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㉖ **Scandate cathode.**

㉗ By providing at least the top layer of the matrix of a scandate cathode with an alloy or compound which exhibits scandium segregation, a satisfactory recovery for cathodes with a high emission can be achieved after ion bombardment.

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### Scandate cathode.

The invention relates to a scandate cathode having a cathode body comprising a matrix of at least a high melting-point metal and/or alloy, whilst a barium compound which can supply barium to the emissive surface by chemical reaction with the matrix material is present at least in the matrix and in contact with the matrix material.

The invention also relates to methods of manufacturing such a cathode and to an electron beam tube comprising such a cathode.

Cathodes of the type mentioned above are described in the Article "properties and manufacture of top-layer scandate cathodes", Applied Surface Science 26 (1986), 173-195, J. Hasker, J. v. Esdonk and J.E. Crombeen. In the cathodes described in this Article scandium oxide ( $\text{Sc}_2\text{O}_3$ ) grains of several microns or tungsten (W) grains which are partially coated with either scandium (Sc) or scandium hydride ( $\text{Sc H}_2$ ) are processed at least in the top layer of the cathode body. The cathode body is manufactured by means of pressing and sintering whereafter the pores are impregnated with barium-calcium-aluminate. By chemical reaction with the tungsten of the matrix during operation of the cathode, the barium-calcium-aluminate supplies barium to the emissive surface in order to maintain the electron emission. To be able to realize a very high cathode load after assembly in, for example, a cathode ray tube and activation of the cathode, it is important that a scandium-containing layer having a thickness of some monolayers has formed on the cathode surface during impregnation by reaction with the impregnant. To this end the impregnation process must be performed very carefully. As compared with an impregnated tungsten cathode, which is either or not coated with, for example osmium, this may be considered a drawback.

As has been proved by experiments described in the abovementioned Article, an ion bombardment which may occur in practice, for example during the manufacture of television tubes, may entirely or partly remove the scandium containing layer, with the attendant detrimental results for the emission. Since  $\text{Sc}_2\text{O}_3$  is not very mobile (in the cathodes manufactured by means of W partially coated with Sc or  $\text{Sc H}_2$  oxidation occurs during impregnation) the said scandium-containing layer cannot be fully regenerated by reactivating the cathode. According to the experiments described a regeneration sufficient for a complete recovery of the emission was not achieved. As compared with an impregnated tungsten cathode, this may also be considered a drawback.

The object of the invention is to provide scan-

date cathodes which are improved with respect to the drawbacks mentioned hereinbefore. The invention is based on the recognition that this can be achieved by using scandium-containing materials which segregate scandium to their surface upon heating. Due to the relatively low surface energy of scandium there are scandium compounds and scandium alloys which exhibit this scandium segregation. At an elevated temperature in vacuo a monolayer of scandium is deposited on the surface of these compounds and alloys. After removal of this layer - by means of ion bombardment or another process - a new layer of scandium will be deposited on the surface at a sufficiently high temperature. This can of course be repeated until the scandium is depleted.

To this end a scandate cathode according to the invention is characterized in that at least the top layer of the cathode body comprises a scandium compound or scandium alloy which can exhibit scandium segregation.

The speed at which the scandium is dispensed to the emissive surface may also depend on chemical reactions between the barium compound used and the source supplying scandium.

The compound or alloy preferably yields scandium already at the operating temperature of the cathode, but this is not absolutely necessary. If the scandium is dispensed at a higher temperature, the emission may decrease during operation due to evaporation and/or ion bombardment, but then it can in principle be restored by reactivating the cathode at a sufficiently high temperature. The scandium may also segregate if the temperature becomes high enough during the manufacture (for example during impregnation).

Notably compounds and/or alloys of scandium comprising one or more of the metals rhenium (Re), ruthenium (Ru), hafnium (Hf), nickel (Ni), cobalt (Co), palladium (Pd), zirconium (Zr) or tungsten (W) were found to be satisfactory.

