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H. E. KERN ETAL

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ZIRCONIUM-NIOBIUM-NICKEL CATHODES

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2 Sheets-Sheet 1

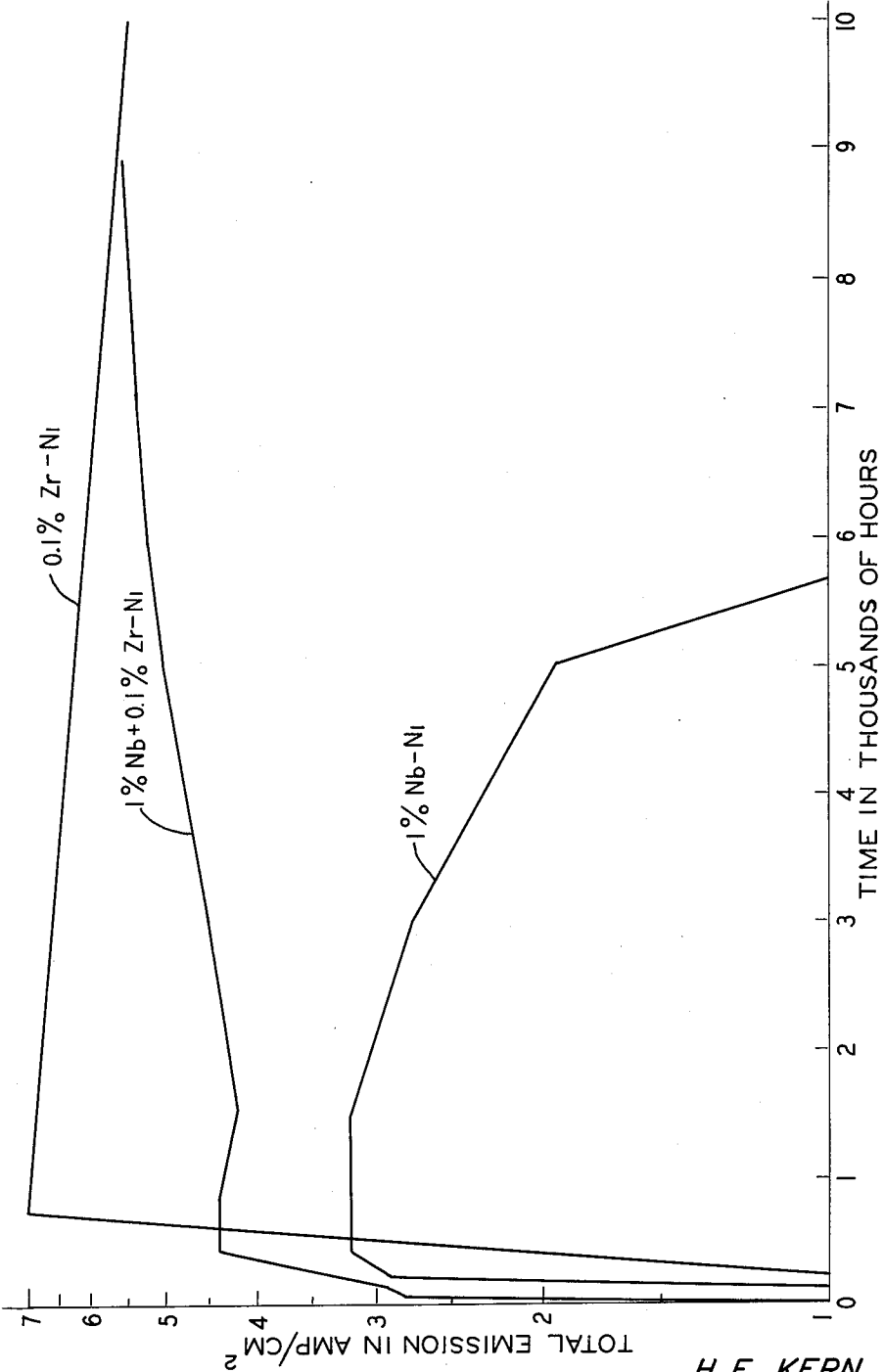


FIG. 1

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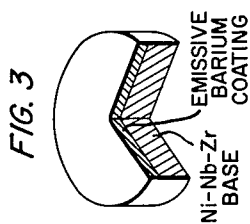
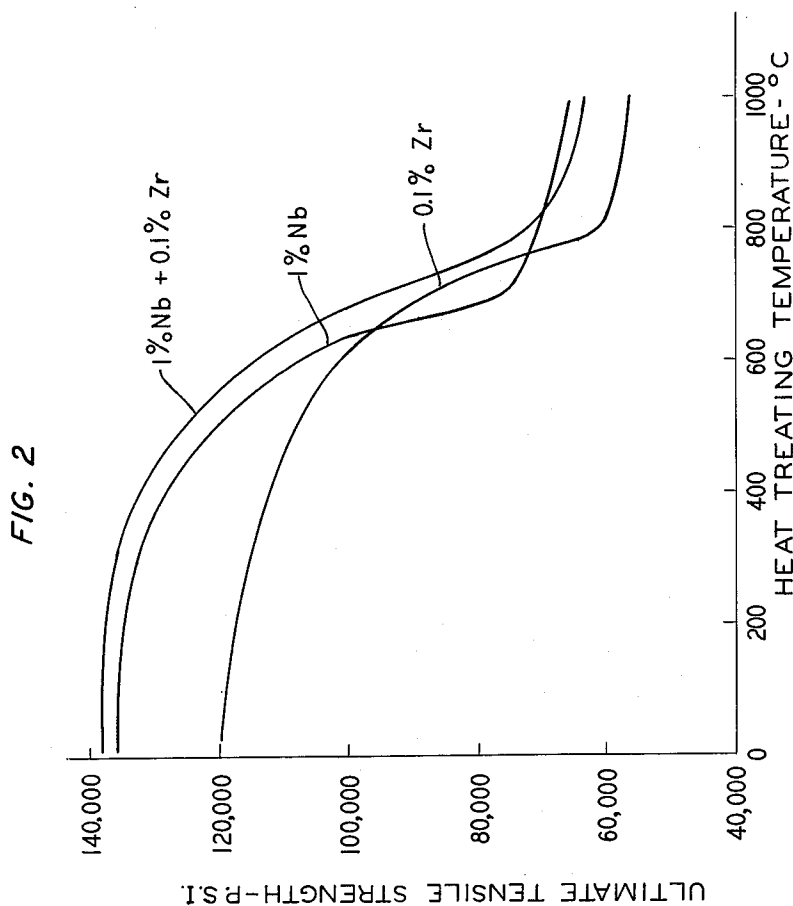
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ZIRCONIUM-NIOBIUM-NICKEL CATHODES

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6 Claims. (Cl. 117-223)

This invention relates to cathode elements of the indirectly-heated type which are destined for use in thermionic tubes.

The most conventional type of cathode in commercial use at the present time is known as the "coated" cathode and typically comprises a nickel base having a coating of alkaline earth metal oxides, generally including barium oxide, and a binder which enables the various coatings to adhere to the cathode base. In addition to the components recited, an activating agent, which performs the function of producing the emission characteristics of the structure, is added to the base member. Among the more effective of such activators is zirconium, which produces emission within about one hour on station, but which begins falling off after about 700 hours.

In accordance with the present invention, nickel-zirconium-niobium cathodes evidence an increase in total emission from 1500 to greater than 9000 hours on life test and evidence superior tensile strength properties as compared with the nickel-zirconium cathodes.

The invention will be more fully understood and other aspects will become apparent from the description of the invention, which will be made with reference to the accompanying drawing, forming a part of the specification, and wherein:

FIG. 1 is a graphical representation on coordinates of total thermionic emission in amperes per square centimeter against time in hours, showing the life test data for nickel-zirconium, nickel-niobium and nickel-niobium-zirconium cathodes; and

FIG. 2 is a graphical representation on coordinates of tensile strength in pounds per square inch against temperature of heating showing the tensile strength at room temperature of nickel-zirconium, nickel-niobium and nickel-niobium-zirconium coated cathodes;

FIG. 3 is a cross-sectional view of a nickel-niobium-zirconium cathode prepared in the described manner.

