June 19, 1951 N. F. CERULLI ET AL 2,557,372

MANUFACTURE OF THORIA CATHODES

Filed Feb. 21, 1948

Fig. 1.

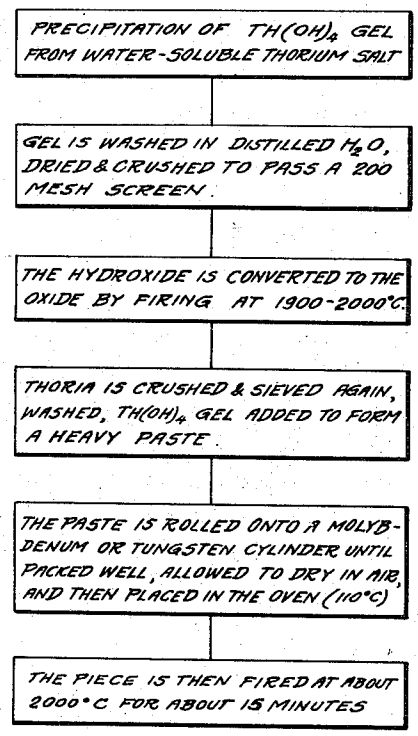


Fig. 2.

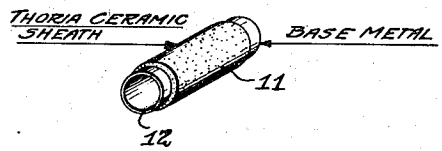


Fig. 3.

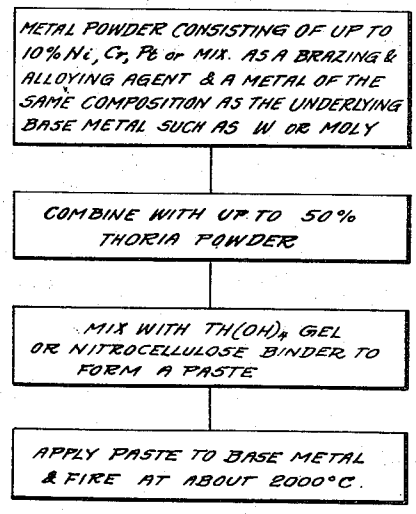


Fig. 5.

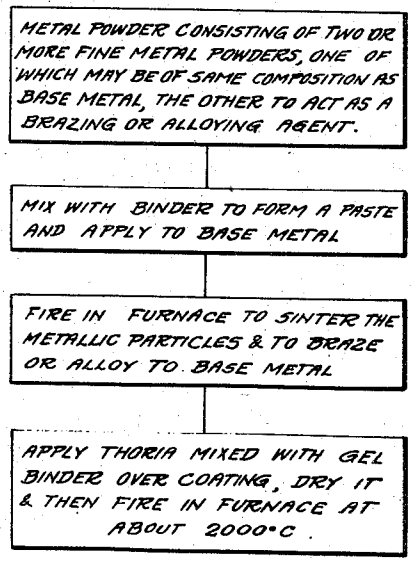


Fig. 4.

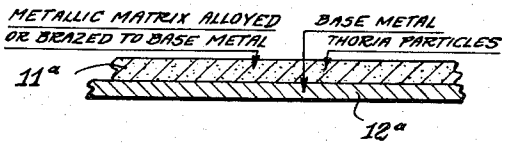
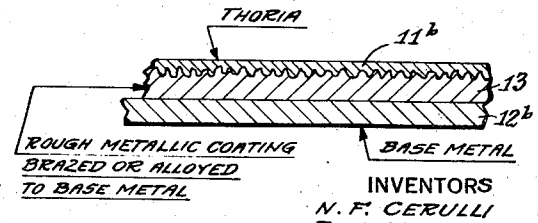


Fig. 6.



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MANUFACTURE OF THORIA CATHODES

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1

This invention relates to the manufacture of thoria cathodes and, more particularly, to such having improved characteristics.

