressed and fired mixture generally of nickel powder together with a compound of the same alkali earth metal.

In general, each of the two types of cathode structures has certain advantages and disadvantages which dictate selection for a particular use. For a given configuration and operating conditions, the oxide coated cathode is capable of delivering a considerably higher current density than is the molded type. On the other hand, the molded cathode contains a deeper layer of emitting material, which may serve as a reservoir to furnish such material as it becomes depleted in use. For this reason, the molded type of structure is considered more desirable for use under more adverse conditions as, for example, where there is a high degree of back bombardment, or under other conditions which may cause deterioration of the relatively thin oxide coating of the more conventional structure.

Although the oxide coated cathode is capable of a higher level of current density, it has been found that in actual use and under certain conditions, there may be chemical effects or other deleterious influence which prevent the attainment of a high level of current density over sustained periods. It has been observed, for example, that during use the resistivity of the cathode path across the body and the layer of the element may increase by several orders of magnitude; for example, from an initial resistance of 1 ohm for a particular configuration to of the order of 50 ohms or greater. This increase in resistivity not only has the effect of decreasing current density under particular operating conditions due to that influence, but it is observed that an accompanying influence has the effect of decreasing the rate of activation of the emissive material in the coating so as to cause a still greater decline in operating level.

It is popularly theorized that the increasing resistivity and decreasing activation observed in the coated cathode type of structure is a result of the formation of an interfacial compound between the coating and the body of the element, such compound being the reaction product of the barium in the coating and the activator material in the body. So, for example, where elemental aluminum is used as the activator material and where barium oxide is used as a source of emissive material, such reaction may result in the formation of the compound $BaAl_2O_4$. Due to the nature of the coated structure, most of the formation of such interfacial compound, i.e., barium aluminate, occurs at the interface between the coating and the base of the structure. Ultimately, such formation results in a substantially continuous interfacial material which produces the effects described. Although this reaction, of necessity, takes place between the activator material and the emissive oxide in a molded structure, the comparatively greater depth of the molded layer results in a wider distribution of the compound formed so as to prevent formation of a substantial concentration affecting the

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electrical path. A further advantage of the molded type of structure resides in the presence of a large amount of elemental nickel powder which forms a metallic matrix, thereby providing a low resistivity electrical path through the device.

Most common activator materials react with barium to form such an interfacial compound. Such compounds are formed by any of the common activator materials such as aluminum, zirconium titanium, zirconium hydride and titanium hydride. Although carbon does not result in the formation of interfacial compounds, it is subject to other drawbacks. First, it is a very rapid diffuser and can therefore result in an overabundance of free barium in the coating, which may, in turn, result in inactivity and also in relatively large barium deposits throughout the tube envelope. Secondly, the formation of free barium resulting from carbon reduction results in the evolution of large quantities of gas within the envelope, thereby causing inactivation and also a drift in tube characteristics due to the generation of ions within the envelope.

On the premise that certain of the disadvantageous features of the coated cathode are due to the formation of such interfacial compound, attention has been directed to the development of a coated configuration designed to avoid the phenomenon. Among those described is the structure of United States Patent 2,792,273. In accordance with the disclosure there contained, an oxide coated element without activator material either in the coating or the base is first prepared. A second element, biased anodically, having a coating of barium carbonate on a base of titanium is next provided. During activation the anodic element is heated sufficiently to result in the breakdown of the barium carbonate to barium oxide and in the evaporation of free barium, the spacing between the anodic element and the cathode structure being such that a large part of the elemental barium so released is deposited on the surface of the cathode. The barium so deposited on the cathode element performs its usual function in decreasing the work function of the semiconductor material there contained so as to result in emission in use. Although such a configuration does avoid the formation of an interfacial compound between the coating and the body of the cathode, certain other disadvantages result in use. Proper activation of such a device requires a very delicate balance between the operating conditions of the cathode and anodic structures, it being necessary to deposit the requisite amount of elemental barium on the cathode while at the same time preventing reoxidation of the material. Reactivation of such a device is involved and may require the same type of activation procedure as that followed initially.

