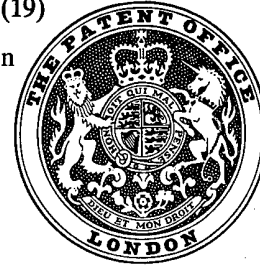


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## (54) METAL BASE PLATE FOR DIRECTLY HEATED OXIDE CATHODE

(71) We, HITACHI, LTD., a Japanese Body Corporate 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:-

- 5 The present invention relates to a metal base plate for a directly heated oxide cathode. 5  
 In general, cathodes are used in, for example, a receiving tube, a discharge tube or a cathode-ray tube. It is generally required for ones used in the cathode-ray tube to be able to operate rapidly and display an image instantaneously after electric power is supplied. In other words, when the starting time is required to be short.  
 10 The above-mentioned cathodes may be classified into indirectly heated ones and directly heated one. In the case of indirectly heated ones, the starting time is almost 20 seconds, while the time can be as short as 1 to 2 seconds in the case of directly heated ones. The directly heated oxide cathodes are most suitable as quick operating cathodes. 10  
 In directly heated oxide cathodes, the metal base plate material should satisfy the following conditions: 15  
 (1) Its mechanical strengths at high temperature should be as high as possible. 15  
 (2) Its specific electric resistance should be higher than a predetermined value, for example,  $90\mu\Omega$  cm at  $900^\circ\text{C}$ .  
 (3) The electron emission of the alkaline earth metal oxide cathode should be 20 satisfactory. 20  
 As the base plate for such a cathode, alloys comprising nickel as main component, 20 to 30% by weight of tungsten and an impurity amount of a reducing agent such as Mg, Si, Ti, Al or Zr are known [see Japanese Patent Kokoku (post-Exam Publ.) No. 21,008/69]: MISUMI, who is one of the present inventors has suggested an improved base metal which 25 can maintain its electron emission for a long period of time and which is fundamentally an Ni-W-Zr alloy containing 20 to 30% by weight of tungsten and 0.3 to 5.0% by weight of zirconium. The main reason why tungsten is added here is that it satisfies the above-mentioned conditions required for the base material. It is most suitable to add 20 to 30% by weight of tungsten. 25  
 30 When a metal plate material having the above-mentioned composition is used as the base, however, the material has a defect in that, in the step of producing a cathode-ray tube and during the operation of the cathode, a larger amount of a tungstate interface layer is formed between the base and the oxide layer and the oxide layer is easily peeled off owing to this tungstate interface layer [Japanese Patent Kokoku (Post-Examination Publ.) No. 12,266/69]. Further, it is stated in the Japanese patent publication that it is more difficult to 35

form an interface layer with molybdenum than with tungsten.

In order to obviate the above-mentioned defect, therefore, the present inventors previously attempted to improve the directly heated oxide cathode by replacing tungsten by molybdenum. Since molybdenum is lower than tungsten in reactivity with the oxide layer, a molybdate interface layer is substantially not formed. It was also confirmed that the peeling of the oxide layer occurred only with difficulty as compared with the use of tungsten when molybdenum was used in place of tungsten. Also, mechanical strengths at high temperatures, specific electric resistance and the diffusion velocity of zirconium were also similar to those obtained when using tungsten.

For example, when the mechanical strengths at high temperatures, specific electric resistance and zirconium diffusion velocity for the directly heated oxide cathode formed from an alloy comprising 82.1% by weight of nickel, 17.5% by weight of molybdenum and 0.4% by weight of zirconium were measured, it was found that this cathode had almost identical properties to a cathode formed with a Ni-W-Zr alloy comprising 72.1% by weight of nickel, 27.5% by weight of tungsten and 0.4% by weight of zirconium as shown in the following Table:

Table

		Specific electric resistance (20°C, $\mu\Omega\text{cm}$ )	Tensile strength (800°C, $\text{kg/mm}^2$ )	Zr diffusion coefficient D 800°C, $\text{cm}^2/\text{sec}$ )	
	Ni-Mo-Zr	89	37	$1.5 \times 10^{-11}$	
	Ni-W-Zr	84	40	$1.4 \times 10^{-11}$	

Also, a ternary carbonate comprising  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$  was coated onto a fixed surface at the top of said base formed with the above-mentioned Ni-Mo-Zr alloy and the resulting coating was subjected to heat treatment in a vacuum atmosphere at 1000°C for about 10 hours to convert the carbonate layer into an oxide layer. When the adhesive strength of the oxide layer was examined by scratching the oxide layer with the tip of a setting pin in a vacuum, the oxide layer peeled off in the case of the Ni-W-Zr alloy material but did not peel at all in the case of the Ni-Mo-Zr alloy material. Also, with regard to the same examples, X-ray diffraction test was carried out after the samples were taken out in the air and freed from the oxide layer with methanol. A tungstate interface layer was detected in the case of the Ni-W-Zr alloy material but a molybdate interface layer was not detected at all in the case of the Ni-Mo-Zr alloy material.