The principal object of our invention, generally considered, is to produce cathodes of conductive refractory materials, such as metals or alloys of high melting points, carrying coatings of thoria of good mechanical strength and electron emission.

Another object of our invention is to produce electrodes with coatings of thoria bonded to a base by a gel of thorium hydroxide giving increased strength.

A further object of our invention is to produce electrodes with coatings containing thoria up to 50% and admixed metal such as nickel, chromium, platinum, or a mixture thereof, up to 10%, with the balance consisting of metal such as tungsten, tantalum, molybdenum, or a mixture thereof, corresponding with that of the base.

A still further object of our invention is to produce electrodes with coatings of two or more fine metal powders, one of which may be metal like that of the base with a binder of thorium hydroxide gel, to which coating is applied thoria bonded by a gel of thorium hydroxide.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Figure 1 is a flow diagram indicating one method of manufacturing cathodes in accordance with our invention.

Figure 2 is a perspective view of a cathode manufactured in accordance with the method of the diagram of Figure 1.

Figure 3 is a flow diagram of another embodiment of our invention.

Figure 4 is a sectional view of a cathode manufactured in accordance with the method of the diagram of Figure 3.

Figure 5 is a flow diagram of still another embodiment of our invention.

Figure 6 is a sectional view of a cathode manufactured in accordance with the method of the diagram of Figure 5.

Thoria cathodes manufactured in accordance with prior methods are characterized by a very low mechanical strength. We have, therefore, endeavored to produce such cathodes having not only improved mechanical strength but also better electron-emitting properties.

Referring to the drawing in detail, and first considering the Figures 1 and 2 embodiment of our invention, which figures illustrate the manufacture of a thermionic cathode consisting of a ceramic sheath of thoria on a base, preferably hollow cylindrical, formed of refractory conductive material such as molybdenum, tantalum, tungsten, other refractory metal, or a refractory alloy thereof.

2

The first step in our improved process may be the precipitation of a heavy gel of thorium hydroxide from a water-soluble salt of thorium. Suitable salts for the purpose are thorium nitrate, $Th(NO_3)_4$, thorium chloride, $ThCl_4$, and thorium sulphate, $Th(SO_4)_2$. The gel is washed thoroughly, preferably with distilled water in order to remove the by-product of the precipitation, such as the ammonium salt resulting from use of a preferred precipitating agent, ammonium hydroxide, NH_4OH.

The gel is then dried, as in an oven, at about 110° C., and crushed to a fine powder, as in a porcelain mortar, so that it will pass a 200 mesh screen. The powdered thorium hydroxide is dehydrated and converted to thoria, as by placing in a molybdenum crucible and firing at between about 1900° C. and 2000° C. in an atmosphere of hydrogen, inert gas, or in a vacuum. Such thoria, by virtue of dehydration from the hydroxide, consists of particles that are much finer than those of fused thoria that has been crushed and sieved, and has an apparent density that compares favorably with fused thoria.

After removal from the hydrogen furnace, the thoria is crushed again and sieved. Some thorium hydroxide gel, freed from ammonium salts or other by-products by washing as explained above, is added to the thoria to form a heavy paste. The paste, indicated at 11, is applied to the cathode base, such as a hollow conductive or metal cylinder 12, as illustrated in Figure 2, for example, and the coated cylinder then rolled on filter paper placed on a smooth hard surface, in order to pack the thoria and make the coating uniform.

The piece is then allowed to dry for several hours at room temperature, after which it is placed in an oven and baked at a temperature of about 110° C. for about one half hour. It is then placed in a hydrogen, inert gas, or vacuum furnace and dehydrated by being slowly brought to a temperature of about 2,000° C. and kept at such a temperature for about 15 minutes. The piece is then brought slowly to room temperature and removed from the furnace. The coated thoria ceramic is relatively hard, being scratched by a knife point with difficulty, and is relatively free from cracks and strains.

