

# PATENT SPECIFICATION

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## (54) DIRECTLY HEATED OXIDE CATHODE

5 (71) We, HITACHI LTD., a corporation organized under the laws of Japan of 5-1, 1-Chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a directly heated oxide cathode, and more particularly to a directly heated oxide cathode structure having a metal core deposited with an oxide of an alkaline earth metal.

15 A cathode is used in, for example, a receiving tube, discharge tube or cathode-ray tube. The cathode used in a cathode ray tube must act quickly to display images instantaneously, that is, its starting time must be quick.

20 On the other hand, the cathode is classified into two types, that is, indirectly heated oxide cathode and directly heated oxide cathode. In the indirectly heated oxide cathode the starting time is almost 20 seconds, whereas in the directly heated oxide cathode, the starting time may be as short as 1 to 2 seconds. Thus, the directly heated oxide cathode is most suitable as a quick start type.

25 The present invention provides in a directly heated oxide cathode of the type having: (i) a metal core capable of generating heat when an electric current is passed therethrough, the metal core being of an alloy containing Ni as host material, (ii) a top coating of an electron emissable oxide of an alkaline earth metal deposited on one surface of the metal core and (iii) an intermediate coating of a metal powder deposited on the cathode core beneath the top coating and sintered to the cathode core, the metal powder being Ni, Co, an Ni-Co alloy or an alloy containing Ni, Co, or Ni-Co as major component, an improvement which comprises a further coating of metal powder which is Ni, Co, an

50 Ni-Co alloy or an alloy containing Ni, Co, or Ni-Co as major component, respectively deposited on the surface of the cathode core opposite to the surface bearing the intermediate and top coatings.

55 The present invention also provides a method of manufacturing the cathode of this invention which comprises depositing the metal powder on two opposite surfaces of the metal core, sintering the metal powder and depositing a coating of the electron emissable oxide of an alkaline earth metal on one surface of the metal core which bears a coating of the metal powder.

60 The present invention will now be described, by way of example, with reference to the accompanying drawings in which:

65 Figure 1 is a cross-sectional, enlarged view of one example of the conventional directly heated oxide cathode structure;

70 Figure 2 is a characteristic diagram showing changes in the deformation of base metal with time;

75 Figure 3 is a characteristic diagram showing changes in the cut-off voltage with time; and

80 Figure 4 is a cross-sectional, enlarged view of one embodiment of the present directly heated oxide cathode structure.

85 Figure 1 shows a metal core 1 capable of generating heat when a current is passed therethrough, which is formed, for example, from a Ni alloy containing a high melting point metal capable of increasing mechanical strength, such as W, and a reducing agent such as Mg, Al, Si, and Zr. A deposit of an oxide 2 of an alkaline earth metal having an electron emissability is applied onto the metal core 1, the surface of the base metal to which the oxide 2 is applied being roughened by grains of powder 3 of particle sizes of a few  $\mu\text{m}$  suitably up to 20  $\mu\text{m}$  containing Ni as major component. The grains of powder 3 are, for example, sprayed onto the metal core in an amount of a few milligrams per 1  $\text{cm}^2$  of the

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metal core and then sintered in a vacuum or in a hydrogen gas atmosphere. The metal core 1 can then be firmly coated with the oxide 2.

5 However, in such a directly heated oxide cathode structure, a diffusion rate of the Ni powder 3 into the metal core 1 is increased with the heat generation of the metal core 1, and consequently a strain develops at the 10 surface of the metal core 1 at the side in contact with the Ni powder 3, thereby deforming the metal core 1 towards the grid electrode side into a convex, spherical shape. The curvature of deformation, that is, reciprocal number of radius R (cm), is increased with increasing periods of use of the cathode structure, as is shown in Figure 2, where the time (min.) is plotted on the abscissa, and the log of the reciprocal number of radius R is plotted on the ordinate as deformatuon. Curve A is plotted for the metal core temperature of 950°C, curve B for 1000°C, and curve C for 1050°C. As a result, the distance between the oxide 2 and a grid electrode is gradually changed, and consequently the cutoff voltage is changed. In Figure 3, a change  $\Delta E_{co}$  in the cutoff voltage  $E_{co}$  is plotted against time. Thus, in the case of a color cathode-ray tube based on such a cathode structure, the operating point of a three electron gun changes during use of the cathode-ray tube, and white balance is lost. If the deformation of the metal core 1 is further increased, the oxide 2 will peel off.