Due to the high melting point and the fact that rhenium or ruthenium do not evaporate during operation and manufacture,  $\text{Re}_{24}\text{Sc}_5$ ,  $\text{Re}_2\text{Sc}$  and  $\text{Ru}_2\text{Sc}$  are extremely suitable, particularly the rhenium compounds because they exhibit scandium segregation already at the operating temperature.

A first method of manufacturing a scandate cathode according to the invention is characterized in that a porous body comprising the scandium compound or scandium alloy at least in the top layer is obtained by means of mixing, pressing and sintering powders of a high melting-point metal and/or alloy and a scandium compound or scan-

dium alloy which can exhibit scandium segregation, whereafter said body is at least partly provided by means of impregnation with a barium compound which can supply barium to the emissive surface by chemical reaction with the high melting-point metal and/or alloy.

Another method is characterized in that the cathode body comprising in at least its top layer a scandium compound or scandium alloy which can exhibit scandium segregation is obtained by means of mixing, pressing and sintering powders of a high melting-point metal and/or alloy and of the scandium compound or scandium alloy combined with the powder of a barium compound which can supply barium to the emissive surface by chemical reaction with the high melting-point metal and/or alloy during operation of the cathode. In this method the sintering temperature is the highest temperature the cathode body ever acquires. This temperature may be substantially lower than the impregnation temperature which is generally used in the previous method. Consequently, the reaction of the barium compound with the scandium compound or scandium alloy is reduced. In fact, a too vigorous reaction may give rise to a considerable scandium oxidation so that the supply of scandium is reduced.

The invention will now be described in greater detail, by way of example, with reference to the accompanying drawing in which

Figure 1 shows diagrammatically an experimental setup for testing scandium compounds and alloys,

Figure 2 shows a result of measurements on a scandium compound,

Figure 3 is a diagrammatic representation of a cathode according to the invention, and

Figure 4 is a diagrammatic representation of another cathode according to the invention.

Figure 1 is a longitudinal sectional view of an experimental set-up. A pulverulent scandium compound or scandium alloy 2 is pressed and sintered in the molybdenum tray 1. Subsequently, it is welded onto the shaft 3 comprising a heating element 4. The assembly is mounted in a Scanning Auger Microscope to measure the scandium concentration on the surface. This concentration can be reduced by means of ion bombardment and it may increase again after this bombardment due to scandium segregation. In this way various scandium compounds and scandium alloys have been tested, such as  $\text{Re}_{24}\text{Sc}_5$ ,  $\text{Re}_2\text{Sc}$ ,  $\text{Ru}_2\text{Sc}$ ,  $\text{Co}_2\text{Sc}$ ,  $\text{Pd}_2\text{Sc}$ ,  $\text{Ni}_2\text{Sc}$ ,  $\text{Sc}_{50}\text{Zr}_{43}\text{W}_7$ ,  $\text{Sc}_{63}\text{Hf}_{24}\text{W}_8$  and  $\text{Sc}_{47}\text{Hf}_{41}\text{W}_{12}$ .

Figure 2 shows a measuring result for the compound  $\text{Re}_{24}\text{Sc}_5$ . The measurement indicated by curve a is considered first. Prior to the instant t

= 0 in the Figure the experimental set-up had been at a temperature of  $950^\circ\text{C}$  for some time and this temperature was also maintained during the measurement. At the instant t = 0 - approximately one mono-layer of scandium is then present on the surface - the experimental set-up was exposed to an ion bombardment. Consequently, the scandium concentration on the surface decreased until at t =  $t_1$  a balance was achieved between the supply and removal of scandium. After the ion bombardment had been switched off at t =  $t_2$  the original concentration was achieved again in a short time by scandium segregation. No scandium depletion was observed when the experiment was repeated several times. Curve b shows a similar result measured on the same experimental set-up at a temperature of  $1100^\circ\text{C}$ . The balance during bombardment was set at a higher concentration than at  $950^\circ\text{C}$ . Scandium depletion was neither observed when the experiment was repeated several times. Another result of the investigations was that the compound  $\text{Ru}_2\text{Sc}$  at the operating temperature (approximately  $950^\circ\text{C}$ ) or the usual temperature for activating a scandate cathode (approximately  $1100^\circ\text{C}$ ) did not exhibit any scandium segregation.