In a directly heated oxide cathode having a base of the above-mentioned Ni-Mo-Zr composition, however, the molybdenum contained in the base is low in reducing (deoxidising) velocity and thereby the deoxidation is carried out mainly by the zirconium. In this case, zirconium as a deoxidising agent gradually decreases during the operation of the cathode while deoxidising the oxide layer until it is exhausted and the electron emissive activity of the oxide layer is lost. The electron emissive ability can be maintained for a long period of time by increasing the zirconium content. However, there is an upper limit for the zirconium content since a low melting eutectic is produced and thereby mechanical strengths at high temperatures are reduced at a zirconium content exceeding 5% by weight. Therefore, the duration of electron emissive ability is limited by the amount of zirconium.

The disadvantages outlined above had been overcome to a large extent by the present invention wherein a part of the tungsten in the Ni-W-Zr alloy used for forming the metal base plate is replaced by molybdenum.

The present invention provides a metal base plate for a directly heated oxide cathode comprising an alloy which consists of 10 to 22% by weight of molybdenum, 1 to 8% by weight of tungsten, 0.1 to 5% by weight of zirconium and optionally a deoxidising amount of at least one of magnesium, silicon and aluminium, the balance being nickel and incidental ingredients and impurities.

The metal base plate for a directly heated oxide cathode according to the present invention, contains molybdenum, thereby its mechanical strengths at high temperatures and specific electric resistance are increased. Also, the metal base plate contains an amount of tungsten such that a larger amount of a tungstate interface layer is not formed in the step of forming the oxide layer by the thermal decomposition of alkaline earth metal carbonates and at the beginning of its life when the atmosphere in the tube is bad. Thus, the electron emissive ability of the oxide cathode can be maintained when the zirconium is exhausted

and sufficient supplement of the zirconium become impossible.

Figure 1 is a sectional view of the principal part of one example of a prior art directly heated oxide cathode,

Figure 2 is a sectional view of the principal part of one example of a directly heated oxide cathode using a metal base plate according to the present invention,

Figure 3 shows the relationship between electron emission and operating time for a directly heated oxide cathode according to the present invention (I) and a prior art directly heated oxide cathode (II).

Figure 1 illustrates a base 1 which is heated by the supply of an electric current, and has terminals 2. An alkaline earth metal oxide layer 3 which emits electrons is provided on the base 1, for example, a layer of a mixture of barium oxide, strontium oxide and calcium oxide. The oxide layer 3 is provided at a fixed part on one surface of base 1 to form a directly heated oxide cathode. It is desirable in this prior art cathode for the base 1 to be 100  $\mu\text{m}$  or less, and preferably 60  $\mu\text{m}$  or less, in thickness so that its electric resistance may be as large as possible, its thermal capacity may be reduced and its starting time may be short.

In Figure 2 which is a sectional view of the principal part of one example of directly heated oxide cathodes using a metal base plate according to the present invention, a base 4 has terminals 2 and an alkaline earth metal oxide layer 3.

The base 4 according to the present invention is preferably produced by forming an alloy ingot comprising 15% by weight of molybdenum, 4% by weight of tungsten, 0.4% by weight of zirconium and the balance nickel according to a standard powder metallurgy process, and then forming a base for a cathode of about 30  $\mu\text{m}$  in thickness by cold rolling while the ingot is repeatedly subjected to vacuum annealing. A directly heated oxide cathode can then be formed from this plate.

In the directly heated oxide cathode thus formed, the mechanical strengths at high temperatures, specific electric resistance and zirconium diffusion velocity were measured. As a result, it was found that this plate material formed with an alloy comprising 80.6% by weight of nickel, 15% by weight of molybdenum, 0.4% by weight of zirconium and 4% by weight of tungsten was substantially identical in all the above-mentioned properties as a tungsten-free plate material formed with an alloy comprising 82.1% by weight of nickel, 17.5% by weight of molybdenum and 0.4% by weight of zirconium. Thus, prescribed values of strengths at high temperatures and specific electric resistance can be obtained by the use of 15% by weight of molybdenum. Also, since a small amount (4% by weight) of tungsten is added, this tungsten reduces the oxide layer 3 and the electron emissive ability of the oxide cathode can be maintained for a long period of time even after the zirconium (0.4% by weight) as deoxidising agent is exhausted.