15 In the cathode of the present invention, metallic powders are deposited also onto the opposite surface of the metal core 1 so that diffusion of the metal of the powder occurs at both sides of the metal core 1.

20 In Figure 4, one embodiment of a cathode structure of direct heating type according to the present invention is shown, where the reference numerals 1, 2 and 3 have the same meanings as in Figure 1. In Figure 4, a powder 30 comprising for example Ni as major component, is deposited onto the surface of the metal core side opposite to the surface to which the powder 3 is deposited. The metal powder 3 is Ni, Co, an Ni-Co alloy or an alloy containing Ni, Co or Ni-Co as major component, and the metal powder 30 is accordingly Ni, Co, an Ni-Co alloy or an alloy containing Ni, Co or Ni-Co as major component, respectively.

25 The powder 30 is sintered at the same time as the powder 3 is sintered. In a preferred cathode, carbonyl nickel powder usually having a particle size of a few  $\mu\text{m}$  is deposited as powder 3 in a deposition amount of 1.5  $\text{mg/cm}^2$ , and the same carbonyl nickel powder having a particle size of a few  $\mu\text{m}$  is deposited on the opposite surface of the metal core 1 as powder 30 in the same deposition amount of

30 1.5  $\text{mg/cm}^2$ . In such a cathode structure, Ni diffusion proceeds at both sides of the metal core 1 by the heat generation of the metal core 1, and the strains developed and added to the metal core 1 can be balanced at both face and back surfaces of the metal core 1, thereby minimizing the deformation. That is, loss of the white balance and peeling of the oxide can be substantially prevented thereby.

35 The metal powders 3 and 30 to be deposited onto the face and back surfaces of the metal core 1 can be powders of nickel simple substances as mentioned above powders of Co simple substance, powders of Ni-Co alloy, or powders of alloys containing Ni, Co or Ni-Co as major component. The powders can also contain a small amount of elements having no adverse effect upon the cathode itself, such as a reducing agent. In the case of powders of Ni-Co alloy, a mixing ratio of Ni to Co can be selected as desired.

40 As to the amount of the powders deposited, 1.5  $\text{mg/cm}^2$  has been mentioned. When the amount deposited is less than 0.3  $\text{mg/cm}^2$ , there is a risk of oxide peeling, and when the amount deposited exceeds 4.0  $\text{mg/cm}^2$ , there is a tendency for there to be a large deformation of the cathode and a large fluctuation in the cathode temperature. Thus, the practical range of deposition of the powders is generally 0.3 to 4.0  $\text{mg/cm}^2$ .

45 Even in the foregoing cathode structure, there is a disadvantage that a reducing agent to be supplied from the metal core to the oxide prepared by heating and decomposing a carbonate in vacuum is quickly decreased, because the metal core of a directly heated oxide cathode structure is thinner than that of an indirectly heated oxide cathode, and a sufficient amount of the reducing agent cannot be stored in the metal core. That is, the reducing agent cannot be supplied sufficiently, and the life of the cathode will be shortened.

50 According to a further embodiment of the present invention, a reducing agent, for example, Zr, is contained in the metal powders. This enables a sufficient supply of the reducing agent to the oxide thereby improving the electron emissability of the oxide.