Figure 3 is a longitudinal sectional view of a scandate cathode according to the invention. The cathode body 13 has a top layer 23 and an emissive surface 33. This body, having a diameter of 1.8 mm, is obtained by pressing a matrix of W powder with a top layer on it comprising a mixture of W powder and a powder of a scandium compound or scandium alloy according to the invention. After pressing a sintering operation is carried out at  $1500^\circ\text{C}$  in a hydrogen atmosphere. The thickness of the matrix is then approximately 0.5 mm and that of the top layer is approximately 0.1 mm. The pressure during pressing of the cathode body is such that the increase in weight is substantially 4.5% after impregnation with  $4\text{BaO}\cdot 1\text{CaO}\cdot 1\text{Al}_2\text{O}_3$  in a hydrogen atmosphere. The impregnated cathode body, either or not provided with an envelope 43, is welded onto the cathode shaft 53. A coiled cathode filament 63 which may consist of a helically wound metal core 73 with an aluminium oxide insulation layer 83 is present in the shaft 53. The emission of such a cathode, after assembly and activation, is measured in a diode arrangement with a cathode-anode gap of 0.3 mm at a 1000 Volt pulse load. Cathodes were manufactured as examples with top layers consisting of W with 25 and 50% by weight of  $\text{Re}_2\text{Sc}$  and with top layers consisting of W with 10 and 25% by weight of  $\text{Re}_{24}\text{Sc}_5$ . In all cases the measured emission was substantially  $100\text{ A/cm}^2$  at an operating temperature of approximately  $950^\circ\text{C}$ . In another example the top layer consisted of W with 10 and 25% by weight of  $\text{Ru}_2\text{Sc}$ . The emission was again substan-

tially 100 A/cm<sup>2</sup> but, unlike the previous examples, it exhibited a decrease of approximately 30% after 8000 hours of a continuous load of 1.5 A/cm<sup>2</sup>. In yet another example the top layer consisted of W with 5, 10 and 20% by weight of Sc<sub>68</sub>Hf<sub>24</sub>W<sub>8</sub>. The measured emission varied between approximately 70 and 90 A/cm<sup>2</sup>. The above examples show that the high emissions characteristic of scandate cathodes can be realized by using scandium compounds or scandium alloys according to the invention.

Figure 4 is a longitudinal sectional view of another scandate cathode according to the invention. The cathode body 14 has an emissive surface 24. This body, with a diameter of 1.8 mm and a thickness of approximately 0.5 mm is obtained by pressing a mixture of W powder and 10% by weight of Re<sub>24</sub>Sc<sub>5</sub> powder and 7% by weight of barium-calcium-aluminate powder (4BaO-1CaO-1Al<sub>2</sub>O<sub>3</sub>) and by subsequently sintering at 1500 °C in a hydrogen atmosphere. The cathode body, either or not provided with a molybdenum envelope 34, is then welded onto the cathode shaft 44. The shaft 44 accommodates a coiled filament 54 which may consist of a helically wound metal core 64 having an aluminium oxide insulation layer 74. The measured emission after activation was approximately 100 A/cm<sup>2</sup> at a cathode temperature of 950 °C. An advantage of this cathode is the simple method of its manufacture: impregnation and subsequent cleaning is not necessary. Auger measurements have proved that the scandium concentration on the surface is very low before activation. During activation, as described in the Article mentioned in the opening paragraph, the scandium concentration required for the measured emission is formed on the surface.

The invention is of course not limited to the examples shown, but several variations within the scope of the invention are possible to those skilled in the art. The emissive material may be present in a storage space under the actual matrix (L-cathode), whilst many design variations are also possible. Moreover, the barium supply to the emissive surface is not necessarily confined to the mechanism described herein but can also be imagined to originate e.g. from segregation from barium compounds or alloys because the surface energy of barium is lower than that of scandium.

