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(54) BASE METAL PLATE FOR DIRECTLY HEATED OXIDE CATHODE AND METHOD FOR PREPARING THE SAME

(71) We, HITACHI LTD, a corporation organised 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:-

This invention relates to a base metal plate for a directly heated oxide cathode for electron tubes.

In the field of camera tubes, cathode-ray tubes for various purposes including television picture tubes, development of the so-called quick start electron tubes, capable of being put in operation within about one second after an electric source switch is turned on, have been recently in great demand, and various systems have been proposed for realizing the quick-start electron tubes.

The present invention provides a base metal plate for the so-called directly heated oxide cathode.

The present invention will be described in detail, referring to the accompanying drawings in which

Figure 1 is a cross-sectional, enlarged view of a directly heated oxide cathode.

Figure 2 is a graph showing changes in electron emission with time for known base metal plates for directly heated oxide cathodes containing very small amounts of various previously well known reducing elements and having different plate thick-

nesses.

Figure 3 is a graph showing the relationship between the contents of Mg, Zr, Al, and Si added to the base metal plates for a directly heated oxide cathode and the period of electron emission.

As shown schematically in Figure 1, a directly heated oxide cathode is comprised of a base metal plate 1 and a layer 2 of oxide of an alkaline earth metal, an electron emitting material, the layer having a thickness of 50 to 100 μ . An electric current is directly passed through the base metal plate 1 from one end plate 3 to another to heat the base metal plate 1 and also heat the layer 2 of alkaline earth metal oxide, thereby bringing about thermionic emission from oxide layer 2.

In producing a directly heated oxide cathode, the most important problem is whether or not a suitable base metal plate can be obtained. The characteristics required for the base metal plate are as follows:

(A) That sufficient electron emission can be effected for a long period of time (in practice, at least 20,000 hours).

(B) That there should be sufficient strength at an elevated temperature, for example, enough to assure supporting the oxide layer having a thickness of at least 50 μ at an operating temperature of 750° to 850°C without any deformation or breakage occurring.

(C) That the electric resistivity should

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be large enough to prevent any deviation of the cathode temperature from its normal operating temperature due to the contact resistance, of the electron tube socket or others.

To meet the foregoing requirements, a Ni-Co alloy has previously been proposed, but is not now used in practice because of its low strength at elevated temperature, and its small electric resistivity. Furthermore, Ni alloys containing 20 to 30 % by weight of W and trace amounts of a reducing element such as Mg, Si, Al or Zr have been also proposed for this purpose, but they cannot maintain electron emission over a long enough period of time, as will be described later, although they do have satisfactory strength at elevated temperature, and sufficient electric resistivity.

If it is possible to use a directly heated oxide cathode whose base metal plate has a thickness similar to that of the indirectly heated oxide cathode, that is, about 0.2 to about 1.2 mm, a very small amount, for example, of a reducing element could be added to the metal for a base plate, for example, Ni, as in the indirectly heated oxide cathode, and the resulting base metal could be used, as in the ordinary indirectly heated oxide cathode, to provide a satisfactory directly heated oxide cathode, but such is quite impossible to do for the following reasons.

As is obvious from electro-heating alloys, the electrical resistivity of the metal at the operating temperature of an oxide cathode, that is, about 750° to about 850°C, is generally not more than 150 $\mu\Omega$ cm. It is therefore necessary to reduce the cross-sectional area of the base metal plate to the current flow so as to produce a sufficiently large electrical resistance of the base metal than the contact resistance of electron tube socket, and also to assure a stable cathode temperature in a practical range of current for heating the cathode of an electron tube, for example, less than about 1A in the case of television picture tube. However, the electron-emitting face of the oxide cathode layer (the face designated by numeral 4 in Figure 1) must be of a sufficient area, for example, more than that of a disc having a diameter of 1.0 mm in the case of a television picture tube, to effect normal operation of the electron tube. Therefore, unless the thickness of the base metal plate is made as small as possible, the electrical resistance of the base metal plate for heating the cathode cannot be increased sufficiently to permit the electron tube to perform its normal function. We find that it is impossible to design a cathode capable of operating normally unless the thickness of the base metal plate is made as small as possible, for example, not more than about 30 μ , or not

more than 50 μ at most, in the case of color television picture tubes. Therefore, for a directly heated oxide cathode to be used in camera tubes, cathode-ray tubes for various purposes including television picture tubes, it is necessary that the thickness of the base metal plate be not more than 50 μ , preferably not more than 30 μ . However, for a base metal plate having such a small thickness, a plate containing only trace amounts of the reducing elements, as in the conventional indirectly heated oxide cathode, cannot maintain electron emission from the electron-emitting oxide deposited on the base metal plate for a sufficiently long period of time.