A general outline of a method suitable for use in the manufacture of a thermionic tube in accordance with the method of this invention is set forth below. Certain operating parameters and ranges as well as the type of materials employed are indicated.

The cathode base of the present invention is an alloy of nickel, niobium and zirconium, the latter two being designated activators. The grade of nickel chosen should be as nearly pure as practical so as not to contain any contaminant which may impair the emitting characteristics of the cathode. Any conventional cathode grade nickel such as carbonyl nickel powder has been found suitable in this use. It is, likewise, desirable to employ metallic zirconium and niobium which are as pure as practical, such materials being of high purity and obtainable from commercial sources.

Any of the emitting mixtures well known in the preparation of sprayed and molded cathodes may be used in the cathode described herein. These materials contain a barium compound which will be converted to barium oxide upon thermal decomposition in a vacuum or by some other means as, for example, in a hydrogen atmosphere. Typically, this compound is a carbonate. Among the materials preferred for this purpose are the single carbonate material, barium carbonate; the double car-

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bonate material, coprecipitated barium-strontium carbonate; and the triple carbonate material, coprecipitated barium-strontium-calcium carbonate. The most commonly available material for this purpose is a coprecipitant of equimolar portions of barium carbonate and strontium carbonate.

In addition to the carbonates listed above, there may be added to the emitting mixture a binder material. The binder is considered to function as an adherent and suitable materials for this purpose are well known to those skilled in the cathode art. Common binder materials which will operate satisfactorily include nitrocellulose or acetone solutions of stearic acid or isobutylmethacrylate. Binders are added to the mixture in minimum quantities to assure maximum density and to avoid possible contamination due to impurities contained therein.

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

The first step in the preparative technique involves preparing the cathode base which is an alloy of nickel, zirconium and niobium. To this end, carbonyl nickel powder obtained from commercial sources and initially containing minimum quantities of oxygen and carbon is subjected to wet hydrogen reduction, thereby lowering the concentration of oxygen and carbon to a satisfactory level.

The reduction is effected by sintering a desired quantity of powder, typically of the order of 25 pounds, in a suitable container, such as magnesium oxide, at temperatures of the order of 800° C. in the presence of wet hydrogen for a time period within the range of 12 to 16 hours.

Alloying is conducted in a suitable furnace, such as a controlled atmosphere induction furnace. These furnaces typically include a central crucible contained within an induction coil and a bin and chute for additions to the melt. The crucible employed is preferably one from which minimum contamination might be expected, magnesium oxide having been found suitable in such use.

The hydrogen reduced nickel slugs are next charged into the magnesium oxide crucible and the alloying agent comprising essentially pure zirconium and niobium are placed in the addition hopper of the furnace, after which the furnace is closed. The zirconium is added in an amount within the range of 0.04 to 0.05 percent by weight based on the weight of the total alloy composition. The addition of zirconium in amounts appreciable below the indicated minimum result in a slower rate of activation than is considered practical and a shorter life for the resultant structure. The upper limit of 0.5 percent is dictated by considerations of the solubility of zirconium in nickel. Niobium is added in an amount within the range of 0.1 to 2 percent by weight based on the total weight of the alloy. Although the indicated minimum percentage of niobium is not absolute, it will be understood that such amounts are considered necessary to produce a noticeable effect upon the properties of the resultant structure, whereas exceeding the indicated maximum produces no further beneficial effect.

Next, the system is evacuated to a pressure of approximately 1 millimeter of mercury by means of a mechanical pump. Dry hydrogen having a dew point of the order of -20° F. is then introduced into the system until a continuous flow of approximately 20 cubic feet per hour at one atmosphere of pressure is attained. Then, the nickel charge is heated inductively using a suitable generator, such as a 1920 cycle, 450 volt, 100 kilowatt generator, to a temperature within the range of 1455 to 1650° C. Complete melting is found to occur in approximately one hour. In order to assure complete miscibility,

the molten charge is held an additional 10 minutes in dry hydrogen.

After melting, the dry hydrogen is purged from the system with dry helium, the system re-evacuated to a pressure of the order of one millimeter and dry hydrogen again introduced in order to further reduce the oxygen and carbon content. Following, the system is again flushed with dry helium and evacuated.