Various experiments were carried out in the above-mentioned construction to confirm the effects of the construction. A ternary carbonate mixture comprising  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$  was coated on the fixed surface at the top of said base 4 and the resulting coating was subjected to thermal decomposition in a vacuum atmosphere at 1000°C for about 10 hours to convert the carbonate layer into an oxide layer 3. When the adhesive strength of the oxide layer 3 was examined by scratching the oxide layer 3 with the tip of a setting pin in a vacuum, the oxide layer 3 did not peel at all. Also, an X-ray diffraction test was carried out after the sample was taken out into the air and freed from the oxide layer 3 with methanol, and neither a molybdate interface layer nor a tungstate interface layer was detected. The relationship between electron emission and operating time found when said oxide layer 3 comprising  $\text{BaO}$ ,  $\text{SrO}$  and  $\text{CaO}$  is formed on a fixed surface of the top of the base 4 and the directly heated oxide cathode thus obtained is actually installed in a color television cathode-ray tube is shown in Figure 3. In Figure 3, curve (I) shows the electron emission life of a cathode formed with a metal base plate (thickness 30  $\mu\text{m}$ ) according to the present invention comprising 15% by weight of molybdenum, 4% by weight of tungsten, 0.4% by weight of zirconium and the balance being nickel and impurities. Curve (II) shows the electron emission life of a cathode formed with a prior art metal base plate comprising 27.5% by weight of tungsten, 0.4% by weight of zirconium and the balance being nickel. As is clear from Figure 3, a directly heated oxide cathode formed with a metal base plate according to the present invention has a remarkably prolonged electron emission life.

The above-mentioned example of a metal base plate of the invention had a composition containing 15% by weight of molybdenum, 4% by weight of tungsten and 0.4% by weight of zirconium. It has been found that if the amount of molybdenum is less than 10% by weight, satisfactory specific electric resistance and mechanical strengths at high temperatures cannot be secured. Also, an amount of molybdenum of more than 22% by weight exceeds the solid solution limit and separation of molybdenum is caused by repeated heating and cooling. Therefore, the amount of molybdenum must be 10 to 22% by weight. Also, an amount of tungsten of less than 1% by weight is insufficient to maintain the electron emissive ability of an oxide cathode for a long enough period, while when the

tungsten exceeds 8% by weight, a tungstate interface layer is formed during thermal decomposition of alkaline earth metal carbonates in the step of producing an oxide layer and in the initial stage of operation. This causes peeling of the oxide and prevents the tungsten from reacting with the oxide layer, in other words, prevents the deoxidising action of tungsten. Therefore, the amount of tungsten must be 1 to 8% by weight. Further, as for the amount of zirconium, good initial properties cannot be obtained if the amount of zirconium is less than 0.1% by weight, while a low melting eutectic is formed and the mechanical strength at high temperatures is reduced when the amount of zirconium exceeds 5% by weight. Therefore, the amount of zirconium must be 0.01 to 5% by weight.

Thus, by use of the base plate of the present invention, the formation of a tungstate interface layer between the base plate and the oxide layer can be substantially prevented and thereby the peeling of the oxide layer can be prevented. Further, a satisfactory amount of alkaline earth metals such as Ba, Ca and Sr can be generated and the electron emissive ability of the oxide layer can be maintained for a long period of time. As a result, the life of the directly heated oxide cathode formed with the metal base plate of the present invention can be remarkably prolonged.

WHAT WE CLAIM IS:-

1. A metal base plate for a directly heated oxide cathode comprising an alloy which consists of 10 to 22% by weight of molybdenum, 1 to 8% by weight of tungsten, 0.1 to 5% by weight of zirconium and optionally a deoxidising amount of at least one of magnesium, silicon and aluminium, the balance being nickel and incidental ingredients and impurities.

2. A base plate according to claim 1 wherein the alloy comprises 80.6% by weight of nickel, 15.0% by weight of molybdenum, 0.4% by weight of zirconium and 4.0% by weight of tungsten.

3. A base plate according to claim 1 or 2, coated with an alkaline earth metal oxide which emits electrons when heated.

4. A base plate according to claim 1, substantially as hereinbefore described.

5. A directly heated oxide cathode comprising a metal base plate as claimed in any one of the preceding claims.

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

FIG.1

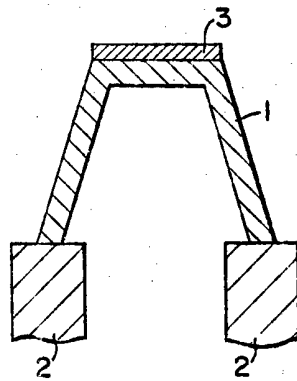


FIG.2

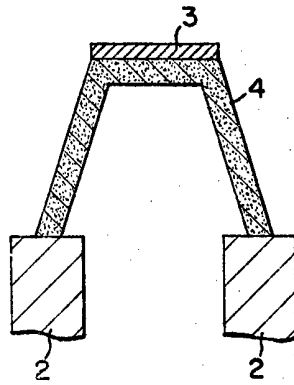


FIG.3