55 In the cathode containing Zr in the metal powder, reduction of the oxide takes place according to the following reaction:

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$$3\text{BaO} + \text{Zr} \longrightarrow \text{BaZrO}_3 + 2\text{Ba}\uparrow$$

65 The reducing agent Zr may be supplied both from the metal core and from the metal powders at the front and back surfaces of the metal core continuously for a long period of time, and thus the oxide can maintain its electron emissability and its life for a longer period of time. The amount of

Zr to be added to the metal powders is not restricted to a solid solution range of Zr in the alloy powders. The solid solubility of Zr in an Ni-based alloy is generally 0.2 to 0.3% by weight, but Zr in excess of the solid solubility exists as an intermetallic compound in the powders. When Zr within the solid solubility range is consumed according to the reaction for reducing the oxide, the intermetallic compound is then decomposed to keep Zr in the solid solution phase at 0.2 to 0.3% by weight, and thus the intermetallic compound acts as a storage house. Therefore, the powders containing Zr above its solid solution range continue to supply Zr at the same rate as that of the powders containing 0.2 to 0.3% by weight of Zr until the intermetallic compound disappears. Thus, such powders can keep the reduction going for a very long period of time and can maintain the electron emissability of the oxide for a longer period of time.

As to the amount of the reducing agent Zr in the powders, an amount of less than 0.04% by weight of Zr is not substantially effective for the prolongation of the cathode life, and its upper limit is determined by the point at which it becomes incapable of forming a lower melting point intermetallic compound. Thus, the practically preferable range of Zr is 0.1 to 10% by weight.

In the foregoing embodiment, the description has been restricted to the use of powders of Ni-Zr alloy, but it is also possible to use a mixture of a powder of an alloy free from Zr and a powder containing Zr to adjust the Zr content, practically the same effect can be obtained using this mixture as when powder of a Zr alloy having a lower Zr concentration is used.

Other reducing agents than Zr, for example, C, Mg, Si and Al, have a similar effect in principle to that of Zr, but side reactions which are not encountered in the case of Zr sometimes occur, and thus a sufficient care should be taken when using these other reducing agents. That is, for example, in the case of C, it is difficult to obtain powders in which C in the amount in excess of the solid solubility (approximately 0.1% by weight) is uniformly distributed, and special precaution must be taken to ensure that the quality is even. In the case of Mg, an increase in Mg content gives rise to vigorous evaporation of Mg, and a low melting point compound is more liable to form. Thus, an Mg alloy at a Mg concentration as low as possible should be used. The practical range for Mg content is generally 0.1 to 1.0% by weight. In the case of Si and Al, their solid solution limits are as high as about 7% by weight, and when powders having a higher Al or Si content are used, the supply rate of

Al or Si is excessively high, increasing the resistance of the intermediate powder layer, and consequently adversely effecting the function of the oxide cathode. Thus, in using these reducing agents, it is necessary to take into account the characteristics of the cathode they are to be applied to.

#### WHAT WE CLAIM IS:—

1. In a directly heated oxide cathode of the type having: (i) a metal core capable of generating heat when an electric current is passed therethrough, the metal core being of an alloy containing Ni as host material, (ii) a top coating of an electron emissable oxide of an alkaline earth metal deposited on one surface of the metal core and (iii) an intermediate coating of a metal powder deposited on the cathode core beneath the top coating and sintered to the cathode core, the metal powder being Ni, Co, an Ni-Co alloy or an alloy containing Ni, Co or Ni-Co as major component, an improvement which comprises a further coating of metal powder which is Ni, Co, an Ni-Co alloy or an alloy containing Ni, Co or Ni-Co as major component, respectively, deposited on the surface of the cathode core opposite to the surface bearing the intermediate and top coatings. 75
2. A directly heated oxide cathode according to claim 1, wherein the metal core contains W and a reducing agent. 90
3. A directly heated oxide cathode according to claim 2, wherein the reducing agent is Mg, Al, Si or Zr. 100
4. A directly heated oxide cathode according to any one of the preceding claims wherein the metal powder contains a reducing agent.. 105
5. A directly heated oxide cathode according to claim 4, wherein the reducing agent is C, Mg, Si or Al. 110
6. A directly heated oxide cathode according to claim 4, wherein the reducing agent is Zr. 115
7. A directly heated oxide cathode according to claim 4, 5 or 6, wherein the metal powder is an alloy containing Ni as major component. 120
8. A directly heated oxide cathode according to claim 7, wherein the alloy contains 0.1 to 10% by weight of Zr. 125
9. A directly heated oxide cathode according to claim 4, 5 or 6, wherein the metal powder is a mixture of a powder of an alloy containing a reducing agent and Ni as major component and a powder of an alloy containing Ni as major component which alloy is free from a reducing agent.
10. A directly heated oxide cathode according to any one of claims 1 to 4, wherein the metal powder is deposited in an amount of 0.3 to 4.0 mg/cm<sup>2</sup>.

