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(54) **Method of manufacturing an electrode tube cathode.**

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EP 0 421 372 B1

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Description

This invention concerns a method of manufacturing an electrode tube cathode used in cathode ray tubes or other electron tubes.

The cathodes conventionally used in cathode ray tubes or other electron tubes were most often oxide cathodes comprising a base metal having nickel as the principal component and containing also minute quantities of reducing agents such as magnesium and silicon, on which a layer of oxide of alkaline earth metal including Ba was formed. These oxide cathodes were prepared by thermally decomposing an alkaline earth metal carbonate to convert it to the oxide and allowing reducing agents to react with the oxide so as to liberate free atoms, the free atoms then acting as electron donors to promote electron emission.

The reason why this complex procedure was used is that, although Ba has excellent electron emission properties, it is extremely reactive, and reacts with moisture in the air to produce barium hydroxide. As it is very difficult to produce free barium from barium hydroxide in an electron tube, the carbonate was chosen as the starting material due to its chemical stability. The carbonate may be the single element carbonate such as $BaCO_3$ or a multi-element carbonate such as (Ba, Sr, Ca) CO_3, but as the basic mechanism of activation forming the donor is the same for all of the above salts, we shall take the single element carbonate as an example, and describe the mechanism in detail with reference to Fig. 3.

Fig. 3 is a schematic sectional view of a conventional oxide cathode. In the figure, the cathode 1 comprises a cathode sleeve 1a and a cathode cap 1b. A heater 2 is installed inside the cathode sleeve 1a so as to be able to heat the interior of the sleeve. The cathode cap 1b performs the role of a base metal for cathode 1, and a layer of electron emissive substance 3 is formed on the cathode. This layer 3 is initially formed as a barium carbonate layer. The layer 3 is formed for example by spraying, electro-depositing or coating, onto the surface of cathode cap 1b, barium carbonate mixed and stirred into a solution of a resin such as nitrocellulose in an organic solvent. The oxide cathode so formed is assembled in an electron tube, and when the temperature is raised to approx. 1000°C by heater 2 in the evacuation process to place the interior of the tube under vacuum, the barium carbonate of the layer 3 is thermally decomposed according to formula (I) below into barium oxide:

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (I)$$

The carbon dioxide produced by the above reaction is evacuated outside the tube. At the same time, the nitrocellulose or other organic materials are also thermally decomposed into gases, and the gases are evacuated outside the tube together with the carbon dioxide.

Conventional cathodes however suffered from the disadvantage that, when the above reaction (I) took place, an oxidizing atmosphere of carbon monoxide, oxygen or the like was produced in the tube, and the nickel and reducing agents such as Si or Mg which play an important role in the reduction reaction are oxidized on the surface of cathode cap 1b at the same time.

After reaction (I), the interface between electron emission layer 3 and cathode cap 1b is in the state shown in Fig. 4. 11 is the interface between the cathode cap 1b and the barium carbonate layer 3. Fig. 4 is a partial enlarged sectional view to describe the area near the interface 11 between cathode cap 1b and electron emission layer 3 in more detail. In general, minute rod-shaped crystals of barium oxide 8 agglomerate to form crystal grains 9 of several microns - several tens of microns in size, and there are interstices 10 of an appropriate size between these grains which make layer 3 porous. The barium oxide in this layer 3 reacts with reducing agents such as Si and Mg in the cathode cap 1b at the interface 11 with the cap, and is reduced to free barium. This is due to the fact that the reducing agents diffuse and migrate between the grain boundaries 7 of the nickel crystals 6 in cap 1b, and give rise to the following reductions (II) and (III) in the vicinity of the interface 11.

$$2BaO + Si \rightarrow 2Ba + SiO_2 \qquad (II)$$

$$BaO + Mg \rightarrow Ba + MgO \qquad (III)$$

As can be seen from the above reactions (II) and (III), the free barium (Ba) obtained as a result of the reduction of barium oxide acts as an electron donor.