For example, cathodes comprised of a base metal plate of a Ni-W alloy containing 27.5 % by weight of W and trace amounts of Mg, Zr, Al or Si as reducing elements, proposed earlier, and a layer of alkaline earth metal oxide deposited on said base metal plate, are actually inserted in color television picture tubes as a directly heated oxide cathode to measure the electron emission and duration of electron emission. That is, in an oxide cathode comprised of a base metal plate 1 and a layer 2 of alkaline earth metal oxide deposited on the base metal plate 1, as shown in Figure 1, variation in electron emission in color television picture tubes with time are measured. Ni-W alloys containing 27.5 % by weight of W and, as typical reducing elements 0.07 % by weight of any of Mg, Zr, Al and Si are used as the base metal plates with a thickness of 0.03 mm, the thickness that must be used in the directly heated system, and, for comparison purpose, with a thickness of 0.1 mm, the thickness corresponding to one-half of 0.2 mm, the thickness now used in ordinary color television picture tubes having indirectly heated oxide cathodes. The results are shown in Figure 2. The reason why a thickness of 0.1 mm is used in place of the 0.2 mm of the ordinary indirectly heated type, for comparative purposes is that the 0.2 mm base metal plates are so low in heating resistance for the directly heated type that a large amount of electric current is required for cathode heating, and it is actually impossible to prepare a color television picture tube for such a large amount of electric current.

It is apparent from the graph of Figure 2, especially analysis of groups (I) and (II), that the duration of electron emission from the cathodes decisively depends upon the thickness of the base metal plate.

In Figure 2, curves II-A and II-B in group (II) contain 0.07 % by weight of Mg and Zr, respectively, as the reducing element. We have found that the duration of electron emission shown by curves II-A and II-B is mainly based on consumption of Mg and Zr

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contained in the base metal plates. On the other hand, in the case of base metal plates containing 0.07 % by weight of Al, shown by curve II-C in Figure 2, a phenomenon of peeling of the alkaline earth metal oxide from the base metal plate is seen after 3,000 hours from the start of operation, and most of the sample fails to effect electron emission at all after several thousand hours. That is, exact data on the duration of electron emission are not obtainable, and thus, the dotted line in Figure 2 indicates an assumption. The base metal plate containing 0.07 % by weight of Si has the characteristics shown by curve II-D in Figure 2, where the duration of electron emission is mainly dependent upon the presence of an intermediate layer having a high electrical resistance formed between Si and the alkaline earth metal oxide. Once such intermediate layer is formed, the voltage drop at that layer is so large that it is difficult, in an actual color television picture tube, to make electrons emit from the cathode, so failing to maintain a satisfactory function. If a much higher voltage is applied between the cathode and electrode for extracting the electrons to produce electron emission, the alkaline earth metal oxide is damaged by the heat generation in the intermediate layer of high electric resistance, so reducing the life span of the cathode.

The base metal plates of Group (I) in Figure 2 are of the same base metal as those of Group (II), but have a different thickness, 0.03 mm. The variation in electron emission with time of the base metal plates of Group (I) are shown by curves I-A for the Mg containing alloy, I-B for Zr containing alloy, I-C for Al containing alloy and I-D for the Si containing alloy in Figure 2. In the case of the base metal plate containing Al, the similar phenomenon of peeling of the alkaline earth metal oxide layer appears, as shown by curve I-C. On the other hand, in the case of the base metal plates containing the reducing elements other than Al, that is, those containing Mg, Zr or Si, the reducing elements contained in the base metal plates are consumed, and electron emission ceases. This means that for base metal plates containing Mg, Zr, Al, or Si, reducing elements for an ordinary oxide cathode, to the same extent as used in indirectly heated oxide cathodes, no useful electron emitting duration can be obtained, because of the small thickness of the base metal plate.

To overcome the disadvantages of the prior art as described above, we have made extensive studies of new Ni-W-based alloys containing the reducing element not only in an alloy form but also in other forms, such as intermetallic compounds, to provide a new material on the basis of the study of the

conventional oxide cathode using a base metal plate of large thickness, and, as a result, we have found that, among the reducing elements, only Zr can form the intermetallic compound meeting the characteristics required for the base metal plate for the directly heated oxide cathode.