## Claims

1. A scandate cathode having a cathode body comprising a matrix of at least a high melting-point metal and/or alloy, whilst a barium compound which can supply barium to the emissive surface by chemical reaction with the matrix material is present at least in the matrix and in contact with the matrix material, characterized in that at least the top layer of the cathode body comprises a scandium compound or scandium alloy which can exhibit scandium segregation.
2. A scandate cathode as claimed in Claim 1, characterized in that the scandium compound or scandium alloy exhibits scandium segregation at the operating temperature of the cathode.
3. A scandate cathode as claimed in Claim 1, characterized in that the scandium compound or scandium alloy exhibits scandium segregation at an activation temperature which is higher than the operating temperature of the cathode.
4. A scandate cathode as claimed in Claim 1, characterized in that the scandium compound or scandium alloy exhibits scandium segregation at a temperature to which the cathode is subjected during one of its manufacturing steps.
5. A scandate cathode as claimed in any one of the preceding Claims, characterized in that the scandium compound or scandium alloy is a compound of scandium with one or more of the metals rhenium (Re), ruthenium (Ru), hafnium (Hf), nickel (Ni), cobalt (Co), palladium (Pd), zirconium (Zr) or tungsten (W).
6. A scandate cathode as claimed in Claim 5, characterized in that the scandium compound or scandium alloy is associated with the group of Re<sub>24</sub>Sc<sub>5</sub>, Re<sub>2</sub>Sc, Ru<sub>2</sub>Sc, Co<sub>2</sub>Sc, Pd<sub>2</sub>Sc, Ni<sub>2</sub>Sc, Sc<sub>50</sub>Zr<sub>43</sub>W<sub>7</sub>, Sc<sub>68</sub>Hf<sub>24</sub>W<sub>8</sub> and Sc<sub>47</sub>Hf<sub>41</sub>W<sub>12</sub>.
7. A scandate cathode as claimed in Claim 2, characterized in that the scandium compound is Re<sub>2</sub>Sc or Re<sub>24</sub>Sc<sub>5</sub>.
8. A scandate cathode as claimed in Claim 7, characterized in that at least the top layer of the cathode body comprises 5 to 50% by weight of Re<sub>2</sub>Sc or Re<sub>24</sub>Sc<sub>5</sub>.
9. A scandate cathode as claimed in any one of the preceding Claims, characterized in that the barium compound is provided in the cathode body by means of impregnation.
10. A scandate cathode as claimed in any one of Claims 1 to 8, characterized in that matrix material, barium compound and the scandium compound or scandium alloy are simultaneously pressed and subsequently sintered.
11. A method of manufacturing a scandate cathode, characterized in that a porous body comprising the scandium compound or scandium alloy at least in the top layer is obtained by means of mixing, pressing and sintering powders of a high melting-point metal and/or alloy and a scandium compound or scandium alloy which can exhibit scandium segregation, whereafter said body is at least partly provided by means of impregnation

with a barium compound which can supply barium to the emissive surface by chemical reaction with the high melting-point metal and/or alloy.

12. A method of manufacturing a scandate cathode characterized in that the cathode body comprising in at least its top layer a scandium compound or scandium alloy which can exhibit scandium segregation is obtained by means of mixing, pressing and sintering powders of a high melting-point metal and/or alloy and of the scandium compound or scandium alloy combined with the powder of a barium compound which can supply barium to the emissive surface by chemical reaction with the high melting-point metal and/or alloy during operation of the cathode.

13. A method as claimed in Claim 11 or 12, characterized in that the scandium compound or scandium alloy is a compound or alloy comprising one or more of the metals rhenium (Re), ruthenium (Ru), hafnium (Hf), nickel (Ni), cobalt (Co), palladium (Pd), zirconium (Zr) or tungsten (W).