At the same time, barium silicate (Ba_2SiO_4) is also produced by the following reaction (IV):

$$SiO_2 + 2BaO \rightarrow Ba_2SiO_4 \qquad (IV)$$

As described above, the electron donor Ba is produced at the interface 11 between electron emission layer 3 and cathode cap 1b, migrates through the interstices 10 of layer 3, emerges on the surface and fulfils its function of emitting electrons. It also evaporates and reacts with residual CO, CO_2, O_2 and H_2O gases in the electron tube to be eliminated. It is therefore necessary to supply Ba continuously by means of the above reactions, and these reductions take place continuously during the operation of the cathode. To ensure that an equilibrium is maintained between supply and elimination of Ba, the cathode is usually operated at a high temperature of approx. 800°C. While the cathode is being operated, the reaction products 12 of reactions (II) and (IV), that is SiO_2, Ba_2SiO_4 or the like are produced at the interface 11 of layer 3 and cap 1b, and accumulate continuously at the interface 11 or at the crystal grain boundaries 7. When the reaction products 12 accumulate at the interface 11, however, layer 3 and cap 1b tend to join together at the interface. The result is that reaction products 12 provide a barrier (generally referred to as an intermediate layer) to the passage of Si or the like, reactions (II) and (III) tend to slow down, and the pro-

duction of electron donor Ba becomes difficult. Further. as the intermediate layer has a high resistance, it interferes with the free flow of emission electrons.

In conventional electron tube cathodes, therefore, in the decomposition of carbonates and reduction reactions to produce electron emission donors, the reducing agents were oxidized and reaction products 12 accumulated. Also. during operation of the cathode, reaction products 12 accumulated in the vicinity of the interface 11 between cathode cap 1b and electron emission layer 3, and in particular at the nickel crystal grain boundaries 7 in the vicinity of the surface of cap 1b. An intermediate layer was therefore formed and prevented the passage of Si or the like, and as this intermediate layer had a high resistance, it interfered with the flow of electron emission current and gradually obstructed the diffusion of reducing agents into layer 3. Consequently, it was impossible to obtain satisfactory electron emission properties with a high current density over a long period of time.

To overcome the above problems, Japanese Patent Application Kokai Publication No. 61-271732 (referred to hereafter as the prior art) was proposed. According to this prior art, powder of scandium oxide is dispersed in the electron emission layer to dissociate reaction products such as Ba_2SiO_4, and thereby break up the intermediate layer. As a result, the passage of reducing agents such as Si between the crystal grain boundaries 7 is facilitated, reactions (II) and (III) are promoted, and the electron donor Ba is produced more easily.

In the scandium oxide dispersed cathode of the prior art, the production of electron donor Ba is promoted and electron emission properties are improved. As the electron emission layer has a high density, however, when the cathod ray tube was switched on and off, a large stress was produced due to the difference in thermal expansion coefficient between this layer and the cathode cap. This sometimes caused the electron emission layer to blister and swell up in places at the interface with the cap, and in severe cases even caused it to peel away completely.

We shall explain the swelling phenomenon with reference to Fig. 2. Fig. 2 is a schematic front view of the surface of the cathode cap after the electron emission layer of the cathode has been carefully peeled off in a life test. In the figure, the peripheral area A is the part corresponding to barium silicate which is one of the above reaction products 12, and the central part B corresponds to nickel. The presence of both the barium silicate and nickel was confirmed by X-ray diffraction.

This indicates that in the peripheral area A, reaction (IV) occurred at the interface between the base metal of the cathode cap and the electron emission layer; whereas in the central area B, no reaction occurred as the base metal and the electron emission layer are not in contact. It may thus be conjectured that local swelling of the electron emission layer took place in the central area.

SUMMARY OF THE INVENTION

This invention was conceived to overcome the above problem. It aims to provide a method of manufacturing an electron tube cathode with superior electron emission properties wherein the electron emission layer does not swell up or peel away at the interface with the cathode cap.

The inventional method starts from the following method described in the above cited prior art (JP 61-271732):

forming a suspension by suspending an alkaline earth metal carbonate powder and scandium oxide powder in an organic solvent solution of nitrocellulose, and regulating the particle size of said powders;

applying said suspension onto a nickel base metal surface so that after evaporation of the solvent a layer of alkaline earth metal carbonate is formed; and

heating said layer of alkaline earth metal carbonate in vacuum to a temperature of 800 - 1200 °C to decompose said carbonate into oxide, thereby forming a porous electron emission layer wherein scandium oxide is dispersed in an alkaline earth metal oxide on said nickel base metal surface.

