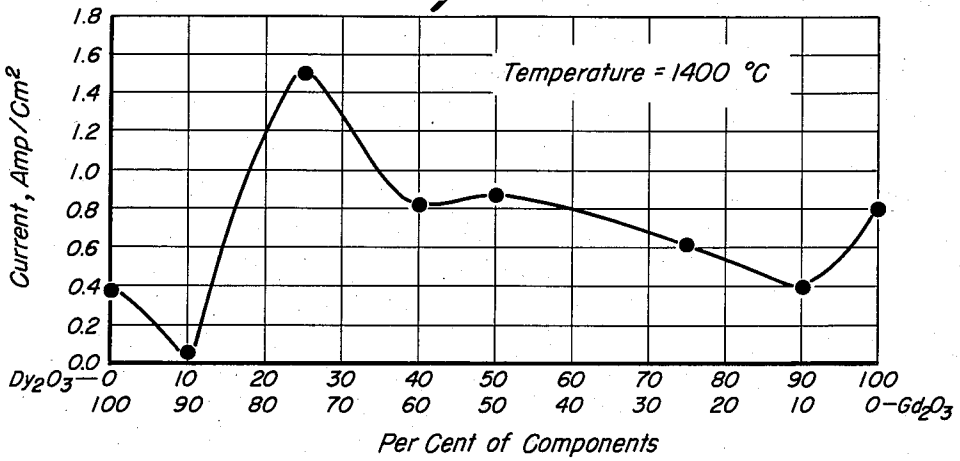
May 1, 1956 F. C. TODD ET AL 2,744,073

THERMIONIC EMITTER MATERIALS

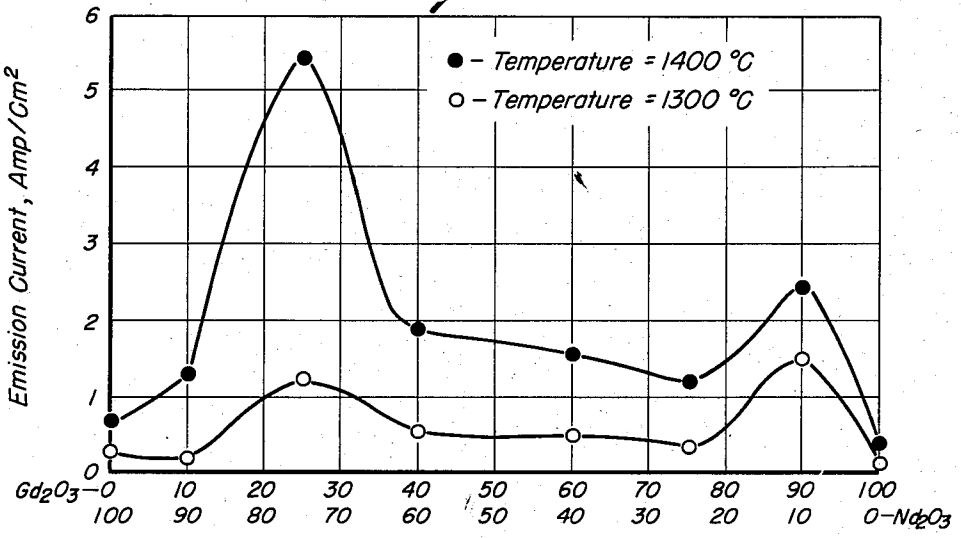
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FIG 1



PULSE EMISSION CURRENT FROM MIXTURES OF GADOLINIUM OXIDE WITH DYSPROSIUM OXIDE

FIG 2



PULSE EMISSION OF VARIOUS MIXTURES OF NEODYMIUM OXIDE WITH GADOLINIUM OXIDE

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THERMIONIC EMITTER MATERIALS

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1 Claim. (Cl. 252—521)

This invention relates to electron emission and, particularly, to materials for thermionic emitters.

For many years work has been carried on to develop materials which would give a high thermionic emission current when used as cathode surfaces in vacuum tubes. In addition to a high thermionic emission, the materials should be stable at high temperatures in vacuua and should be mechanically strong. The materials should not be adversely affected by positive ion bombardment and should possess long life under the operating conditions for which they are designed.