As another embodiment of our invention, illustrated in Figures 3 and 4, we have produced an electron emissive cathode consisting of thoria in a metallic matrix, upon a base of molybdenum, tantalum, tungsten, other refractory metal, or refractory alloy thereof, in hollow cylindrical or other desired form. The procedure desirably consists in using a powder of about 200 mesh containing the following ingredients:

1. Thoria
2. A metal such as nickel, chromium, platinum, an alloy or mixture thereof, or the like, in powdered form, which will act as a brazing or alloying agent, and
3. A metal powder which may be of a composition the same or similar to the underlying metal of the electrode base.

The percentage composition of the powder may be varied within a wide range, depending upon the metal used in the powder, the metal of the base, and other factors. Typical compositions used on a base of a refractory metal, such as molybdenum, tantalum, tungsten, or a high melting point alloy thereof are, for example:

1. Thoria, 12.5%; platinum, 10%; molybdenum, 77.5%.
2. Thoria, 25%; nickel, 10%; molybdenum 65%.
3. Thoria, 12.5%; nickel, 10%; molybdenum, 77.5%.
4. Thoria, 50%; chromium, 10%; molybdenum, 40%.
5. Thoria, 10 to 50%; metal or mixtures of the nickel, platinum, chromium group, 1 to 10%; refractory metal corresponding with that of base, remainder.

As a general rule the thoria content may be as high as 50%, while the brazing or alloying metal is usually not greater than 10%. The remaining metal, corresponding with that of the base, may be as high as 77.5%, as indicated by the foregoing examples.

The powder may be applied to the base metal by making a paste with thorium hydroxide gel, or by mixing the powder with a nitrocellulose binder. The application of this paste may be as described in connection with the first embodiment. The coated cylinder or other base may then be dehydrated by being fired at about 2000° C. in hydrogen, inert gas, or in vacuum, as in connection with the first embodiment. The fired piece consists of a base of refractory metal 12[a], as indicated in Figure 4, upon the outer surface of which has been fastened by means of the brazing or alloying metal, a metallic matrix 11[a] having thoria distributed at random throughout its structure.

In order to concentrate the thoria content near the emitting surface, the procedure of the second embodiment, above described, may as illustrated in Figures 5 and 6, be divided into two steps as follows:

1. The application of a rough and porous metallic coating to the base metal by means of two or more fine metal powders, one or more of which may be the same as, or similar in composition to, the underlying base metal, and at least one other of which, constituting the remaining metal, metals and/or alloy or alloys, may act as a brazing or alloying agent.

2. There is superimposed upon this metal coating, a coating of thoria.

The base coating of metal and/or alloy powder may be applied by means of a nitrocellulose binder and fired in a hydrogen, inert gas, or vacuum furnace, at a temperature that will cause the metal particles to sinter together, or braze or alloy to the base metal. This coating is represented by the reference character 13 in Figure 6, as applied to the base 12[b]. The metal coating is kept thick enough so that rough metallic portions thereof will project well into the exterior coating of thoria, which is indicated by the reference character 11[b], and may be applied using a thorium hydroxide gel binder, as in the first embodiment. After the coatings have been applied, the article is allowed to dry, and fired again, as in a hydrogen, inert gas or vacuum furnace, at about 2000° C. to dehydrate the binder to thoria.

The most obvious advantage of the last mentioned procedure over the second embodiment is that here the outside emitting surface is composed almost entirely of thoria.

Although preferred embodiments of our invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. An electrode for electric discharge devices comprising a refractory conductive base carrying a coating of unusually fine particles of thoria bonded to said base by a dehydrated gel of thorium hydroxide.

2. An electrode for electric discharge devices comprising a base of a material of the group consisting of molybdenum, tantalum, tungsten and refractory alloys thereof, carrying a coating of unusually fine particles of thoria bonded to said base by a dehydrated gel of thorium hydroxide.

3. An electrode for electric discharge devices comprising a base of material of the group consisting of molybdenum, tantalum, tungsten, and refractory alloys thereof, to which has been directly applied a coating of thoria bonded to said base by a dehydrated gel of thorium hydroxide.

