

United States Patent

[11] 3,615,901

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 [21] Appl. No. **881,265**
 [22] Filed **Dec. 1, 1969**
 [45] Patented **Oct. 26, 1971**

[54] **METHOD OF MAKING A PLASTICALLY
 SHAPEABLE CATHODE MATERIAL**
7 Claims, No Drawings

[52] U.S. Cl. **148/11.5 R,**
29/25.11, 29/182.5, 29/420.5, 75/206, 75/208,
117/223, 148/126

[51] Int. Cl. **C22f 1/10,**
B44d 1/18, H01j 63/02

[50] Field of Search **148/11.5 R,**
126, 31.5; 29/25.11, 182.5, 420.5; 117/223;
75/206, 208

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ABSTRACT: A plastically shapeable cathode material is prepared by depositing on a nickel substrate a layer of a mixture of nickel or nickel oxide powder and barium, strontium and calcium carbonates; sintering in a neutral or reducing atmosphere the nickel substrate with deposited layer; compressing the sintered material; cold rolling the sintered and compressed material; annealing the resulting cold-rolled material; and repeating the latter two steps until the nickel substrate with deposited layer has a desired thickness.

METHOD OF MAKING A PLASTICALLY SHAPEABLE CATHODE MATERIAL

This invention is concerned with a process for preparing a plastically shapeable cathode material. In one aspect it relates to a cathode material prepared by the aforementioned process.

As shown in the prior art, thermionic cathodes can be made by compressing and sintering a mixture of nickel powder with barium, strontium and calcium carbonates. The resulting product either has the desired form, or it is shaped by machining, e.g., by turning, drilling, milling, or the like. Such cathodes have excellent properties with respect to poisoning, exposure to the atmosphere, and resistance to cathode sputtering as well as related effects. The cathode material of the present invention is an improvement over the prior art material in that it provides many additional advantages.

It is an object of this invention to provide an improved cathode material.

Another object of the invention is to provide a shapeable cathode material which can be worked by any of the conventional metalworking processes, such as shearing, punching, bending, welding, shear forming or spinning, deep drawing, and the like.

A further object of the invention is to provide a cathode material which has improved emission characteristics and a longer life than the prior art cathodes.

Still another object of the invention is to provide a material which is suitable for direct ohmic heating.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

In a preferred embodiment, the present invention resides in a cathode material that is prepared by depositing on a nickel substrate an active layer of nickel powder or nickel oxide powder and alkaline earth metal carbonates; sintering in a reducing or neutral atmosphere the nickel substrate with deposited layer; compressing the sintered material; cold rolling the sintered and compressed material; annealing the cold-rolled material in a reducing or neutral atmosphere; and repeating the latter two steps until the nickel substrate with deposited layer has a desired thickness.

A cathode formed by the process of this invention is superior in many respects to the prior art cathodes. Since the cathode is plastically deformable, it can be shaped by any conventional metalworking process. As a result wastage of material is reduced to a minimum while making it possible to fabricate a cathode of any desired configuration. The cathode can be stored without deterioration for extended periods in the atmosphere. The cathode can be readily spotwelded, and it is suitable for direct ohmic heating. Furthermore, the cathode often has better emission and longer life than conventional cathodes.

The thickness of the nickel sheet material used as a substrate can vary over a wide range. Generally, the thickness of the substrate is in the approximate range of 0.25 to 5 mm. although it is to be understood that a nickel sheet of any desired thickness can be used in the practice of the present invention. For example, in large production runs, it is advantageous to commence with a piece of nickel having a thickness ranging from a few centimeters to 10 to 15 centimeters. A mixture of nickel or nickel oxide powder and barium, strontium and/or calcium carbonate is deposited as by sieving on the substrate as an active layer of substantially uniform thickness. The alkaline earth metal carbonates generally constitute about 20 to 65 weight percent of the mixture, the remainder of the mixture being nickel or nickel oxide powder. The mechanical properties of the layer can be varied over a wide range by changing the amount of nickel or nickel oxide powder present in the mixture. As to the amount of the alkaline earth metal carbonates, each is usually present in an amount equal to zero to 75 weight percent of the total amount of carbonates, and at least two of the carbonates are present. The ratio of the thickness of the layer of nickel or nickel oxide powder and alkaline earth metal carbonates to the thickness

of the nickel sheet can be varied within rather wide limits in order to adjust the malleability of the cathode material for different degrees and kinds of plastic deformation. It is also within the scope of the invention to adjust the concentration of nickel powder in the layer mixture so that it is higher at the substrate surface. In a preferred procedure nickel or nickel oxide powder is first sieved onto the nickel substrate followed by the deposition of the mixture of nickel or nickel oxide powder and alkaline earth metal carbonates. By proceeding in this manner, the deformation properties of the cathode material can be improved. However, the ratio of layer thickness to substrate thickness generally falls in the range of 10:1 to 1:10. To improve adherence the surface of the substrate can be scarred or roughened by chemical or electrochemical etching or by mechanical means prior to depositing the layer thereon.