The inventional method is characterized in that the alkaline earth metal carbonate layer has a density not greater than 2 mg/mm^3.

According to this invention, the electron emission layer is formed by the thermal decomposition of the alkaline earth metal carbonate layer of coating density not greater than 2 mg/mm^3, so the electron emission layer has a coarse porous structure. As a result, the stress due to the difference in thermal expansion coefficient between the electron emission layer and the base metal is reduced. This appears to suppress the swelling of the layer and the peeling of the layer away from the surface of the base metal, so that a highly reliable electron tube cathode is obtained.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic view showing the structure of one embodiment of the electron tube cathode of this invention.

Fig. 2 is an enlarged frontal view schematically showing the surface of the cathode cap where part of the electron emission substance has swollen up.

Fig. 3 is a schematic structural view showing one example of a conventional oxide cathode.

Fig. 4 is a partial enlarged sectional view to provide a detailed description of the area near the interface between the base metal and the electron emission layer.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

We shall now describe one embodiment of this invention in more detail with reference to the drawings.

Fig. 1 is a schematic view of the structure of one embodiment of the electron tube cathode manufactured by this invention. In the figure, components which are identical to those of the conventional example shown in Fig. 3 are given the same numbers, and their description is omitted.

In Fig. 1, 30 is a electron emission layer, and it is formed on the surface of a cathode cap 1b comprising nickel base metal and Si or Mg as reducing agents. This electron emission layer 30 has an alkaline earth metal oxide as its principal constituent, and scandium oxide is dispersed in it. The alkaline earth metal oxide is preferably barium oxide, but it may also be a ternary oxide containing Sr and Ca in addition to Ba. Further, the proportion of the scandium oxide is preferably in the range 0.1 - 20 weight %.

The electron emission layer of the above electron tube cathode must be formed from an alkaline earth metal carbonate layer of coating density not greater than 2 mg/mm^3, but the coating density is preferably not greater than 1.6 mg/mm^3 and more preferably 0.8 mg/mm^3.

The electron tube cathode may be manufactured advantageously by the following method.

Firstly, a powder of an alkaline earth metal carbonate and scandium oxide powder are suspended in an organic solvent solution of nitrocellulose, and the particle size of the powders is then adjusted so as to obtain a suitable suspension.

The above suspension may be similar to conventional suspensions. It may for example be prepared by blending barium carbonate and scandium oxide with a solution of a resin such as nitrocellulose in an organic solvent in the desired weight % (calculated on the assumption that the carbonate will be converted to oxide), and then crushing the product in a ball mill or other device to obtain a suitable particle size. The barium carbonate may also be a ternary carbonate containing Sr and Ca in addition to Ba.

Next, a layer of alkaline earth metal carbonate is formed by applying the, above suspension to a nickel base metal surface such that the coating density is not greater than 2 mg/mm^3. As soon as the suspension is applied to the surface, the organic solvent evaporates, and leaves an alkaline earth metal carbonate layer comprised of barium carbonate, scandium oxide and nitrocellulose. In this specification, therefore, the term "coating density" refers to the density of this alkaline earth metal carbonate layer formed from the suspension. Further, it is preferable that the suspension is applied such that the coating density of the layer is not greater than 1.6 mg/mm^3, and more preferable that it is not greater than 0.8 mg/mm^3.

The alkaline earth metal carbonate layer is normally formed by spraying. Apart from spraying, electro-deposition or a coating method such as spin coating or blade coating may also be used. The term "apply" or "application" as used in the appended claims should be construed to cover "spraying", "electro-deposition", "coating", "spray coating", "blade coating" and other types of film formation.

There is no particular restriction on the method used to form the layer, but spraying is to be preferred as it gives a porous film which is important to obtain good contact between the cathode cap and electron emission layer, and as good electron emission properties are obtained.

Next, the alkaline earth metal carbonate layer is heated in vacuum to a temperature of 800 - 1200°C to decompose the carbonate to oxide, and a porous electron emission layer of alkaline earth metal oxide containing a dispersion of scandium oxide is thus formed on the surface of the nickel base metal surface.

The heating of the alkaline earth metal carbonate layer is preferably carried out at a temperature of no less than 1000°C for several 10 seconds to several minutes.