The oxide-coated cathode which is now generally employed in vacuum tubes is not satisfactory for use in magnetrons or other vacuum tubes where high emission current is required from the cathode. In pulse operation, this type of cathode sparks when high currents are drawn from it for long pulses, and when heated to high temperatures it evaporates excessively, coating other parts of the tube. The thoriated tungsten cathode is unsatisfactory for use in vacuum tubes where potentials are more than about 10,000 volts. When the operating potentials exceed about 10,000 volts, the thoriated tungsten cathode is deactivated by positive ion bombardment. Tungsten possesses the necessary electrical ruggedness required of a cathode and is not adversely affected by positive ion bombardment. Tungsten is not an efficient electron emitter, however, and it must be heated to very high temperatures before sufficient electron emission can be obtained.

It has been discovered, as a part of this invention, that various mixtures of the rare earth oxides give higher pulse emission than either of the pure components of the mixture. No sparking has been observed for cathodes coated with such mixtures at field strengths of the order of 30,000 volts per centimeter. Even when subjected to severe arcing, the cathode surface suffers no apparent damage or deactivation. With continued operation at temperatures of 1500° C. brightness the cathode coatings of the rare earth oxide mixtures have shown no indications of excessive evaporation. The rare earth oxide mixtures have good chemical stability in vacuua at high temperatures. All of these properties go together to produce a cathode coating with good emission properties and a long useful life. This type of material is particularly useful for application in magnetron cathodes where high electrical fields are required and where long life of the tube is desired. Cathodes of this type can also be applied to any high-voltage, high-power tube where sparking and excessive evaporation of the conventional cathode are limiting factors.

Electron emitter materials according to the present invention comprise rare-earth compounds (including compounds of lanthanum) in solid solution. By mixing these

compounds, the work function of the pure components of the mixture may be altered. The vapor pressure of the mixtures is lower than that of the pure component of the mixture with the highest vapor pressure. In addition, cathodes made from such mixtures appear to be easier to activate than the pure components which they contain and are very resistant to emission poisoning.

It is a primary object of this invention, therefore, to provide thermionic emitter materials comprising rare-earth compounds (including lanthanum compounds in such classification) in solid solution.

It is also an object of this invention to provide thermionic emitter materials comprising solid solutions of rare-earth compounds to obtain the foregoing and other desirable properties and advantages.

It is a further object of this invention to provide such solid solutions in which the components are present in such proportions as to provide: (*a*) substantially maximum solubility of one existing crystal phase in another crystal phase present in the solid solution; (*b*) substantially the lowest rate of diffusion and migration therein; (*c*) substantially the maximum distortion of the crystal lattice in the solution.

It is another important object of this invention to provide solid solutions of rare-earth compounds wherein the pulse thermionic emission of the solid solution exceeds that of any of its components.

Other objects and advantages will be apparent from the following detailed description.

In the drawings:

Fig. 1 comprises a graph, in rectangular coordinants, of pulse thermionic emission at 1400° C. for various mixtures of dysprosium oxide with gadolinium oxide; and

Fig. 2 comprises a graph, in rectangular coordinants, of pulse thermionic emission at 1300° C. and at 1400° C. for various mixtures of neodymium oxide with gadolinium oxide.

These figures illustrate advantages of this invention.

An electron emitter material according to this invention is composed of a solid solution of one component in one or more other components, or in solid solutions of the other components. When the materials are placed in solid solution, the pulse emission current is found to be greater than that for either of the two components, when only two components are used. If only a mixture of the two components were involved, then one would expect the pulse emission current to be a linear function of the percentage composition and lie between the values obtained for the two pure components separately. Since this is not the case, then one might expect that one of the components is going into solid solution with a single-crystal phase formed by the two components. It has been discovered as a part of this invention that the maximum pulse emission current is realized when substantially the maximum solubility limit of one of the components in a solid solution of the two components is reached. The same type of explanation applies where more than two components are present. The emission current would then be expected to vary between values obtained from solid solutions of the components and not from the values obtained from the pure components, but the discoveries of this invention show that greater emission currents can be obtained.