Helium is now reintroduced into the system and the zirconium and niobium added to the molten nickel from the addition hopper by means of a chute leading directly into the magnesium oxide crucible.

Finally, the molten charge is poured under dry helium maintained at a pressure of approximately one atmosphere and a temperature of 1500 to 1600° C. into an aluminum-coated steel mold and permitted to cool.

The resultant ingots are then hot rolled, annealed and machined by conventional metallurgical techniques.

The base material having been completed, the next step in the preparation of a cathode involves machine spraying the formed cathode with any of the noted emitting mixtures, for example, a triple carbonate containing 1% by weight of nitrocellulose, 49% BaCO₃, 44% SrCO₃ and 7% CaCO₃. The coating area may typically be 0.05 cm.² with a coating density of 2.0 gm./cm.³ and a thickness of 0.5 mil or a coating density of 1.0 gm./cm.³ and a thickness of 1.5 mils. The resultant cathode structure is shown in a cross-sectional view in FIG. 3. All that remains in the manufacture of a usable cathode is to assemble the element in a tube envelope, convert the carbonates to the oxides and seal the tube. Since this procedure is well known to those skilled in the art, it will not be described in detail. In brief, the procedure involves sealing a tube structure containing 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 temperature of the order of 950° C. until the carbonates are broken down to the oxides. This heating procedure, which may take of the order of zero to 30 minutes for an emitting layer thickness of approximately 1-4 mils is terminated when substantially all of the carbonates are converted to oxides. 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 2 minutes. Finally, the temperature of the structure is dropped to about 740° C. and total current measured by pulse measurement.

In order that those skilled in the art may more fully understand the inventive concept herein presented, the following example is given by way of illustration and not limitation.

Example I

25 pounds of carbonyl nickel powder obtained from commercial sources and having an oxygen content of 0.2 percent by weight and a carbon content of 0.07 percent by weight were inserted into a magnesium oxide crucible which was inserted in a nichrome pot through which wet hydrogen flowed continually at a temperature of 800° C. in a muffle furnace for 14 hours, so reducing the carbon and oxygen content to less than 0.01 percent by weight.

The resultant slugs were next charged into a magnesium oxide crucible contained in a controlled atmosphere induction furnace containing an addition hopper to which there was added 0.25 pound of metallic niobium obtained from commercial sources and having a purity of 99.9+ percent and 0.025 pound of metallic zirconium obtained from commercial sources and having a purity of 99.8+ percent. The furnace was then closed and the system evacuated by means of a mechanical pump to a pressure of one millimeter of mercury.

Dry hydrogen having a dew point of -20° F. was then admitted to the system until a continuous flow of 20 cubic

feet per hour was established. The furnace was next heated to a temperature of 1550° C. and maintained at that level for 70 minutes to melt the contents.

Following heating, the system was pumped with dry helium (dew point approximately -20° F.), re-evacuated to a pressure of one millimeter of mercury, and dry hydrogen readmitted to the system.

Next, the system was flushed with dry helium, evacuated again and dry helium readmitted. At this stage, the zirconium-niobium mixture contained in the addition hopper was added to the molten mixture. The resultant charge was then poured under dry helium maintained at a pressure of one atmosphere at 1550° C. into an aluminum-coated steel mold and permitted to cool.

The resultant ingot, having a composition of 1% by weight Nb, 0.1% by weight Zr, remainder Ni, was then removed from the mold and hot rolled in air at 1000° C. to ½ inch plate, the surfaces machined to remove oxide scale and cold rolled to 0.020 inch strips with an intermediate anneal at 0.080 inch in hydrogen at 800° C. Several sample lengths were re-annealed and rolled further to 0.003 inch, annealing being conducted by continuously passing the strip through a heated muffle at 1.5 feet per minute.

The completed base material was then machine sprayed with a triple carbonate containing 49% by weight barium carbonate, 44% by weight strontium carbonate and 7% by weight calcium carbonate, and 1% by weight nitrocellulose binder. The coating area was 0.05 cm.² and had a density of 2.0 gm./cm.³ and a thickness of 0.5 mil.