In accordance with the present invention, a new type of oxide coated cathode element has been developed. This element, which includes an oxide coating over a molded layer containing an activator material, which layer is, in turn, affixed to the surface of, or is pressed into, a composite structure including a base member, exhibits a degree of current density for a given configuration and operating conditions which is greater than that obtainable by use of a conventional coated structure. In addition, certain of the advantages inherent in the molded type of structure are retained so that, for example, there is an ever-present available reservoir of emissive material in the molded layer which may be fed into the coating upon demand. Cathodes of this invention have been successfully operated at current densities of the order of twice as great and larger than those available by use of a conventional coated structure. Operation at such high emissive has been continued for several thousand hours without visible deterioration. Cathodes of the type here described have an inherent advantage in that an interfacial compound is not formed at the oxide layer-base interface.

To facilitate the teaching of this invention, reference is had to the following drawings in which:

FIG. 1 is a schematic front elevational view in section of a diode utilizing a cathode structure of this invention;

FIGS. 2A and 2B are elevational sectional and plan views, respectively, of a cathode structure described herein;

FIGS. 3A and 3B are elevational sectional and plan views, respectively, of an alternate structure of this invention;

FIGS. 4A and 4B are front elevational and end views both in section of a tubular coated configuration in accordance with this invention;

FIG. 5 is a schematic front elevational view in section of a diode structure utilized in the testing of certain of the elements here described; and

FIG. 6 on three-halves power paper and on coordinates of plate current against plate voltage is an E-I diagram showing the emissive characteristics of three elements including one of the instant invention, said characteristics having been measured by use of the device of FIG. 5.

Referring again to FIG. 1, the diode device depicted includes a cathode element 1 having a disk-shaped body 2 of, for example, solid nickel or sintered nickel powder having an outside diameter of about 200 mils and a thickness of the order of 50 mils. Body 2 may contain an activator material such as zirconium hydride as herein described. Molded layer 3, which in this instance is predominantly nickel powder, also containing an emissive oxide including barium and an activator material such as zirconium hydride, is embedded within body 2 as shown. This molded component is disk-shaped, in this example, of the order of 100 mils in diameter and 25 mils in depth. Coated layer 4, which is predominantly an oxide of barium together with any strontium oxide or calcium oxide which may be included in the emissive material, contains no activator. This layer 4, which is shown exaggerated in thickness, is generally of the order of 1 mil thick and is also a disk-shaped configuration generally corresponding with the surface of molded portion 3.

The remainder of the diode shown schematically in FIG. 1 includes anode 5. Cathode element 1 is biased cathodically via electrode 1, and positive connection is made to anode 5 through electrode 7. The potential source is not shown.

In use, barium oxide in molded layer 3 is reduced by zirconium or other activator material present both in that layer and in body 2 so as to release elemental barium. This material then migrates across the interface from molded body 3 into coating 4. This excess barium, which may be transported either through the grains of the oxide coating, over the surfaces of the grains, or through the pores by successive evaporation, enhances both the electrical conductivity and the electron emissivity of the coating. Heating of coating 4 by an indirect heating element, not shown, results in an electron stream originating from coating 4 and terminating on anode or plate 5 in the conventional manner. The exact mechanism by which the work function of the material contained in the oxide coating is reduced so as to result in the liberation of such electrons is described in detail elsewhere. (See "The Oxide Coated Cathode," Herrman and Wagener, Chapman and Hall, Ltd., 1951.)

The cathode elements of FIGS. 2A and 2B include a body member 10 generally predominating in elemental nickel which may be pressed in the form shown or machined either from a pressed compact or from a solid body. Molded portion 11, predominantly nickel but also containing emissive oxide material such as barium and strontium oxides together with an activator material, is pressed into the structure as shown. Such a molded portion may, for example, be about 200 mils in diameter and 20 mils in depth. Coating 12, covering the entire surface of molded portion 11 and overlapping portions of nickel body 10 as shown, completes the structure. This

coating is a conventional oxide material containing no activator and may be of a thickness of the order of 1 mil.