The present invention provides a base metal plate for a directly heated oxide cathode, which comprises a plate of Ni-W-Zr alloy consisting of 20 to 30 % by weight of W 0.3 to 5.0% by weight of Zr, and the balance nickel and incidental ingredients and impurities, the plate having a thickness of not more than 50 μ .

The plate of the invention may be modified by replacing a part of the nickel in the alloy by one or more of Mg, Si, Al or C in a quantity sufficient to act as a reducing agent for the oxide cathode.

Embodiments of the present invention will be described, referring to Figure 3.

Ni-W alloy plates containing 27.5 % by weight of W and varied amounts of Mg, Zr, Al or Si as the reducing element and having a plate thickness of 0.03 mm, are inserted into color television picture tubes as the base metal plates in a directly heated oxide cathode to measure the duration of electron emission of the respective cathodes, where the duration of electron emission of the cathodes is defined as the time taken for the value of electron emission to fall to 50 % of the initial value. The results are shown in Figure 3.

Curve A in Figure 3 relates to base metals of a Ni-W alloy containing Mg as reducing element. When the Mg content exceeds 0.1 % by weight in the Ni-W-Mg alloy, a low melting compound is formed in the Ni-W-Mg alloy, resulting in considerable decrease in the strength of the alloy at the elevated temperature, and the base metal plate is broken during the test. This is the reason why curve A is plotted only up to 0.1 % by weight in Figure 3. Consequently, the allowable range for the Mg content in the base metal plate is not more than 0.1 % by weight, and the duration of electron emission of the alloy is as short as or shorter than 3×10^3 to 4×10^3 hours owing to the high Mg consumption rate. Consequently, these Mg modified plates are not of practical value.

Curve C in Figure 3 relates to base metal plates of the Ni-W alloy containing Al as the reducing element. When the Al content exceeds 0.05 % by weight in the Ni-W-Al alloy, peeling of the alkaline earth metal oxide layer from the base metal plate occurs (in Figure 3, the dotted line of curve C shows the appearance of the peeling phenomenon), and no electron emission takes place at all in most of the tested tubes as a result of the peeling of the oxide layer.

Consequently, this Ni-W alloy containing Al as a principal reducing element is not of practical value for a directly heated oxide cathode.

5 Curve D in Figure 3 relates to base metal plates of the Ni-W alloy containing Si as reducing element. When the Si content exceeds 0.14 % by weight in the Ni-W-Si alloy, an intermediate layer, having a large
10 electric resistance, is formed between the base metal plate and the oxide layer, and the electron emission is reduced by the influence of the large electrical resistance, and, in an extreme case, the alkaline earth
15 metal oxide layer is broken by the heat generated. Thus, the Ni-W alloy containing Si as a principal reducing element is not of practical value for a base metal plate for the directly heated oxide cathode.

20 Curve B in Figure 3 relates to base metal plates of the Ni-W alloy containing Zr as the reducing element. In this case, the duration of electron emission is increased with increasing Zr content, as shown by Curve B.
25 This is because the Zr solid solution limit in the Ni-W alloy is small (we find it to be 0.2 % by weight in the operating temperature range of the oxide cathode). Even if the Zr content is increased further, the reaction rate of Zr with the alkaline earth metal
30 oxide layer in the initial period is still relatively small, and is not significantly greater than that when the Zr content is only 0.2 % by weight. We have found that Zr deposited as an intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, is decomposed to compensate for the consumption of Zr in the solid
35 solution phase, and the decomposition reaction continues until the intermetallic compound has been consumed, and so the intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, acts as a source of Zr. We have also found that the higher the Zr content, the longer the life
40 time of electron emission. Furthermore, we have found that, since the intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, deposited as very fine grains has a high melting point, a Zr content up to 5 % by weight has substantially
45 no influence upon the strength of the base metal plate at the elevated temperature. That is, the base metal plate containing 0.3 to 5 % by weight of Zr and having a thickness as low as 30μ has a satisfactory strength at the elevated temperature and a
50 good life time of electron emission, and is acceptable in practice as a base metal plate for the directly heated oxide cathode. Compared with the base metal plates containing Mg, Al or Si as the reducing element, only
55 the Ni-W-Zr alloy can provide a satisfactory material for the base metal plate for the directly heated oxide cathode.

65 As a result of further extensive studies and tests we have made on the Ni-W-Zr alloy by varying the Zr content in the range

0.3 to 5 % by weight, and the W content in the range 20 to 30 % by weight, but replacing part of the Ni by one or more of the preferred reducing elements Mg, Al or Si, in the small amounts mentioned above, this does not cause any adverse effects, for example, decreasing the strength at the elevated temperature, peeling of the oxide layer or increasing the resistance of the intermediate layer, so that such modified Ni-W-Zr alloys can be used as the base metal plate for a directly heated oxide cathode.