The materials which are used in mixtures of the rare-earth compounds should go into solid solution one with the other, or others. The most desirable case is where the materials used have low vapor pressure and give high thermionic emission current, i. e., materials with a low

work function. Since quite a number of the good electron emitters in the rare-earth series have a high vapor pressure, a good emitter of this type may be mixed with a rare-earth compound which has a lower vapor pressure, but probably a higher work function, to provide an improved emitter material. In this case, the vapor pressure of the solid solution formed by such a mixture is lower than that of the component of the mixture with the higher vapor pressure. According to Vegard's law, the lattice constant of the solid solution of two components in each other is given by $a=a_2+(a_1-a_2)A_1$, where a_2 is the lattice dimension of the rare-earth oxide with the smallest lattice spacing, a_1 is the corresponding lattice dimension of the other rare-earth oxide, and A_1 is the fraction of the latter rare-earth oxide in the mixture. Since the vapor pressure is dependent upon the lattice spacing, this law provides a means of predicting the effect on the vapor pressure when solid solution is formed.

The solid solution is formed by co-precipitating solutions of the materials together in a suitable medium, such as oxalic acid, and the resulting precipitate is calcined at a suitable temperature, such as approximates 1000° C. Since the rare-earth oxides are not particularly unstable in air, no special precautions are necessary in their handling except in the case of lanthanum oxide. Lanthanum must be handled as the carbonate to avoid the formation of hydrates. This does not impose a serious handicap upon the use of a lanthanum oxide emitter since it may be treated in the same manner as the ordinary present-day oxide cathode.

For the maximum efficiency a mixture should be chosen which gives the maximum emission current at the desired temperature of operation. The composition of such a mixture may be determined experimentally by actually making emission measurements for various mixtures. It has been found for those mixtures upon which measurements have been made that the maximum pulse emission current is obtained near the low concentration of one or the other of the components and not for the half-and-half mixture. Since the position of the maximum in pulse emission current as a function of the proportions of the components present appears to depend upon the degree of solid solution, it is difficult to predict by calculation where the peaks in pulse emission current might occur because of the lack of information of the chemical and physical properties of the pure rare-earth compounds. For those mixtures upon which measurements have been made, several peaks in emission current have been observed. X-ray diffraction data have shown that these peaks occur near the solubility limit of one or the other components in the crystal phase of the solid solution of the components involved.

The crystal properties of the materials chosen for a mixture should be close enough alike that a solid solution can be formed over a maximum range of compositions. For a solid solution to occur for all proportions of a mixture, it is necessary that the crystal structure be identical, and the dimensions of the lattice should be almost identical. The crystal dimensions and configuration may be determined by X-ray diffraction measurements.

After a mixture is once made, the material may be coated onto the cathode base by any of the commonly accepted techniques, such as spraying, for coating oxide cathodes. After the cathode is coated, no special activation, other than thorough outgassing by heating and drawing emission current, is required. Mixtures of the rare-earth oxides do not attack any of the commonly used cathode base materials.

The proportions of the mixtures of materials should be such that the solubility limit of one of the components in a solid solution of the other components is reached. In some mixtures several peaks in the emission current may occur over a range of proportions of the components. In other only one peak might occur over a range of proportions.

Cathodes coated with mixtures of neodymium oxide with gadolinium oxide, dysprosium oxide with gadolinium oxide, and neodymium oxide with cerium oxide, have been operated as thermionic emitters in an experimental diode. Gadolinium oxide with neodymium oxide, and gadolinium oxide with dysprosium oxide, were tested in several mixtures. The mixtures of gadolinium oxide with neodymium oxide ranged in composition from zero per cent gadolinium oxide to zero per cent neodymium oxide. The mixtures of the gadolinium oxide with dysprosium oxide ranged in composition from zero per cent gadolinium oxide to zero per cent dysprosium oxide. It was found that the maximum pulse emission current was obtained from a cathode coated with a mixture of twenty-five per cent gadolinium oxide with seventy-five per cent neodymium oxide by weight. The pulse emission current from this mixture was about six times greater than that from the pure component of the mixture with the higher emission current. A mixture of only one composition was tried for neodymium oxide with cerium oxide. The pulse emission current was much higher than that obtained from either of the components of the mixtures. The maximum emission current for the mixtures of gadolinium oxide occurred when the composition approximated seventy-five per cent gadolinium oxide and twenty-five per cent dysprosium oxide by weight.

These results are set forth in greater detail in Fig. 1 and Fig. 2 and in the following examples and tables. The thermionic emission measurements in the examples were made by the following method.