The nickel substrate with deposited layer of nickel or nickel oxide powder and alkaline earth metal carbonates is then sintered. The sintering step is carried out by heating the substrate and adhering layer to a temperature below the melting point of nickel for a period sufficient to reduce the alkaline earth metal carbonates to oxygen-containing compounds and, when used, the nickel oxide powder to nickel. The exact composition of the compounds obtained in the sintering step is not known with certainty, but corresponding alkaline earth metal oxides as well as alkaline earth metal nickelates, e.g., calcium nickelate ($\text{Ca}(\text{NiO}_4)_2$), are apparently formed. This is accomplished by placing the substrate and adhering layer in a furnace maintained at a temperature below about 1,400° C., e.g., at a temperature in the range of 900° to 1,300° C. In general, the higher the temperature the shorter the time the material must remain in the furnace, but in any event the time and temperature are adjusted so as to obtain substantially complete reduction of the nickel oxide and decomposition of the carbonates. Although the sintering is preferably conducted in a reducing atmosphere, e.g., in the presence of hydrogen, it is within the purview of the invention to carry it out in a neutral atmosphere, such as argon or helium. It is preferred to employ nickel oxide since a more homogeneous mixture is thereby obtained. And when nickel oxide is used, it is necessary to carry out the sintering in a reducing atmosphere. An important purpose of the sintering step is to obtain uniform adherence between the substrate and the active layer. In order to ensure that this is accomplished, it may be desirable to apply a slight pressure to the layer, e.g., by placing a weight on the layer so as to exert 1 to 5 pounds per square inch pressure.

The sintered material, i.e., the nickel substrate with deposited layer, is then compressed without delay at a high pressure. Any suitable pressure inducing means can be employed although it is preferred to use a hydraulic press. The pressure is usually in the range of 5,000 to 20,000 pounds per square inch absolute (p.s.i.a.) although higher and lower pressures can be used without departing from the spirit or scope of the invention. It is not necessary to subject the substrate with deposited layer to the pressure for an extended period of time. It is usually sufficient merely to apply the pressure and then immediately release the pressure in order to cause nickel and alkaline earth metal compounds to adhere and form a unitary mass bonded to the substrate.

In the preferred procedure, the sintering and compression steps are carried out in that order. By proceeding in this manner, the layer is in a porous state during sintering as compared to a compacted state after the compression step. As a result gases formed during sintering, such as carbon dioxide, are driven out of the porous layer by the heat or are squeezed out of the layer upon being compacted during the compression step. The possibility of gases being entrapped in the layer is thereby reduced to a minimum as is the chance of carbon deposits being formed during use of the cathode material.

Immediately after the compression step, the nickel substrate with adhering layer is removed from the hydraulic press and cold rolled. The cold rolling is continued until such time as the material can no longer be worked and annealing becomes

necessary. The substrate with bonded layer is then annealed by heating it to a temperature in the range of 500° to 800° C. The annealing step is conducted in a reducing or neutral atmosphere as is the sintering step. The cold rolling and the annealing steps are thereafter repeated, as necessary, to obtain a cathode material having a desired thickness. It is also within the scope of the invention to carry out the annealing step immediately after the compression step after which the material is then cold rolled.

The cold-rolling step homogenizes and compacts the active layer of nickel or nickel oxide powder and alkaline earth metal carbonates. The rolling also gives the layer a unique grain structure which is responsible for its plasticity or malleability. Thus, it is important to roll the material in one direction in order that the grains of nickel powder may approach the shape of filaments.

A desirable property of any cathode material is that it may be readily degassed. Accordingly, it is advantageous to take steps to ensure to the extent possible that hydrogen is the only gas evolving during the degassing process. Thus, it is preferred to conduct not only the sintering and annealing steps but also at least the first rolling cycle in the presence of hydrogen since hydrogen diffuses readily through hot nickel.

The cathode material as described above comprises a nickel substrate with an active layer bonded to one of its surfaces. However, it is to be understood that the substrate can have an active layer bonded to both of its surfaces. Such a cathode material is in general prepared in accordance with the method described hereinabove. It is usually preferred, however, to deposit the layer of nickel or nickel oxide powder and alkaline earth metal carbonates first on one surface of the substrate followed by sintering after which the same procedure is followed for the other surface. It may be desirable to reverse the sintering and compression steps in this embodiment since the adherence of the layer to the substrate may be greater after the compression step. Alternatively, the sintering and compression steps can be carried out on one side after which a layer is formed on the other side. This layer is then subjected to the sintering and compression steps in the preferred order. A cathode material comprising a nickel substrate with an active layer bonded to both of its surfaces is particularly desirable for directly heated cathodes.

