Oct. 28, 1958 M. P. WARIN 2,858,207

THERMIONIC CATHODE CORES COMPOSED OF NICKEL-RHENIUM ALLOY

Filed Dec. 22, 1955

Fig. 2

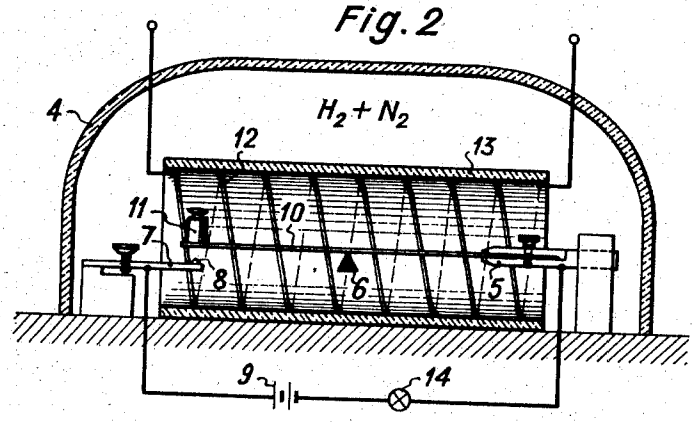


Fig. 1

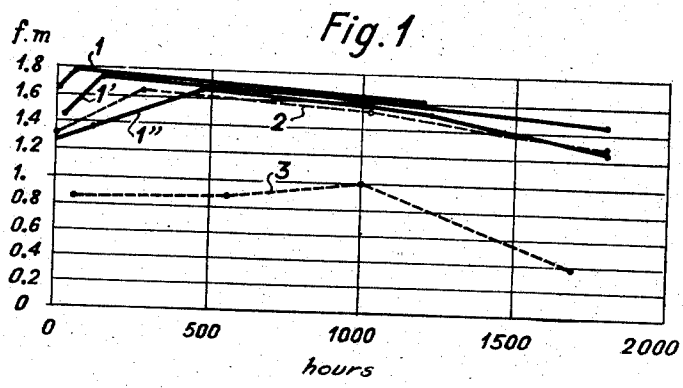
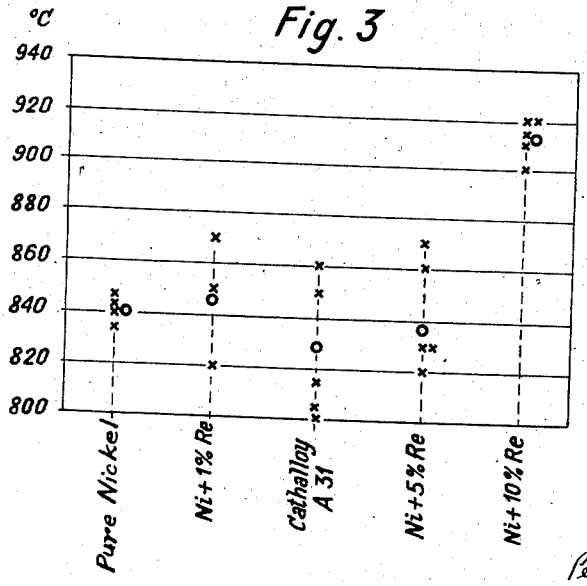


Fig. 3



INVENTOR
Maurice P. Warin

BY
Pennie Edmonds, Morton, Barrows & Taylor

ATTORNEYS

United States Patent Office 2,858,207
Patented Oct. 28, 1958

2,858,207

THERMIONIC CATHODE CORES COMPOSED OF NICKEL-RHENIUM ALLOY

Maurice P. Warin, Clichy, France, assignor to Etablissements Charles Bertolus, Paris, France, a French company

Application December 22, 1955, Serial No. 554,907

Claims priority, application France December 24, 1954

3 Claims. (Cl. 75—170)

The present invention relates to metallic cores for thermionic cathodes which have alkaline earth oxide coatings.

For many years thermionic cathodes of the alkaline earth oxide type have employed electrolytic nickel as a base metal or core. It has however been proposed, in order to obtain more dependable and uniform operation, to add to relatively pure nickel small amounts of reducing metals whose function is to reduce the alkaline earth oxides with which the cathodes are coated.

For example magnesium can reduce barium oxide according to the reaction.

$$BaO+Mg \rightarrow MgO+Ba$$

According to presently accepted views, a satisfactorily emissive cathode of the alkaline earth oxide type is to be considered as a semiconductor of type N including a sufficient proportion of an impurity provided by free atoms of the alkaline earth metals, particularly free atoms of barium.