The cathode shown in FIGS. 3A and 3B is a structure alternative to that of FIGS. 2A and 2B. This device, which may be of the same general dimensions as that of FIGS. 2A and 2B, includes a nickel body 20 which may contain an activator material, an embedded molded portion 21 predominantly nickel but also containing an emissive oxide material together with a suitable activator, and a coating 22 consisting only of an emissive material. Emissive coating 22 is of approximately the same diameter as that of embedded portion 21 and does not overlap any part of the nickel surface of body 20.

The configuration shown in FIG. 4 is tube-shaped and is generally exemplary of the type of structure used in underwater telephony cables. This structure, which operated in the same manner as those of the preceding figures, includes an inner tube 30 which is generally solid nickel, having a wall thickness of the order of 20 mils, a pressed concentric molded member 31 predominantly nickel and also containing an emissive barium compound together with an activator material of a thickness of the order of 10 mils, and an outermost coated layer 32 of the order of 1 mil in thickness of an oxide material containing barium.

The diode device depicted in FIG. 5 is of the structure used in collecting the operating data presented in the form of the curves of FIG. 6 and elsewhere herein. Such structure includes outer envelope 40, containing cathode element 41 which is disk-shaped, of an outside diameter of approximately 200 mils, having a thickness of approximately 50 mils and having an emissive surface 42 which is disk-shaped, of a diameter of 100 mils and is 20 mils distant from anode element 43. The particular cathode element 41 depicted is in accordance with the instant invention and is of the general type of that of FIG. 3A including body 44, embedded molded portion 45 and coating 42. In operation, cathode element 41 is heated by heater element 47, said heater element being enclosed within tube 48, which in this instance is made of nickel. Paired electrical leads 49, 50 and 51 make connection with heater 47, cathode 41 and anode 43, respectively, and pass through glass base 52, which is hermetically sealed with envelope 40.

FIG. 6 on three-halves power graph paper and on coordinates of plate current in amperes per square centimeter on the ordinate and plate voltage in volts on the abscissa contains three E-I curves for three cathode elements tested in the structure of FIG. 5. All three elements of identical emissive dimensions and anode-to-cathode spacing were operated at a constant temperature of 800° C. The dimensions of the elements were those of element 41 of FIG. 5. Curve 60 of this figure corresponds with tests run on a molded cathode structure of the nature described in United States Patent 2,543,439. This cathode was made up using a triple carbonate of barium, strontium and calcium together with zirconium hydride as the activator material. As is seen from this curve, the plate current started to drop off at an applied voltage of about 20 volts and reached a maximum current density of about 0.75 amp./cm.² at about 50 volts. Curve 61 corresponds with a conventional sprayed cathode of the same dimensions also made up utilizing the triple carbonate and zirconium hydride as activator material. Although the plate current of this cathode started to fall off very shortly after the device of curve 60, it reached a maximum plate current density of about 1.4 amp./cm.² at an applied voltage of the order of 70 volts. Curve 62 is plotted from data taken from such test made on a cathode of this invention. The emissive materials and also the activator material used were identical to those of the cathodes of curves 60 and 61. Disregarding the additional coating, such as coating 42 of FIG. 5, the element was identical to that of the molded device of curve 60. It is seen from curve 62 that this element showed no substantial falling-off of plate current after reaching a

value of 2 amp./cm.², corresponding with an applied voltage of about 48 volts. Increasing the applied plate voltage resulted in an increase in plate current, the curve showing the same essentially linear characteristics to a value of about 2.5 amp./cm.² at an applied potential of 70 volts. As is discussed herein, the current density of 2.5 amp./cm.² here attained does not represent a maximum value for this type of coating. Further increase in plate current, however, requires a provision for cooling not included in the test device of FIG. 5. Cathodes of this invention, including that corresponding with curve 62 of FIG. 6, have been operated at a current density of 2 amp./cm.² and higher for periods of 2,000 hours and greater without noticeable inactivation.

A general outline of a method suitable for use in the manufacture of a cathode element of this invention is set forth below. Certain operating parameters and ranges and types of starting materials are indicated. This particular process utilizes a composite pressed powder body and is in other ways illustrative of suitable procedures for use herein.