After a coating has been prepared on a cathode, the cathode is inserted in a vacuum system. The system is exhausted to a pressure of about 10^{-6} mm. of mercury before heating the cathode is initiated. The temperature of the cathode is slowly raised while outgassing occurs. After the temperature of the cathode is raised to 1500° C. or more without substantially lowering the pressure, the D. C. voltage is applied across the diode comprising the cathode and an auxiliary anode covering a platinum anode. The voltage is then slowly raised until the emission current reaches the maximum safe value for the auxiliary anode. With the cathode still hot, the auxiliary anode is raised and the clean platinum anode is exposed for the remainder of the conditioning period and for the emission measurements. The voltage is then raised slowly until the saturation current is reached. This whole process may take as long as 48 hours of operation before a steady pressure and a constant emission current are obtained. After this state of equilibrium is reached, the actual thermionic-emission measurements are initiated. These measurements are obtained by decreasing the voltage and the temperature in steps, in order to maintain the cathode in a reasonably constant state of activation. Alternate D. C. and pulse measurements are taken so that the cathode is in the same state of activation for both types of measurement. The usual procedure is to make at least three D. C. measurements and two pulse measurements. The saturation currents are determined from the characteristics curves. The results are reproducible.

EXAMPLE I

Thermionic-emission measurements were made as described above for cathode coatings of neodymium oxide, of cerium oxide, and of a solid solution comprising seventy-five per cent neodymium oxide and twenty-five per cent cerium oxide. Table I lists the emission currents at 1300° C. and at 1400° C., the work functions, and the Richardson constants for these emitter materials. From Table I it is apparent that, although cerium oxide by itself is an unsatisfactory material for thermionic emission, in fact so poor that no measurements could be obtained, the mixture of cerium oxide and neodymium oxide provides nearly twice as much pulse emission current at 1300° C. and three times as much pulse emission current at 1400° C. as does neodymium oxide by itself.

Table I

Mixture	Type Emission	Emission Current, Amp./cm.²		Emission Constants	
		1,300° C.	1,400° C.	ϕ Electron Volts	A Amp./cm.² °K.²
0 CeO_2, 100% Nd_2O_3	D. C	0.041	0.220	2.18	0.158
	Pulse	0.222	0.601	1.99	0.211
25% CeO_2+75% Nd_2O_3	D. C	0.068	0.220	1.83	0.02
	Pulse	0.394	1.80	2.08	0.73
100% CeO_2, 0 Nd_2O_3	Low emission, unstable				

EXAMPLE II

The same type of thermionic emission measurements as were made in the first example were made for cathodes coated with gadolinium oxide, with dysprosium oxide, and with six mixtures of the two compounds in various proportions. The emission currents at 1400° C., the work functions, ϕ, and the Richardson constants, A, for these emitter materials are listed in Table II. The pulse emission currents listed in Table II are plotted in Figure 1 of the drawing. From Table II and Figure 1, it is apparent that increased pulse emission is obtained with various mixtures of the components, particularly with solid solutions having from about 20 per cent to about 30 per cent dysprosium oxide and the balance essentially all gadolinium oxide.

Table II

Mixture	Type Emission	Emission Current, Amp./cm.², 1,400° C.	Emission Constants	
			ϕ Electron Volts	A Amp./cm.² °K²
100% Gd_2O_3, 0 Dy_2O_3	D. C	0.436	2.54	6.70
	Pulse	0.372	2.18	0.500
90% Gd_2O_3+10% Dy_2O_3	D. C	0.012	3.1	5.25
	Pulse	0.052	3.14	27
75% Gd_2O_3+25% Dy_2O_3	D. C	0.388	1.95	0.10
	Pulse	0.745	2.74	44
60% Gd_2O_3+40% Dy_2O_3	D. C	0.145		
	Pulse	0.826	2.46	9.34
50% Gd_2O_3+50% Dy_2O_3	D. C	0.019	2.94	4.8
	Pulse	0.870	3.16	945
25% Gd_2O_3+75% Dy_2O_3	D. C	0.191	1.81	0.02
	Pulse	0.610	1.70	0.03
10% Gd_2O_3+90% Dy_2O_3	D. C	0.110	2.66	4.7
	Pulse	0.410	2.62	8.9
0 Gd_2O_3, 100% Dy_2O_3	D. C	0.550	2.28	1.58
	Pulse	0.790	2.28	2.51