14. A method as claimed in Claim 13, characterized in that the scandium metal compound or scandium alloy is associated with the group of  $\text{Re}_{24}\text{Sc}_5$ ,  $\text{Re}_2\text{Sc}$ ,  $\text{Ru}_2\text{Sc}$ ,  $\text{Co}_2\text{Sc}$ ,  $\text{Pd}_2\text{Sc}$ ,  $\text{Ni}_2\text{Sc}$ ,  $\text{Sc}_{50}\text{Zr}_{43}\text{W}_7$ ,  $\text{Sc}_{68}\text{Hf}_{24}\text{W}_8$  and  $\text{Sc}_{47}\text{Hf}_{41}\text{W}_{12}$ .

15. A method as claimed in Claim 13, characterized in that the scandium compound is  $\text{Re}_2\text{Sc}$  or  $\text{Re}_{24}\text{Sc}_5$ .

16. A method as claimed in Claim 13, characterized in that at least the top layer of the cathode body comprises 5 to 50% by weight of  $\text{Re}_2\text{Sc}$  or  $\text{Re}_{24}\text{Sc}_5$ .

17. An electron beam tube provided with a cathode as claimed in any one of Claims 1 to 10.

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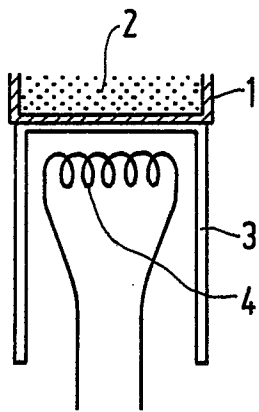