An initial mixture containing nickel powder plus activator is prepared. The grade of nickel powder chosen should be as nearly pure as practicable so as not to contain any contaminant which may impair the emitting characteristics of the final structure. Carbonyl-nickel powder has been found suitable for this use. Electrolytic nickel powder may be substituted. Although the particle size of the nickel powder is not critical, a general preference exists for very fine particles. It has been found that 100-mesh material containing particles of a maximum size of 150 microns produces satisfactory results. In the production of cathodes for use in micro-oscilloscope tubes where a very fine uniform surface is required, particles as small as 4 microns have been used with an accompanying improvement in characteristics as compared with the coarser material.

Any of the powdered emitting mixtures well known in the preparation of sprayed thermionic cathodes may be used in the preparation of the molded cathode. These materials usually contain a barium compound, which will break down on a vacuum station to yield barium oxide. Since the temperature attained on station is usually about 1000° C., for the purpose of the process described herein, it is considered that any barium compound which will thermally decompose at a temperature of less than 1000° C. to yield barium oxide is suitable. Such materials include the single carbonate material, barium carbonate; the double carbonate material, coprecipitated barium-strontium carbonate; and the triple carbonate material, coprecipitated barium-strontium-calcium carbonate. In general, it has been found that the double carbonate is to be preferred over the single and that little further advantage is gained by use of the triple carbonate. The double carbonate most commonly available for this purpose is a coprecipitant of equimolar portions of barium carbonate and strontium carbonate. The particle size of this emitting mixture is not critical, a preference again existing for fine particles. A commercially available coprecipitant containing particles, 90 percent of which are smaller than 10 microns, has been found satisfactory.

Activators which perform the function of producing the emission characteristics of the structure are well known in the sprayed cathode art, and reference may be had to the literature of that field as to available activator materials. Such activators include zirconium hydride, titanium hydride, silicon, aluminum and magnesium. Whichever activator is used, it should be powdered as finely as is feasible. An average particle size of 15 microns has been found satisfactory.

In addition to the nickel powder, the carbonate, and the activator materials listed above, a binder material may be added. Binder materials which may perform the second additional function of acting as a lubricant are well known to those skilled in related fields such as, for

example, the ferrite art. It is a general requirement of such materials that they leave little or no residue in the end product after sintering. Common binder materials which will operate satisfactorily here include acetone solutions of either isobutyl methacrylate or stearic acid. For other common binders and associated characteristics, see "Treatise on Powder Metallurgy" by Goetzl. Binders should be added to the mixture in minimum quantities. Where excessive amounts are present, resultant difficulties include porosity and excessive flexibility of final product, possible contamination due to impurities which may be contained in the binder, and difficulty of removal. Where it is undesirable to use a binder as, for example, when the cathode is sintered in vacuum, the die plungers may be lubricated with paraffin.

The following is an outline of the procedure to be followed in producing a cathode element from the above materials.

To the nickel powder there is added from zero to 2 percent by weight of an activator material. For most uses the preferred amount of activator is of the order of 1 percent by weight of the nickel powder. Use of amounts of activator in excess of about 2 percent results in a falling-off of the activity of the end product. The mixture of nickel powder and activator is thoroughly dry-mixed as, for example, in a mortar and pestle or in a ball mill. Experience indicates that a mixture of about 100 grams may be thoroughly mixed in a mortar and pestle in less than 15 minutes. This mixing step is carried out in air at room temperature.

Where a binder is to be included, an acetone solution of such binder is produced by dissolving from 1 to 2 percent of binder in the acetone in air at room temperature. Although heating will hasten the formation of this solution, it is to be avoided unless proper precautions are taken to prevent fire.

A binder solution in an amount of up to about 2 percent by weight of nickel powder is slowly added to the nickel powder-activator mix in a mortar at such a rate as to maintain a slurry. Mixing is continued with a pestle as the binder solution is added in air at room temperature until the mixture is dry, the acetone evaporating as the binder is added. Again, by reason of the flammability of acetone, this mixing step is desirably carried out in an unheated mortar unless additional precautions are taken.

This mixture is herein referred to as the "nickel mix" and may be stored until required.