EXAMPLE III

Thermionic emission measurements were made as in the first two examples for cathodes coated with neodymium oxide, with gadolinium oxide, and with mixtures of these two compounds in various proportions. Table III lists the emission currents at 1300° C. and at 1400° C., the work functions, and the Richardson constants for these emitter materials. The pulse emission currents at 1300° C. and at 1400° C. listed in Table III are plotted in Figure 2 of the drawing. From Table III and Figure 2, it is apparent that mixtures of the components provide increased pulse emission, particularly the solid solutions having from about 15 per cent to about 35 per cent gadolinium oxide and the balance essentially all neodymium oxide, and those having from about 85 per cent to about 95 per cent gadolinium oxide and the balance essentially all neodymium oxide.

Table III

Mixture	Type Emission	Emission Current, Amp./cm.²		Emission Constants	
		1,300° C.	1,400° C.	ϕ Electron Volts	A Amp./cm.² °K²
100% Nd_2O_3, 0 Gd_2O_3	D. C	0.042	0.220	2.18	0.158
	Pulse	0.227	0.601	1.99	0.211
90% Nd_2O_3+10% Gd_2O_3	D.C	0.089	0.225	1.85	0.03
	Pulse	0.199	1.27	1.74	0.03
75% Nd_2O_3+25% GD_2O_3	D. C	0.332	0.170	2.9	251
	Pulse	1.30	5.35	2.34	1.59
60% Nd_2O_3+40% Gd_2O_3	D. C	0.068	0.172	1.98	0.06
	Pulse	0.541	1.85	1.98	0.48
40% Nd_2O_3+60% Gd_2O_3	D. C	0.079	0.237	2.27	0.58
	Pulse	0.534	1.55	1.84	0.15
25% Nd_2O_3+75% Gd_2O_3	D. C	0.143	0.273	2.12	0.35
	Pulse	0.271	1.17	2.12	0.66
10% Nd_2O_3+90% Gd_2O_3	D. C	0.075	0.265	2.52	3.5
	Pulse	1.51	2.42	1.77	0.28
100% Nd_2O_3, 100% Gd_2O_3	D. C	0.125	0.436	2.54	6.70
	Pulse	0.132	0.372	2.18	0.500

The maximum pulse emission current appears to be obtained when the solubility limit of one of the components in the solid solution of the two or more components is approached. It is possible to prepare mixtures of various rare-earth oxides which will form solid solutions in which one of the crystal phases present approaches the solubility limit of one phase in another. The same mechanism holds

for the rare-earth borides, the rare-earth sulfides, the rare-earth oxides with the rare-earth borides or sulfides, or any combination of refractory compounds of the rare earths suitable for cathode coating materials.

In addition to increasing the thermionic emission over that obtained from the pure compounds used in the rare-earth oxide mixtures, cathodes of this type have shown no temperature rise as a result of drawing pulsed emission current. Chemical stability beyond that of some of the pure components which are used in the mixtures has been observed. It is predicted, because of the known chemical similarities, that mixtures of rare-earth compounds of the *5f* series will also produce the same effect that is observed for mixtures of the rare-earths compounds of the *4f* series. Unavailability of rare earths of the *5f* series has so far prevented any verification of this prediction.

The D. C.-emission data are included in the tables because these data are more nearly in accord with what is normally to be expected from a mixture of ingredients for thermionic emission. The D. C.-emission currents for the mixtures tested lie predominantly between the D. C.-emission currents obtained with the individual components separately, as would be expected. The results of the D. C.-emission measurements, therefore, tend to emphasize the unexpected character of the results for pulse emission of mixtures of rare-earth compounds according to this invention.

It is apparent from the foregoing disclosure that thermionic emitter materials have been provided which comprise rare-earth compounds (including lanthanum compounds in this classification) in solid solutions wherein the pulse thermionic emission exceeds that of any of the components of the solid solution. It will be obvious to those skilled in the art that various changes may be made without departing from the scope of this invention, which is not limited by the particular description above but may be defined in such broader terms as will come within the disclosure.

What is claimed is:

A thermionic emitter material consisting essentially of a solid solution of from about 15% to about 35% gadolinium oxide and the balance essentially neodymium oxide.

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