Cathodes were manufactured with different coating densities of the alkaline earth metal carbonate layer on the surface of the cap base metal, assembled in cathode ray tubes, and subjected to operating tests. The film thickness of the alkaline earth metal carbonate layer was approx. 100 microns.

After 2000 hours had elapsed from the beginning of the operating tests, the cut-off voltage determined by the gap between the cathode and a control electrode was measured, and the following results were obtained.

For cathodes where (a) the coating density exceeded 2 mg/mm^3, abnormal values of cut-off voltage were found which suggested that the electron emission layer had swelled up. When the test cathode ray tubes which had shown these abnormal values were broken, the cathode removed and the electron emission layer observed, the layer was found to have a swelling in the part where the emission electron current was extracted. For cathodes (b) where the coating density did not exceed 1.6 mg/mm^3, on the other hand, there were no abnormalities of cut-off voltage at all. Cathodes (c), where the coating density was 0.8 mg/mm^3, also gave a stable electron emission current and were the most desirable from the viewpoint of performance.

From the results of (a) - (c) above, it is clearly necessary that the coating density of the alkaline earth metal carbonate layer which forms electron emission layer 30 is not greater than 2 mg/mm^3, preferable that it is not greater than 1.6 mg/mm^3, and more preferable that it is not greater than 0.8 mg/mm^3.

The coating density of the alkaline earth metal layer which forms electron emission layer 30 in the cathode of the above embodiment is not greater than 2 mg/mm^3. Layer 30 therefore has a coarse porous structure, it has higher flexibility, and the stress arising from the difference in thermal expansion coefficient between the emission layer 30 and the cathode cap 1b is smaller. The swelling of said layer 30 on the surface of cathode 1b therefore does not occur.

It may be conjectured that when electron emission layer 30 is joined to the surface of the cathode cap 1b, reaction (IV) occurs, and reaction products 12 accumulate in the region of the interface 11 so as to form an intermediate layer. In the electron cathode tube of the above embodiment, however, reaction products 12 decompose and the formation of an intermediate layer is suppressed for the following reason.

During operation of the cathode, the reaction expressed by formula (IV) above does take place. Barium silicate (Ba_2SiO_4), one of the reaction products 12, is however decomposed by scandium oxide (Sc_2O_3) and nickel in the following reactions (V) and (VI):

$$Sc_2O_3 + 10Ni \rightarrow 2ScNi_5 + 3O \quad (V)$$

$$9Ba_2SiO_4 + 16ScNi_5 \rightarrow 4Ba_3Sc_4O_9 + 6Ba + 9Si + 80Ni \quad (VI)$$

The above reactions (V) and (VI) show that even if reaction products 12 such as barium silicate do accumulate in the region of the interface 11 between electron emission layer 30 and cathode cap 1b or the crystal grain boundaries 7, they are broken up and destroyed rapidly by the scandium oxide dispersed in electron emission layer 30.

Due to this decomposing action of scandium oxide, the interstices through which reducing metals such as Si pass are conserved, and the production of Ba which is an electron emission donor is promoted.

The electron cathode tube of this embodiment can therefore be operated without the electron emission layer swelling up, and as a high resistance intermediate layer of barium silicate and other reaction products is not easily formed, there is no obstruction of the electron emission current and the tube can be operated at a high current density.

As described above, the electron cathode of this invention has a constant, stable electron emission without any swelling or peeling of the electron emission layer even when operated for long periods of time.

Further, in the above electron cathode tube, no intermediate layer is formed in the region between the cathode cap and the electron emission layer. The generation of the electron emission donor Ba is thereby promoted, and the electron emission current is not obstructed.

The above electron tube cathode may therefore be used at a high current density over long periods of time.

Claims

1. A method of manufacturing an electrode tube cathode comprising:

   forming a suspension by suspending an alkaline earth metal carbonate powder and scandium oxide powder in an organic solvent solution of nitrocellulose, and regulating the particle size of said powders;

   applying said suspension onto a nickel base metal surface so that after evaporation of the solvent a layer of an alkaline earth metal carbonate is formed;

   heating said layer of alkaline earth metal carbonate in vacuum to a temperature of 800 - 1200°C to decompose said carbonate into oxide, thereby forming a porous electron emission layer wherein scandium oxide is dispersed in an alkaline earth metal oxide on said nickel base metal surface; said method being characterized in that: the alkaline earth metal carbonate layer has a density not greater than 2 mg/mm^3.

