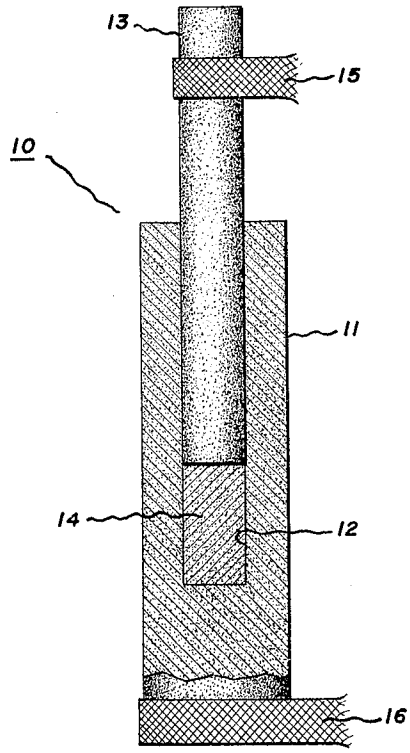
Sept. 27, 1966 R. H. BRISTOW ETAL 3,275,435

METHOD OF PRODUCTION OF A DISPENSER CATHODE

Filed Nov. 1, 1963



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United States Patent Office 3,275,435 Patented Sept. 27, 1966

3,275,435

METHOD OF PRODUCTION OF A DISPENSER CATHODE

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Filed Nov. 1, 1963, Ser. No. 320,725
7 Claims. (Cl. 75—201)

This invention relates to refractory metal dispenser cathodes incorporating a softer additive metal, and more particularly to a high temperature method of compacting dispenser cathode material at reduced pressures.

A dispenser cathode may be defined as a combination of a refractory metal and a compound containing an activator cathode material. The activator cathode material is dispensed to the surface of the cathode in a continuous process and thus maintaining an emissive surface by the activator. One suitable combination is, for example, tungsten as the matrix and a barium compound as the activator cathode material. It is generally known that electron tubes are limited in life and performance by the specific cathode employed. An examination of general factors limiting the frequency and power obtainable from electron tubes also reveals that cathode inadequacies are the most important of these limitations.

One cathode limitation is referred to as "dissipation" which is the result of loss of activator cathode material. This loss is referred to as the evaporation rate of the activator material. Basically, the factors that determine the evaporation rate may be divided into two categories: (1) the rate of production of the activating agent from the activator cathode material such as Ba and BaO from a barium compound; and (2) the transport mechanism by which the active cathode material is dispensed through the matrix and over the emitting surface. The transport of the activator material, for example barium, may be controlled through the pore size or porosity of the matrix material. The porosity and pore size of a dispenser matrix material is governed to a considerable extent both by the particle size and the compacting pressure. Optimum porosity for refractory metal dispenser cathodes requires very high compacting pressures and very high sintering temperatures. These conditions are detrimental to the overall production of dispenser cathodes and further detrimental to the more precise predetermination of porosity.

Accordingly, it is an object of this invention to provide an improved dispenser cathode.

It is another object of this invention to provide an improved method of compacting and sintering a dispenser cathode.

It is a further object of this invention to provide for the addition of predetermined additive materials to reduce high pressures and high temperatures associated with dispenser cathode production.

Briefly described, this invention in one form comprises the addition of small amounts of a Group VIII metal, preferably nickel, in elemental or combined form dispersed throughout a refractory metal which is in powder or small particle form. Upon compressing or compacting the mixture, the additive nickel is operative to reduce the required compacting pressure and facilitate the predetermination of optimum porosity. Sintering temperature of the matrix is also lowered.

This invention will be better understood when taken in connection with the following description and the drawing in which:

The figure is a cross-sectional illustration of one apparatus in which the present invention may be carried out.

Various methods are known in the art by which dispenser cathodes may be produced. For example, the known cold pressed method includes mixing a refractory metal powder and a barium compound and pressing to the desired shape at pressures of about 70 tons per square inch. Thereafter the compact is heated at a temperature of about 1800° C. in vacuum or in a redducing atmosphere for sintering to provide an integral strong cohesive structure.