A second basic mixture is now produced by mixing a portion of the nickel mix above with a portion of single, double or triple carbonate. The amount of carbonate used represents a compromise between pure nickel mix which is best from a mechanical standpoint and pure carbonate which is best for emission. The amount of carbonate is generally in the range of from about 10 percent to about 50 percent by weight of nickel mix, the preferred amount for pressed cathodes having a supporting portion of elemental nickel being about 30 percent by weight. Mixing is carried out in a mortar and pestle or ball mill and is continued until the color is homogeneous. Since the nickel mix is black and the carbonate is an off-white, this final mixture is gray. With a total amount of about 100 grams, mixing in a mortar and pestle takes about 15 minutes. This final mixture is herein referred to as the "emitting mix."

The nickel mix and the emitting mix having been produced, the next step in the process is to press the materials into the desired shape and size. If the final product is to be a composite structure, layers of the nickel mix and the emitting mix may be pressed in one operation. In such a structure, the nickel layer lends mechanical rigidity while the emitting mix layer may be kept relatively shallow so as to keep the time on station to a minimum.

The usual procedure, where the structure is to be composite, is to first insert a layer of nickel mix into a die and after pressing this layer lightly, to then insert a layer

of emitting mix into the same die. The entirety, consisting of the two layers, is then pressed at a pressure of from 20 tons per square inch to 100 tons per square inch. It has been found that a pressure of about 80 tons per square inch, readily available on commercial hydraulic presses, is suitable in producing a dense mass which may be easily machined. Increasing the applied pressure beyond about 100 tons per square inch results in a physical breakdown of the emitting surface.

Alternate procedures may be followed after completing the molded and body portions of the cathode. In accordance with one procedure, a coating material is sprayed, electroplated, or otherwise deposited onto the exposed surface of the molded portion. This coating may or may not overlap any part of the nickel surface as discussed. The coating material may be a triple carbonate of barium, or other emissive material as discussed. After deposition of the emissive coating material, the cathode is mounted as shown in FIG. 5 and the composite body is then heat treated in vacuum and is activated.

Alternately, the body, consisting of the nickel portion and the molded portion, may be heat treated, after which the top coating is added. The body is heat treated in accordance with a suitable temperature schedule and in a desired atmosphere. The chief purpose of the heat treatment is to sinter the nickel in the emitting mix so as to produce a mechanically rigid body. Certain precautions must be taken during heat treatment to avoid contamination, to avoid undue calcification of nickel to achieve good sintering, and to avoid the reduction of the alkaline earth carbonates both in the molded portion and in the layer now present which would react with the atmosphere to produce hydrides.

A particular series of heat treatment steps found suitable in the manufacture of cathode elements of this invention is outlined below. This procedure is discussed in detail elsewhere. See "Journal of Electrochemical Society," volume 107, No. 7, page 395.

The pressed cathode is placed in a boat constructed of a non-contaminating material such as Driver Harris No. 499 which is a high purity passive nickel. The boat is inserted in a suitable furnace such as a one and one-half inch diameter electric globar furnace which is maintained at room temperature and is purged with an inert gas such as purified dry nitrogen containing less than 0.1 percent of impurities for a period of about 2 or 3 minutes. A nitrogen flow rate of the order of about 50 cubic centimeters per second has been found satisfactory. Any inert gas such as helium or argon may be substituted for the nitrogen providing its impurity level is satisfactory.

The nitrogen flow is then replaced by a flow of from 225 to 350 cubic centimeters per second of purified dry hydrogen or prepurified hydrogen (PPH). The exit hydrogen is burned in a pilot at the end of the furnace.

After the exit hydrogen has been ignited, the furnace is put into operation and is heated from room temperature to about 600° C. at a rate of about 100° C. per minute. The purpose of the hydrogen flow is to prevent any substantial oxidation of the nickel particles in the emitting mix and to reduce any nickel oxide which may be present. Heating over this range also has the effect of breaking down a small amount of the carbonate present to oxides with a consequent release of carbon dioxide. If the furnace is heated at a substantially greater rate than 100° C. per minute, the released gases, the oxygen from the nickel oxide and the carbon dioxide from the carbonates may cause eruption and destroy the homogeneity of the pressed body. In general, a slower heating rate during the hydrogen flow period is not objectionable, although reducing to a very low rate as, for example, below the rate of 10° C. per minute may result in breakdown of larger amounts of carbonate.