2. A method as in claim 1 wherein the alkaline earth metal carbonate is barium carbonate.

3. A method as in claim 2 wherein said barium carbonate is a ternary carbonate containing also Sr and Ca.

4. A method as in claim 1, 2 or 3 wherein the coating density of said layer of alkaline earth metal carbonate is not greater than 1,6 mg/mm^3.

5. A method as in claim 4 wherein the coating density of said layer of alkaline earth metal carbonate is not greater than 0,8 mg/mm^3.

6. A method as in any of the claims 1 to 5 wherein the application of said suspension is carried out by spraying.

7. A method as in any of the claims 1 to 6 wherein the heating of said layer of alkaline earthmetal carbonate is carried out in vacuum at a temperatur of not less than 1000 °C.

8. A method as in claim 7 wherein the heating of said layer of alkaline earth metal carbonate is carried out for a period of from several 10 seconds to several minutes.

Patentansprüche

1. Verfahren zum Herstellen einer Elektrodenröhren-Kathode, umfassend:

   Bilden einer Suspension durch Suspen-

dieren eines Erdalkalimetallkarbonatpulvers und Scandiumoxidpulvers in einer Nitrozelluloselösung mit organischem Lösungsmittel, und Regulieren der Partikelgröße des Pulvers;

Aufbringen der Suspension auf eine Nickelbasis-Metalloberfläche, so daß nach der Verdampfung des Lösungsmittels eine Schicht eines Erdalkalimetallkarbonats ausgebildet wird;

Erhitzen dieser Erdalkalimetallkarbonatschicht im Vakuum auf eine Temperatur von 800 bis 1200 °C zur Zersetzung des Karbonats in Oxid, wodurch eine poröse Elektronenemissionsschicht gebildet wird, in der Scandiumoxid in einem Erdalkalimetalloxid auf der Nickelbasis-Metalloberfläche dispergiert ist; welches Verfahren dadurch gekennzeichnet ist, daß:

die Erdalkalimetallkarbonatschicht eine Dichte nicht größer als 2 mg/mm³ aufweist.

2. Verfahren nach Anspruch 1, in welchem das Erdalkalimetallkarbonat Bariumkarbonat ist.

3. Verfahren nach Anspruch 2, in welchem das Bariumkarbonat ein ternäres auch Sr und Ca enthaltendes Karbonat ist.

4. Verfahren nach Anspruch 1, 2 oder 3, in welchem die Beschichtungsdichte der Schicht aus Erdalkalimetallkarbonat nicht größer als 1,6 mg/mm³ ist.

5. Verfahren nach Anspruch 4, in welchem die Beschichtungsdichte der Schicht aus Erdalkalimetallkarbonat nicht größer als 0,8 mg/mm³ ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem die Aufbringung der Suspension durch Spritzen (Sprühen) erfolgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, in welchem die Erhitzung der Erdalkalimetallkarbonatschicht im Vakuum bei einer Temperatur von nicht weniger als 1000 °C ausgeführt wird.

8. Verfahren nach Anspruch 7, in welchem die Erhitzung der Erdalkalimetallkarbonatschicht über eine Periode von einigen 10 Sekunden bis einigen Minuten ausgeführt wird.

Revendications

1. Procédé de fabrication d'une cathode pour tube électronique comprenant:

la formation d'une suspension d'une poudre de carbonate de métal alcalino-terreux et d'une poudre d'oxyde de scandium dans une solution de solvant organique de nitrocellulose, et la régulation de la dimension des particules desdites poudres;

l'application de ladite suspension sur une surface de métal de base en nickel de telle sorte qu'après l'évaporation du solvant une couche d'un carbonate de métal alcalino-terreux est formée;

le chauffage de ladite couche de carbonate de métal alcalino-terreux sous vide à une température de 800-1200°C pour décomposer ledit carbonate en oxyde, afin de former une couche d'émission d'électrons poreuse dans laquelle l'oxyde de scandium est dispersé dans un oxyde de métal alcalino-terreux sur ladite surface de métal de base en nickel; ledit procédé étant caractérisé en ce que:

la couche de carbonate de métal alcalino-terreux a une densité non supérieure à 2 mg/mm³.