A further method of producing a dispenser cathode includes pressing a refractory metal powder, for example tungsten, at about 70 tons per square inch and then sintering the matrix in a reducing atmosphere such as dry hydrogen at about 2500° C. The matrix is then impregnated with molten copper at about 1400° C. The copper-filled matrix is machined to the desired shape and the copper removed by firing at about 2000° C. in vacuum. Thereafter, the pores or interstices of the tungsten matrix are filled with a molten barium compound by hot firing at about 1700° C. in a vacuum or reducing atmosphere.

A further method of producing dispenser cathodes is disclosed and claimed in co-pending application Ser. No. 320,724 assigned to the same assignee as the present invention and filed concurrently herewith. In the mentioned co-pending application the method disclosed includes a combination step of simultaneously pressing and heating a predetermined mix for a dispenser cathode. This combination step is carried out, in one form of the invention, in a carbon crucible to provide a protective atmosphere.

In any of the above-mentioned methods the required pressures may be greatly reduced by the addition of small amounts of one or more of the metals taken from class consisting of those metals of Group VIII of the periodic table of elements. Preferentially these metals include nickel, cobalt, palladium, platinum, ruthenium and rhodium. Best results have been obtained in the practice of this invention where the additive metal contains nickel or cobalt and where the additive metal is of commercial purity.

The additive nickel should be widely dispersed as much as possible throughout the refractory metal matrix for optimum results. Best results are obtained when the amount of additive nickel is maintained at a minimum value and where the amount does not add substantial elemental nickel characteristics to the dispenser cathode. For example, in the practice of this invention in one form, the amount of nickel added is less than 5% and ordinarily about 1% by weight of the refractory metal to be employed. The added amount should be sufficient to provide at least the weight percent (0.3) which will go into solid solution.

The additive nickel may be added by various means known in the art, whether by elemental nickel or through the use of materials or compounds containing nickel which react or otherwise decompose to provide elemental nickel under the conditions of the pressing and sintering. By way of example, such compounds may include nickelous nitrate, nickel oxide, nickel acetate, etcetera.

In one preferred form of this invention, in order to add the required amount of nickel, and in order to obtain excellent dispersion of the nickel, a solution of nickelous nitrate in alcohol was added to 5 micron tungsten powder in such a quantity that 1% by weight of nickel with respect to the matrix material was distributed throughout the matrix.

The effect of the nickel is to reduce the compressing and sintering temperature of the matrix material. The nickel element does not completely line the pores or openings in the refractory material nor is it dispersed in such a manner as to add its particular characteristics to dispenser operation. Of the various metals chosen for the attainment of the given purposes, it has been discovered that nickel combines the salient features of being easily dispersed within a refractory metal matrix and cooperates therewith to reduce the required pressures and temperatures for compacting, and does not chemically or electronically enter into the ordinary dispenser operation to detract therefrom. To the contrary, the effectiveness of the cathode is increased through the addition of nickel. Comparable examples indicate a change in density of the cathode from the former 60% without nickel to 90% with nickel. Nickel coats the tungsten particles so that upon sintering an intimate bond is obtained. This bond is acquired at pressures of about 10 tons per square inch compared to former employed pressures on the order of 70 tons per square inch.

A representative example of the practice of this invention included a dispenser cathode which consisted essentially of tungsten powder of about 5 micron particle size together with one weight percent nickel to provide an 88% by weight refractory matrix. To this powdered matrix there was added 10% by weight barium orthosilicate (Ba_2SiO_4), 1% by weight calcium carbonate ($CaCO_3$), and 1% by weight zirconium hydride (ZrH_2), thereby totaling 100% by weight dispenser cathode. After thoroughly mixing these materials a compact was produced therefrom by pressing the mixture at about 10 tons per square inch and thereafter firing the compact in dry hydrogen at about 1300° C. for about 30 minutes. Dispenser cathodes were machined from the resulting compact and emission tested with good results.

In conjunction with the above representative example and the practices as set forth in the above-mentioned copending application, best results are obtained by the practice of this invention utilizing the other materials and proportions in the example such as Ba_2SiO_4, $CaCO_3$, ZrH_2.