When the temperature of the furnace reaches 600° C., it is held at that temperature as the gas flow is changed from hydrogen to nitrogen or other inert gas as helium

or argon until the exit pilot flame becomes extinguished indicating a removal of residual hydrogen. This generally takes about from 1 to 2 minutes. The flow rate is not critical, but as in purging, a flow rate of about 50 cubic centimeters per second of nitrogen has been found sufficient for the particular furnace configuration.

Although the temperature at which the changeover from hydrogen to nitrogen is carried out is generally held at about 600° C., it has been found that this changeover may satisfactorily be carried out over the range of from 550° C. to 650° C. Changeover below 550° C. results in insufficient reduction of total oxide in the nickel eventually resulting in imperfect sintering, while the presence of a hydrogen atmosphere at a temperature of over 650° C. is undesirable for the reason that too great an amount of the carbonates are reduced to the oxides.

Once the exit pilot is extinguished, the temperature of the furnace is again caused to rise, this time to a temperature of at least 800° C. During this last heating step the nickel powder sinters, substantial sintering taking place at a temperature of about 800° C. A sintering temperature of about 1000° C. is usually preferred. Temperatures above about 1200° C. are unsatisfactory in that larger amounts of carbonate break down.

When the temperature of the furnace attains the desired sintering temperature, the power is turned off and the furnace is allowed to cool to about 600° C. Nitrogen flow through the furnace is maintained during this cooling step. In general, the cooling rate is not critical providing that the rate is not such as to produce serious thermal stress and resultant cracking of the cathode. Maintenance of the furnace at any temperature in the range of over 800° C. results in increased breakdown of the carbonates and should be kept at a minimum.

When the furnace has cooled to about 600° C. the nitrogen flow is stopped and hydrogen is caused to flow through the furnace, the exhaust pilot again being lighted to prevent formation of a combustible mixture outside of the furnace. In this connection, it is again important that, in the temperature range below about 500° C., a reducing atmosphere be maintained within the furnace to remove any reducible oxides which may have formed during the sintering procedure in the higher temperature range.

The furnace is now allowed to cool to room temperature. Although the rate of cooling is not important, it is desirable to cool rapidly to prevent unnecessary contamination of the sintered material. When the furnace is at room temperature the flow of hydrogen is stopped and the furnace is purged with nitrogen or other inert gas until the flame is extinguished. If it is considered desirable, there is no objection to substituting nitrogen for hydrogen in the heating or cooling range between room temperature and a temperature in the range of 300° C. to 400° C. since the hydrogen has little reducing action below about 400° C.

With the process carried out as set forth above, it is possible to produce a sintered product in which no more than about 5 percent of the total carbonate is decomposed to the oxide.

The sintered cathode element may now be machined if such is desired, after which it is coated with barium and/or strontium carbonate either by spraying or electroplating.

All that remains in the manufacture of a usable cathode is the conventional breakdown procedure. Since this procedure is well known to those skilled in the art, it is not here described in detail. In brief, a typical breakdown procedure consists of sealing the element on a vacuum station which is evacuated to a pressure of the order of 10^{-7} millimeters of mercury. The cathode is then heated at a maximum pressure of 10^{-4} millimeters until the carbonates are broken down to oxides. This heating procedure, which may take of the order of 5-15 minutes, is terminated when substantially all of the car-

bonates are broken down. The breakdown point is indicated by a sudden drop in pressure within the chamber. The cathode is then heated to about 1000° C. and is held at this temperature for about 5 minutes. The maximum expected operating anode potential is then applied with the structure at 900° C. and emission current is drawn for a period of 5-10 minutes. The temperature of the structure is then dropped to about 800° C. where the total current is then measured by direct current or pulse measurement.

Measurements made on cathode structures of this invention at this stage on station at an operating temperature of 800° C. indicated pulse current emission intensities of the order of 5 to 15 amp./cm.² and direct current emission current intensities of the order of 1 to 2 amp./cm.².