4. An electrode for electric discharge devices comprising a refractory conductive base carrying a coating of thoria admixed with a relatively small proportion of metal of the group consisting of nickel, chromium, platinum and mixtures thereof and a relatively large proportion of metal of a composition similar to that of the base, and bonded to said base by a dehydrated gel of thorium hydroxide.

5. An electrode for electric discharge devices comprising a refractory conductive base carrying a sintered coating of at least two fine metal powders, at least one of which may be like the metal of said base, applied with a nitrocellulose binder, to which is applied an outer coating of thoria bonded to said sintered coating by a dehydrated gel of thorium hydroxide.

6. The method of bonding thoria to a refractory conductive base in making electrodes, comprising applying to the exterior surface of a refractory conductive base a paste of thoria and thorium hydroxide gel, and dehydrating said gel.

7. The method of making electrodes comprising applying to the exterior surface of a base of refractory material of the group consisting of molybdenum, tantalum, tungsten and refractory alloys thereof, a paste of thoria and thorium hydroxide gel, and firing at about 2000° C. to dehydrate the gel and cause it to bond the thoria to said base.

8. The method of making electrodes comprising applying to a base of material of the group consisting of molybdenum, tantalum, tungsten, and refractory alloys thereof, a coating of thoria

bonded to said base by a gel of thorium hydroxide and dehydrating said gel.

9. The method of making electrodes comprising applying to a base of material of the group consisting of molybdenum, tantalum, tungsten, and refractory alloys thereof, a coating of thoria bonded by a gel of thorium hydroxide, and firing at about 2000° C. to dehydrate the gel and thereby bond the thoria to said base.

10. The method of making electrodes comprising applying to a refractory conductive base, a coating of thoria admixed with a relatively small proportion of metal of the group consisting of nickel, chromium, platinum and mixtures thereof and a relatively large proportion of metal of a composition similar to that of said base, using as a binder a gel of thorium hydroxide, and heating to dehydrate said gel and bond the coating to said base.

11. The method of making electrodes comprising applying to a refractory conductive base, a coating of thoria admixed with a relatively small proportion of metal of the group consisting of nickel, chromium, platinum and mixtures thereof and a relatively large proportion of metal of a composition similar to that of said base of thorium hydroxide made into a paste with a binder, and firing at about 2000° C. to decompose said binder and thereby bond the coating to said base.

12. The method of making electrodes comprising applying to the exterior surface of a refractory conductive base, a coating of at least two fine metal powders, at least one of which may be like the metal of said base, by means of a nitrocellulose binder, applying to said coated base an outer coating of thoria bonded by a gel of thorium hydroxide and heating to dehydrate said gel, and thereby bond the thoria to said coating.

13. An electrode for electric discharge devices comprising a refractory conductive base carrying a coating of thoria admixed with a relatively small proportion of metal of the group consisting of nickel, chromium, platinum, and mixtures thereof, and a relatively large proportion of metal of a composition similar to that of the base, said coating being bonded to said base by a dehydrated gel of thorium hydroxide.

14. An electrode for electric discharge devices comprising a refractory conductive base carrying a sintered coating of at least two fine metal powders, at least one of which may be like the metal of said base, applied with a binder, and to which coating is applied an outer coating of thoria bonded to said sintered coating by a dehydrated gel of thorium hydroxide.

15. An electrode for electric discharge devices comprising a refractory conductive base carrying a coating of 10 to 50% of thoria, from 1 to 10% of a metal of the group consisting of nickel, chromium, platinum, and mixtures thereof, and the remainder consisting of metal of a composition similar to that of the base, said coating being bonded to said base by a dehydrated gel of thorium hydroxide.

16. An electrode for electric discharge devices comprising a refractory conductive base carrying a sintered coating of at least two fine metal powders, at least one of which comprises the major portion and is like the metal of said base, with the remainder selected from the group consisting of nickel, chromium, platinum, and mixtures thereof applied with a nitrocellulose binder, and to which is applied an outer coating of thoria bonded to said sintered base by a dehydrated gel of thorium hydroxide.

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