11. A directly heated oxide cathode according to any one of claims 5 to 9 wherein the metal powder is deposited in an amount of 0.3 to 4.0 mg/cm<sup>2</sup>.

5 12. A directly heated oxide cathode substantially as hereinbefore described with reference to Figure 4 of the accompanying drawings.

10 13. A method of manufacturing a directly heated oxide cathode as claimed in claim 1 which method comprises depositing the metal powder on two opposite surfaces of

the metal core, sintering the metal powder and depositing a coating of the electron emissable oxide of an alkaline earth metal on one surface of the metal core which bears a coating of the metal powder. 15

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14, South Square,  
Gray's Inn,  
London, WC1R 5EU.

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FIG. 1

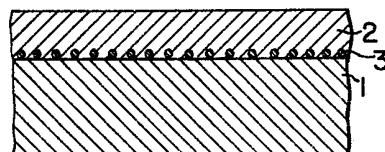


FIG. 2

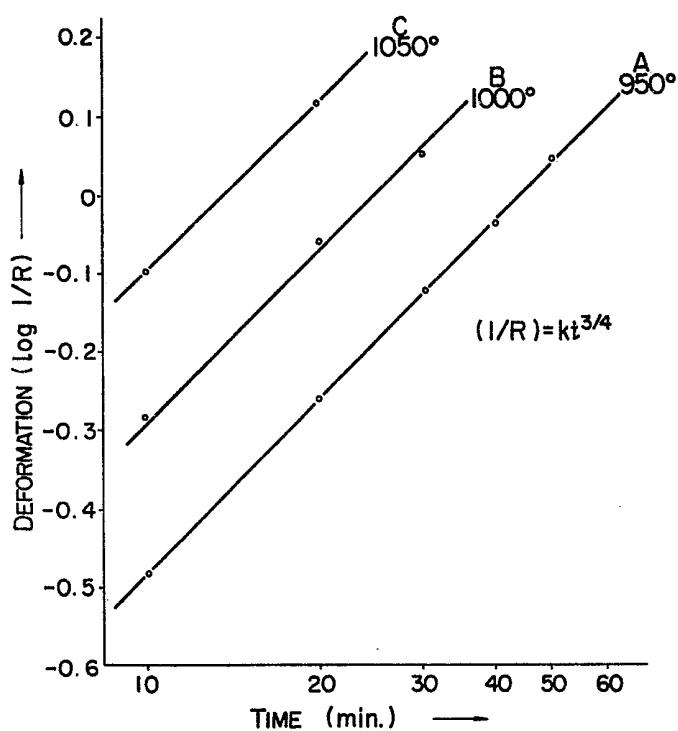


FIG. 3

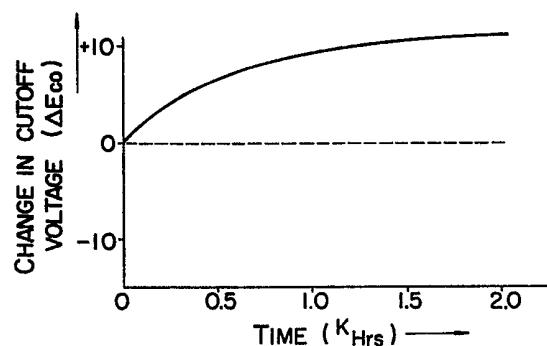


FIG. 4