An alternate method of activation is to keep the cathode element on the pump station and to operate it between 850° C. and 900° C. while drawing electron current to the anode until a satisfactory level of emission is obtained. The full activation period, in accordance with this preferred alternative, is of the order of from 15-20 minutes.

The following examples relate to cathode elements made in accordance with the procedures outlined herein. Current densities for various operating temperatures are indicated.

Example 1

A cathode element of the general configuration shown in FIG. 2 was made as described. This unit had a base diameter of 200 mils, a protruding outside base diameter of 150 mils, a base thickness of 50 mils, a molded portion 100 mils in diameter and 50 mils in depth, and was provided with an oxide coating about 1 mil thick, covering the composite body and molded surface as shown. This element was welded onto a nickel tube three-quarter inches in length of an outside diameter of 210 mils and having a wall thickness of 5 mils. The procedure followed in manufacturing this element is similar to the first outlined above. The quantities and nature of starting materials were as follows.

Base mixture: 0.2 gram carbonyl-nickel powder, of an average particle size of 150 microns and of a chemical purity of 99.9 percent by weight disregarding oxygen;

Molding mix:

0.21 gram carbonyl-nickel powder as described above,

.004 gram zirconium hydride powder as described above,

0.10 gram coprecipitated barium-strontium carbonate;

Coating mix: .05 gram coprecipitated barium-strontium carbonate.

The general processing steps are outlined below:

PROCESSING STEPS

The powders included in the body mix were thoroughly mixed in a four-inch mortar and pestle for 10 minutes. To this there was slowly added 20 cubic centimeters of acetone in which 0.4 gram of isobutyl methacrylate was dissolved as mixing continued. The rate of addition of the isobutyl methacrylate solution to the powder mixture was such as to maintain a slurry in the mortar at all times. Addition time was about 15 minutes. Subsequent to addition, the powders were mixed until all of the acetone was evaporated. Mixing time was about 30 minutes.

The molding mix was next prepared by dry mixing 3 grams of coprecipitated barium-strontium carbonate in a mortar and pestle with 7 grams of body mixture as prepared above. Mixing time was 15 minutes.

A three-piece, double-acting die of circular cross section having a 0.116-inch inside diameter hole and two

sliding plungers was used to mold the nickel mix and emitting mix into a pressed composite body as follows. The lower plunger of the die was inserted in the die body so as to leave a space of a depth of 0.1 inch. The space was filled with nickel mix; the die was tapped gently so as to settle the powder and the excess powder was removed. The nickel mix in the die was then depressed by use of the upper plunger or spacer so as to leave a space of a depth of 0.015 inch. The said space was then filled with emitting mix material prepared as above; the emitting mix material was leveled off at the top of the die and the top plunger was inserted into the die body. The plungers were then centered in the die body; the complete assembly was placed in a hydraulic press and a pressure of 80 tons per square inch was applied between plungers. The plunger and pressed disk were then ejected from the die body. The composite structure so prepared was then placed in a nickel boat and the boat was inserted in a Globar furnace having a one and one-half inch inside diameter. With the furnace at room temperature, it was purged by passing nitrogen gas of a grade known as prepurified nitrogen containing no more than 0.1 percent impurities by volume at a flow rate of 50 cubic centimeters per second for a period of five minutes. After the purging period had terminated, the nitrogen gas flow was replaced by a 250 cubic centimeter per second flow of pure dry hydrogen of a grade known as high purity containing no more than 0.3 percent of impurities by volume. The hydrogen was ignited and burned off at a pilot at the exit end of the furnace.