It is within the scope of the invention to use a very thin substrate as compared to the active layer, e.g., a thickness ratio of substrate to layer of 1 to 10, in preparing the cathode material. Furthermore, if high percentages of nickel or nickel oxide powder, e.g., from 70 to 80 weight percent, are used in preparing the mixture with the carbonates, the substrate may be omitted entirely. By fabricating the cathode material by these methods, it is possible to obtain a homogeneous emitting sheet or ribbon that has a high-ohmic resistance.

A better understanding of the invention can be obtained by referring to the following example which is not intended, however, to be unduly limitative of the invention.

EXAMPLE

Hallow cathodes with the emitting surface on the inside are prepared in the manner described below.

A substrate in the form of a sheet of nickel one and one-half inches wide and 12 inches long has a mixture of nickel powder and barium, strontium and calcium carbonates deposited on one of its surfaces. This is accomplished by first sieving nickel powder onto a substrate surface followed by sieving a mixture of nickel powder and barium, strontium and calcium carbonates onto the nickel powder. The substrate has a thickness of 1 mm. and the ratio of deposited layer thickness to substrate thickness is about 2 to 1. The substrate with deposited layer is placed in a furnace maintained at a temperature of 1,000° C. and containing hydrogen. The material is allowed to remain in the furnace for 30 minutes in the presence of hydrogen, at the end of which period substantially all of the carbonates are reduced. The substrate with adhering active layer is then placed in a hydraulic press whereby it is subjected to a pressure of 10,000 p.s.i.a. The substrate with bonded ac-

tive layer is then cold rolled until such time as it can no longer be worked. The material is then annealed by placing it in a furnace containing hydrogen. The temperature in the furnace is about 600° C., and the material is allowed to remain in the furnace for a time sufficient for it to attain this temperature. The material is then removed from the furnace and the cold rolling and annealing steps are repeated two more times. The substrate with bonded layer has a desired thickness of 1.5 mm.

The sheet of cathode material is cut into six separate pieces each being about one and one-half inches by two inches in size. Each piece is then bent into a cylinder having a diameter of about 1.27 inch and a height of about 1 1/2 inches. The active-layer forms the inner surface of each of the cylinders. The abutting edges of each cylinder are welded so as to provide a rigid structure. Insulated heater wire is then attached to the outer surface of the cylinders to provide means for indirect heating of the cathode material. The cathodes so fabricated are then used in the manufacture of gas-discharge tubes.

The cathode material of this invention is particularly suitable for use in gas-discharge tubes, e.g., mercury and rare gas tubes, as well as gas-laser tubes, such as an argon ion laser tube.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed in light of the foregoing disclosure without departing from the spirit or scope of the invention.

I claim:

1. A process for preparing a plastically shapeable cathode material which comprises depositing on a surface a layer of a mixture of nickel powder or nickel oxide powder and at least two carbonates selected from the group consisting of barium, strontium and calcium carbonates; sintering said layer in a reducing or neutral atmosphere, thereby decomposing said carbonates and reducing said nickel oxide powder; compressing said sintered layer, thereby causing said nickel powder and said reduced compounds to adhere and form a unitary mass; cold rolling said sintered and compressed layer; and annealing said cold-rolled layer in a reducing or neutral atmosphere.

2. A process according to claim 1 in which said surface is a sheet of nickel; said sheet with said layer deposited thereon is sintered in a reducing or neutral atmosphere; said sintered sheet with adhering layer is compressed; said sintered and compressed nickel sheet with said layer bonded thereto is cold rolled; and said cold-rolled nickel sheet and bonded layer are annealed in a reducing or neutral atmosphere.

3. A process according to claim 2 in which said mixture consists essentially of nickel powder or nickel oxide powder, barium carbonate, strontium carbonate and calcium carbonate, said carbonates constituting 20 to 65 weight percent of said mixture with the remainder being nickel or nickel oxide; said nickel sheet has a thickness in the range of 0.25 to 5 mm.; and the ratio of the thickness of said layer to the thickness of said sheet is in the range of 10:1 to 1:10.

4. A process according to claim 2 in which said mixture consists essentially of nickel powder or nickel oxide powder, barium carbonate, strontium carbonate and barium carbonate, said nickel or nickel oxide constituting from 70 to 80 weight percent of said mixture, the remainder being carbonates.

5. A process according to claim 2 in which said layer is formed by sieving nickel powder or nickel oxide powder onto said sheet and then sieving onto said nickel powder or nickel oxide powder a mixture of nickel powder or nickel oxide powder and said carbonates.

6. A process according to claim 3 in which said sintering and said annealing are conducted in a hydrogen atmosphere.

7. A process according to claim 6 in which said sheet with deposited layer is sintered at a temperature in the range of 900° to 1300° C. for a time to reduce substantially all of said carbonates; a pressure between about 5,000 and 20,000 p.s.i.a. is applied to said sintered sheet with adhering layer; said sintered and compressed sheet with bonded layer is cold rolled in one direction until said sheet can no longer be worked; and said cold-rolled nickel sheet with bonded layer is annealed at a temperature in the range of 500° to 800° C.