The above example is representative of a method of producing an optimum cathode carried out in accordance with the teachings of this invention. This process has been repetitiously employed to produce many cathodes. It is to be understood, however, that various other mixtures both as to percentage mixtures and as to materials may be employed within the scope of this invention. For example, nickel may be added from about 0.3 weight percent to about 1 weight percent. Nickel in much greater amounts is unnecessary and should be avoided where high temperature operation of the cathode is contemplated because of its higher vapor pressure. It is preferred to maintain the additive material, nickel, in sufficient amounts to provide about 0.3 weight percent nickel in the tungsten matrix, which is the weight percent of nickel which forms a solid solution with tungsten. While liquid solutions of the metals are desired for additive purposes, in cathode production certain solutions as the chlorides of the mentioned metals are undesirable.

The above example has been repeated with due changes in the process and materials in the prescribed ranges with good results. In addition, this invention has been practiced, in accordance with the above example, with such additive metals as cobalt, platinum and palladium. For example, about 1% by weight of cobalt was added by means of a known concentrate solution of cobalt nitrate dissolved in methanol. In another example about 1% by weight of platinum was added by means of a known concentrate solution of platinum nitrate in methanol. In a still further example, about 1% by weight palladium was added by means of a solution prepared by dissolving palladium in hydrochloric acid, evaporating the solution, and dissolving the residue in methanol. These latter mentioned metal additives also provided excellent dispenser cathodes in accordance with the teachings of this invention, the effects of the additives being similar to those of the preferred nickel additive. In all instances it is preferred to utilize the additives in liquid solution form, and to limit the additive to about 1 weight percent of the cathode. Where desirable, mixtures, including alloys, of the additive metals may also be employed.

Various pressing and heating apparatus and cycles may be employed to carry out this invention. A combined pressing and heating operation in a carbon monoxide or carbon dioxide atmosphere may also be employed, as described in the aforementioned copending application. For example, the operation may be carried out in the presence of carbon where the carbon can react to produce a protective atmosphere. One apparatus to accomplish this result is illustrated in FIG. 1. In FIG. 1 apparatus **10** includes a carbon crucible **11** defining a cylinder **12**. A plunger **13** which also may be of carbon is operative in cylinder **11** to compress a cathode mix **14**. Simultaneous heating of cathode mix **14** is accomplished by connecting the apparatus **10** to a suitable source of power (not shown) by means of electrical conductors **15** and **16**. Material **14** is then heated by electrical resistance heating through the crucible and material **14** or through the crucible alone. Sintering temperature is preferably about 1300° C. for best results. Lower temperatures are insufficient to provide optimum coherency and strength characteristics. Furthermore, sintering beyond about one hour at temperature is unnecessary.

While a particular cathode has been described as an article and by a method of producing, variation of these will become apparent to those skilled in the art without departing from the scope of the disclosed invention. It is therefore intended by the appended claims to include all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A method of producing a dispenser cathode which comprises in combination

(a) providing a refractory metal in particulate form,

(b) adding a material to said refractory metal to coat said refractory metal with an additive metal which is in the range of about 0.3 to 1.0 weight percent of said refractory metal, and not substantially more than will alloy with said refractory metal,

(c) said additive metal including a metal taken from the class consisting of those metals of Group VIII of the Periodic Table of Elements,

(d) adding at least about 8.0 weight percent of a barium compound to said refractory metal,

(e) adding less than about 1.0 weight percent of $CaCO_3$ to said refractory metal,

(f) compressing said mixture at about 10 tons per square inch pressure and

(g) firing said mixture in a reducing atmosphere at about 1300° C. to provide a sintered integral high strength dispenser cathode.

2. The invention as recited in claim **1** wherein said material is a liquid solution containing a metal of those metals of Group VIII of the Periodic Table of Elements.

3. The invention as recited in claim **1** wherein said coating material is nickel solution, said barium compound is barium orthosilicate (Ba_2SiO_4).

4. The invention as recited in claim **1** wherein said additive metal is cobalt.

5. The invention as recited in claim **1** wherein said additive metal is platinum.

6. The invention as recited in claim 1 wherein said additive metal is palladium.

7. The invention as recited in claim 1 wherein said refractory metal is tungsten and said barium compound is barium orthosilicate.

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