The furnace was then switched on and allowed to heat at a rate of 100° C. per minute to a temperature of 600° C. The flow of hydrogen gas was then replaced by a 50 cubic centimeter per second flow of pure dry nitrogen of the grade utilized in initial purging. With nitrogen flowing through, the furnace was maintained at 600° C. for one minute at which time the hydrogen flame was extinguished indicating substantial purging of hydrogen from the system. After extinction of the pilot, the furnace was again allowed to heat, this time at a rate of 250 degrees per minute until a temperature of 1000° C. was attained. Nitrogen flow was maintained through the furnace during the entire heating period from 600° C. to 1000° C. The furnace was allowed to reach a momentary peak temperature of 1000° C. after which it was allowed to cool to a temperature of 600° C. while maintaining the nitrogen flow through the furnace as above set forth. Cooling was accomplished by turning off the power source to the furnace and took 16 minutes. The nitrogen flow was then replaced by hydrogen flow of the grade and flow rate set forth above as utilized during the initial heating procedure while maintaining the furnace at 600° C. The exit flow of hydrogen was again ignited at the exit pilot and the furnace was allowed to cool to room temperature. Cooling from 600° C. to room temperature took 60 minutes. At room temperature the hydrogen within the furnace was purged by a nitrogen flow of the same grade and flow rate as above set forth in initial purging. When the exit pilot was extinguished, indicating substantial purging of the system, the boat was removed from the furnace.

The cathode elements so produced were welded onto a nickel cylinder of an inside dimension of .130 inch, a wall thickness of .005 mil, and a length of 0.3 inch by spot welding.

Finally, the exposed area of the molded portion was spray-coated with barium-strontium carbonate powder suspended in a nitro-cellulose amyl acetate binder.

The device so produced was next placed in the structure described in conjunction with FIG. 5 and was there provided with a heater element, leads and other required details.

The complete diode device was operated at a temperature of 800° C. starting at an applied plate voltage of 20 volts corresponding with a plate current of 30 milli-

amperes and the plate voltage was gradually increased to a value of 50 volts corresponding with a plate current of 50 milliamperes. This plate current is equivalent to a current density of 1 amp./cm.². The device was operated at this applied plate voltage for a period of 3,500 hours. At the end of this period, the current density was invariant at 1 amp./cm.².

Example 2

The device depicted in FIG. 3, having an outside body dimension of 200 mils, a body thickness of 50 mils, molded insert dimensions of 50 mils in diameter and 15 mils in depth, and a coating about .001 mil thick, and of the same diameter as that of the molded portion 21 was produced as described in Example 1. Variations in manufacturing procedures resulted primarily from the difference in configuration between the two structures. All starting materials were the same as those recorded in the preceding example except that no binder materials were used. Directly following molding the cathode was welded to a heater cup (48, FIG. 5); the sintering step as described in Example 1 was eliminated. After welding, the cathode base was masked so as to permit only the exposed area of volume 21 to be sprayed-coated. The coating was barium-strontium carbonate suspended in a binder as described in Example 1.

The device so produced was next placed in the structure described in conjunction with FIG. 5 and was there provided with a heater element, leads and other required details.

The complete diode device was operated at a temperature of 800° C. starting at an applied plate voltage of 30 volts corresponding with a plate current of 12 milliamperes, and the plate voltage was gradually increased to a value of 50 volts corresponding with a plate current of 25 milliamperes. This plate current is equivalent to a current density of 2 amp./cm.². The device was operated at this applied plate voltage for a period of 2,000 hours. At the end of this period, the current density was invariant at 2 amp./cm.².

The invention has necessarily been described in terms of a limited number of embodiments. Variations in the described procedures and resultant devices may be made without departing from the scope of this invention. All known activator materials, emissive materials, and body

materials suitable for use in the manufacture of corresponding elements of deposited or molded type cathode structures are suitable for use in the manufacture of any of the devices herein. Other variations in processing details and configurations are known to those skilled in the art and may be dictated by the specific purpose to be served by the structure.

What is claimed is:

1. A cathode element comprising a metallic body member, a molded element consisting essentially of a sintered mass of metallic powder, at least one alkaline earth oxide including barium oxide and an activator material therefor, and an emissive coating consisting essentially of at least one alkaline earth oxide including barium oxide, the arrangement being such that the said molded element is in intimate contact with the said body element, and such that the said coating substantially covers an entire exposed surface of the said molded element.
2. The cathode of claim 1 in which the said metallic body member is nickel and in which the metallic powder is nickel.
3. The cathode of claim 2 in which the metallic body member is a sintered mass of metallic powder.
4. The cathode of claim 3 in which the said sintered mass includes an activator material for at least one alkaline earth oxide contained in the molded portion.
5. The cathode of claim 1 in which the activator material is zirconium hydride.

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