FIG. 1

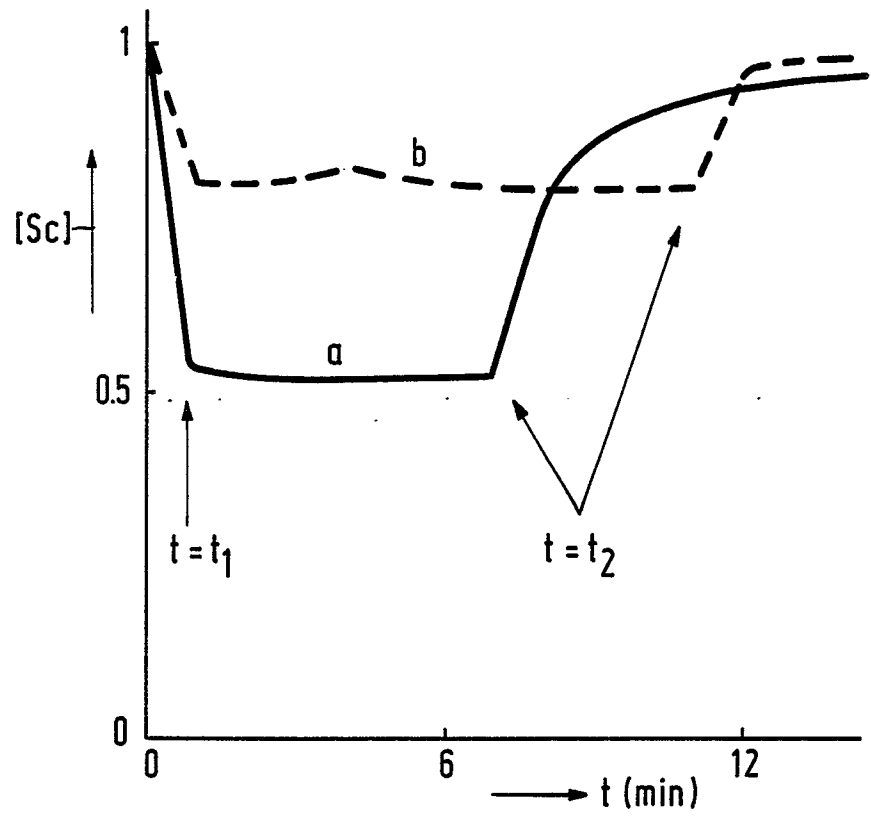


FIG. 2

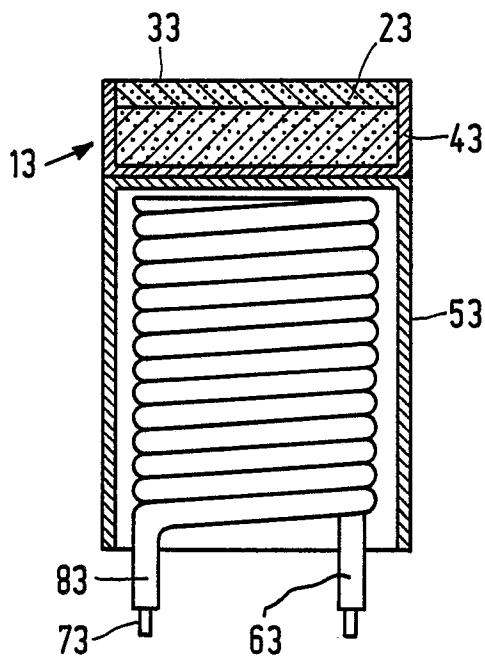


FIG. 3

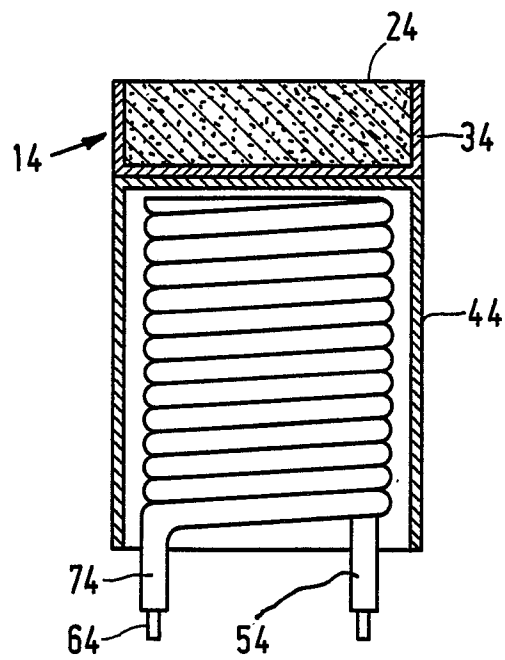


FIG. 4



EINSCHLÄGIGE DOKUMENTE			
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.4)
A	JOURNAL VAC. SCI. TECHNOL., Band 5, Nr. 4, Teil II, Juli-August 1987, Seiten 1299-1302, American Vaccum Society; S. YAMAMOTO et al.: "Impregnated cathode coated with tungsten thin film containing Sc203" * Seite 1300, linke Spalte, Absatz 3; Seite 1302, linke Spalte, Absatz 5 *	1,11,12 ,17	H 01 J 1/28 H 01 J 1/14 H 01 J 9/04
A	US-A-4 626 470 (YAMAMOTO et al.) * Spalte 3, Zeilen 49-55 *	1,11,12 ,17	
A	GB-A-2 170 950 (HITACHI) * Spalte 1, Zeilen 77-83 *	1,11,12 ,17	
A	US-A-4 594 220 (J. HASKER et al.) * Zusammenfassung *	1,11,12 ,17	
A,D	APPLIED SURFACE SCIENCE, Band 26, 1986, Seiten 173-195, Elsevier Science Publishers B.V., Amsterdam, NL; J. HASKER et al.: "Properties and manufacture of top-layer scandate cathodes" * Zusammenfassung *	1,11,12 ,17	
			RECHERCHIERTE SACHGEBIETE (Int. Cl.4)
			H 01 J 1/00 H 01 J 9/00
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt			
Recherchenort	Abschlußdatum der Recherche	Prüfer	
DEN HAAG	15-02-1989	WITH F.B.	
KATEGORIE DER GENANNTEN DOKUMENTE		T : der Erfindung zugrunde liegende Theorien oder Grundsätze	
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