2. Procédé selon la revendication 1 dans lequel le carbonate de métal alcalino-terreux est du carbonate de baryum.

3. Procédé selon la revendication 2 dans lequel le carbonate de baryum est un carbonate ternaire contenant aussi du Sr et du Ca.

4. Procédé selon la revendication 1, 2 ou 3 dans lequel la densité de revêtement de ladite couche de carbonate de métal alcalino-terreux n'est pas supérieure à 1,6 mg/mm³.

5. Procédé selon la revendication 4 dans lequel la densité de revêtement de ladite couche de carbonate de métal alcalino-terreux n'est pas supérieure à 0,8 mg/mm³.

6. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel l'application de ladite suspension est effectuée par vaporisation.

7. Procédé selon l'une quelconque des revendications 1 à 6 dans lequel le chauffage de ladite couche de carbonate de métal alcalino-terreux est effectué sous vide à une température non inférieure à 1000°C.

8. Procédé selon la revendication 7 dans lequel le chauffage de ladite couche de carbonate de métal alcalino-terreux est effectué pendant une période comprise entre plusieurs dizaines de secondes et plusieurs minutes.

FIG. 1

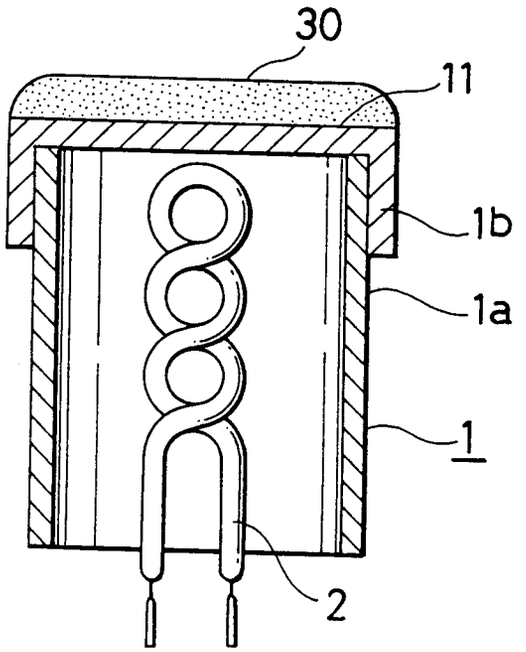


FIG. 2

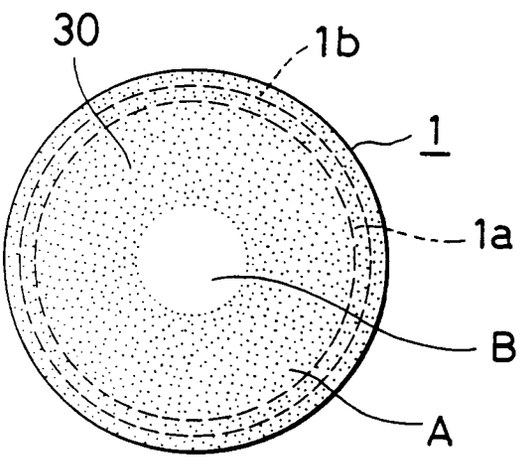


FIG.3

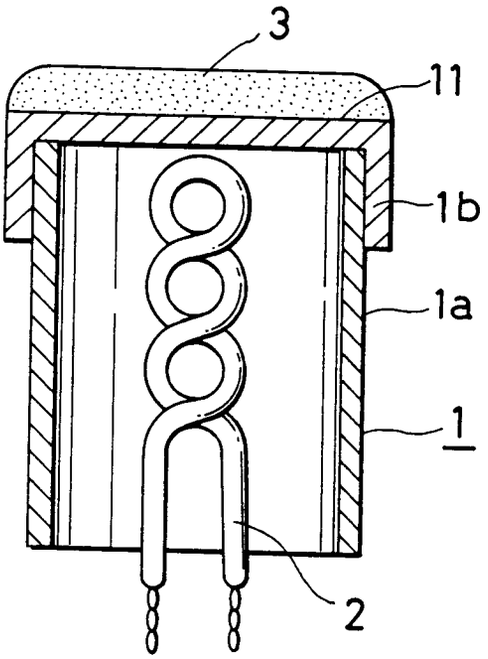


FIG.4