The cathode element was then sealed on a vacuum station and evacuated to a pressure of 10⁻⁷ millimeters of mercury, heated to 950° C. for approximately 10 minutes, after which the temperature was increased to 1000° C. for 2 minutes. The temperature of the structure was then dropped to 740° C. and total current measured by pulse measurement.

For comparative purposes, two cathode elements were prepared in the manner described above, one containing 0.1% zirconium, remainder nickel and one containing 1% niobium, remainder nickel.

Referring again to the figures, FIG. 1 is a graphical representation of total emission in amperes per square centimeter against time in thousands of hours showing total emission data for nickel cathodes containing 0.1% zirconium, 1% niobium and 0.1% zirconium and 1% niobium prepared in accordance with the procedure described in Example I. Total emission is plotted against time and is measured by applying a 400 volt, 6μ second square wave with a repetition rate of one pulse per second. The pulse is superimposed directly over the steady state direct-current operating conditions. The cathode of the present invention activates to 4.35 amperes per square centimeter in about 400 hours and continues at high levels of emission, after falling off slightly at 1500 hours, for over 9000 hours. The nickel niobium cathode activates to 3.2 amperes per square centimeter in about 400 hours, continues at that level until 1500 hours and gradually drops off to terminate life after about 7000 hours. The nickel-zirconium cathode activates to about 7 amperes per square centimeter in about 700 hours and continues at high levels of emission for over 10,000 hours although gradually dropping off. Thus, it is seen from the curves that the cathode of the present invention activates more rapidly than the conventional nickel-zirconium cathode and compares favorably with the emission characteristics of that structure, evidencing an upward trend after 9000 hours as compared with the downward trend of the nickel-zirconium. Further, it is noted that the emission levels of the subject cathode are far superior to the nickel-niobium structure.

FIG. 2 is a graphical representation of tensile strength in pounds per square inch measured at room temperature plotted as a function of cathode heating temperatures for the three structures described with reference to

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FIG. 1. The zirconium-nickel cathode evidenced tensile strengths ranging from 120,000 pounds per square inch before heat treatment to 113,000 pounds per square inch

After heating temperatures up to 400° C. and sharply dropped off to a level of 57,000 pounds per square inch after heating to 1000° C. The niobium-nickel cathode evidenced tensile strengths varying from 135,000 pounds per square inch before heat treatment down to 115,000 pounds per square inch after heating to 600° C. before dropping off sharply to 63,000 pounds per square inch after heating to 1000° C. The cathode of the present invention rather than evidencing properties intermediate the other structures evidenced tensile strengths ranging from 137,000 pounds per square inch before heat treatment down to 116,000 pounds per square inch after heating to 600° C. before dropping off to 63,000 pounds per square inch after heating to 1000° C. Thus, it is noted that the subject cathode unexpectedly shows superior metallurgical properties. The data plotted was obtained by measuring tensile properties of a wire of the subject material after a ½ hour heat treatment in hydrogen at the indicated temperatures followed by cooling to room temperature.

While the invention has been described in detail in the foregoing specification and drawing, it will be appreciated by those skilled in the art that variations may be made without departing from the spirit and scope thereof.

What is claimed is:

1. A cathode element including an alloy consisting

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essentially of 0.1–2% by weight niobium, 0.04–0.5% by weight zirconium, remainder nickel.

2. A cathode element including an alloy consisting essentially of 0.1% by weight zirconium, 1% by weight niobium, remainder nickel.

3. A cathode element destined for use in a thermionic tube comprising a base member, an emissive coating and a binder, said base member consisting essentially of an alloy of 0.1–2% by weight niobium, 0.04–0.5% by weight zirconium, remainder nickel.

4. A cathode in accordance with claim 3 wherein said emissive coating is selected from the group consisting of barium carbonate, barium-strontium carbonate and barium-strontium-calcium carbonate.

5. A cathode in accordance with claim 3 wherein said base member is an alloy consisting essentially of 0.1% by weight zirconium, 1% by weight niobium, remainder nickel.

6. A cathode in accordance with claim 5 wherein said emissive coating is barium-strontium-calcium carbonate.

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