It has been also found that thin plates of the Ni-W-Zr alloy as defined above where Zr is uniformly distributed in the alloy can be prepared only by a powder metallurgical method and such a method forms a further aspect of this invention. An ordinary melting method is not suitable.

WHAT WE CLAIM IS:

1. A base metal plate for a directly heated oxide cathode, which comprises a plate of Ni-W-Zr alloy consisting of 20 to 30 % by weight of W, 0.3 to 5.0 % by weight of Zr, and the balance nickel and incidental ingredients and impurities, the plate having a thickness of not more than 50μ .

2. A plate according to claim 1 in which a part of the nickel in the alloy is replaced by one or more of Mg, Si, Al or C in a quantity sufficient to act as a reducing agent for the oxide cathode.

3. A plate according to claim 1 substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

4. A method of preparing a plate according to any of the preceding claims which comprises preparing an alloy as defined in claim 1 or 2 by powder metallurgy and then forming the alloy into a plate of thickness not more than 50μ .

5. A method according to claim 4 substantially as hereinbefore described.

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Consequently, this Ni-W alloy containing Al as a principal reducing element is not of practical value for a directly heated oxide cathode.

5 Curve D in Figure 3 relates to base metal plates of the Ni-W alloy containing Si as reducing element. When the Si content exceeds 0.14 % by weight in the Ni-W-Si alloy, an intermediate layer, having a large electric resistance, is formed between the base metal plate and the oxide layer, and the electron emission is reduced by the influence of the large electrical resistance, and, in an extreme case, the alkaline earth metal oxide layer is broken by the heat generated. Thus, the Ni-W alloy containing Si as a principal reducing element is not of practical value for a base metal plate for the directly heated oxide cathode.

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20 Curve B in Figure 3 relates to base metal plates of the Ni-W alloy containing Zr as the reducing element. In this case, the duration of electron emission is increased with increasing Zr content, as shown by Curve B. This is because the Zr solid solution limit in the Ni-W alloy is small (we find it to be 0.2 % by weight in the operating temperature range of the oxide cathode). Even if the Zr content is increased further, the reaction rate of Zr with the alkaline earth metal oxide layer in the initial period is still relatively small, and is not significantly greater than that when the Zr content is only 0.2 % by weight. We have found that Zr deposited as an intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, is decomposed to compensate for the consumption of Zr in the solid solution phase, and the decomposition reaction continues until the intermetallic compound has been consumed, and so the intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, acts as a source of Zr. We have also found that the higher the Zr content, the longer the life time of electron emission. Furthermore, we have found that, since the intermetallic compound, $(\text{Ni-W})_x\text{Zr}_y$, deposited as very fine grains has a high melting point, a Zr content up to 5 % by weight has substantially no influence upon the strength of the base metal plate at the elevated temperature. That is, the base metal plate containing 0.3 to 5 % by weight of Zr and having a thickness as low as 30μ has a satisfactory strength at the elevated temperature and a good life time of electron emission, and is acceptable in practice as a base metal plate for the directly heated oxide cathode. Compared with the base metal plates containing Mg, Al or Si as the reducing element, only the Ni-W-Zr alloy can provide a satisfactory material for the base metal plate for the directly heated oxide cathode.

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As a result of further extensive studies and tests we have made on the Ni-W-Zr alloy by varying the Zr content in the range

0.3 to 5 % by weight, and the W content in the range 20 to 30 % by weight, but replacing part of the Ni by one or more of the preferred reducing elements Mg, Al or Si, in the small amounts mentioned above, this does not cause any adverse effects, for example, decreasing the strength at the elevated temperature, peeling of the oxide layer or increasing the resistance of the intermediate layer, so that such modified Ni-W-Zr alloys can be used as the base metal plate for a directly heated oxide cathode.

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2. A plate according to claim 1 in which a part of the nickel in the alloy is replaced by one or more of Mg, Si, Al or C in a quantity sufficient to act as a reducing agent for the oxide cathode.

3. A plate according to claim 1 substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

4. A method of preparing a plate according to any of the preceding claims which comprises preparing an alloy as defined in claim 1 or 2 by powder metallurgy and then forming the alloy into a plate of thickness not more than 50μ .

5. A method according to claim 4 substantially as hereinbefore described.

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