Satisfactory emission is thus dependent upon the liberation of a sufficient quantity of alkaline earth metals from the oxides thereof which are employed as coating materials.

The probability that this reduction of the alkaline earth oxides by the added element will take place and liberate a sufficient quantity of metallic barium increases with the heat of formation of the oxide of the added metallic element. It is this consideration which suggested first the use of powerful reducing agents, i. e. those the formation of whose oxides is accompanied by the liberation of a large amount of heat. The metals selected were accordingly aluminum, magnesium, silicon, titanium, zirconium and others having stable oxides.

The use of these metals is subject to several disadvantages. Some, like magnesium, are volatile and may be eliminated by evaporation either in the heat treatment of the alloy forming the cathode base metal and of the cathodes made therefrom or in the operation of such cathodes in electron tubes.

Others of these metals are susceptible to at least partial oxidation in the course of heat treatment of the alloys or of the cathodes made therefrom. In order however for the reducing agent to reduce the alkaline earth oxides, it must be in a metallic and non-oxidized state.

Lastly it has been recognized that most of the strongly reducing elements develop oxides which combine with the alkaline earth oxide coatings to form interfacial layers between the base metal and the alkaline earth coating.

For example there are formed intermediate layers of the following compounds:

$$Ba_2SiO_4, Ba_2TiO_4, BaAl_2O_4$$

Most of these compounds have the disadvantage of high electrical resistivity which makes the cathodes unsuitable for certain uses.

Certain metals less strongly reducing in their action such as tungsten have been used in higher proportions,

e. g. up to 4% or 5% by weight. In the complete absence of a reducing element other than tungsten the formation of emissive coatings of alkaline earth oxides on nickel-tungsten alloys remains difficult to achieve, probably in consequence of the relatively weak reducing action of tungsten even in the high proportions used.

To remedy this defect, reducing agents such as aluminum, magnesium, silicon and titanium have been added, but the alloys so formed do not wholly avoid the disadvanges mentioned above which accompany the use of very strongly reducing materials.

Tungsten has the disadvantage that it itself develops interfacial layers with the alkaline earth oxides. Among others it develops the basic tungstate of barium Ba_3WO_6. Although this compound does not present appreciable resistance to the passage of the electronic current, it has nonetheless the defect of low emissivity. Moreover it takes on, at operating temperature a rather dark color which increases the loss by radiation and hence lowers the cathode temperature.

Another disadvantage of these interfacial layers is that they promote mechanical separation of the alkaline earth coatings on the cathodes.

Applicant has therefore sought an alloying element for addition to the nickel which would not have the disadvantages of the alloying elements hereinabove discussed and which would moreover have a capacity for improving the mechanical properties of the nickel better than have the additive elements of the prior art. Applicant has sought such an additive element among the transition metals whose oxides are volatile at the operating temperatures of oxide-coated cathodes so that in this way all danger of the formation of interfacial layers would be avoided. In order for this result to be achieved however, it would be necessary for these oxides of the additive element to have relatively low vapor pressure and dissociation pressure, below that normally existing in electron tubes, i. e. of the order of 10^{-6} mm. of mercury or less.

Applicant has discovered that rhenium, the second most refractory metal after tungsten, possesses the desired properties, and the present invention provides thermionic cathodes of the alkaline earth oxide type whose core comprises an alloy of nickel and rhenium.

Applicant first undertook experiments intended to study the behavior of alkaline earth oxides in the presence of pure rhenium. Test diodes were constructed using plane circular cathodes.

For a first series of tests the actively emitting portion of these cathodes comprised a disk of nickel which was itself passive in the sense that it contained only a very small proportion of the reducing elements silicon and magnesium customarily used as activators of nickel cathodes, the proportion being less than 0.01%.

These nickel disks were coated with a layer of rhenium at least 10 microns thick by one of the following processes:

(1) Electrolytic deposition of alkali-metal perrhenates in acid solution.

(2) Coating by thermal dissociation, in a vacuum, of rhenium trichloride vapor, the cathode disk being heated to about 1400° C.

(3) Coating by means of powdered rhenium applied with a pressure of from two to five tons per square centimeter.

In a second series of tests the cathodes or cathode cores were made of solid rhenium prepared from powder sintered at high temperature and brought by successive rolling and annealing operations at 1750° C. to a thickness of 0.2 mm.

For these two series of tests the cathode cores were coated with alkaline earth carbonates. The cathodes so

coated were then assembled into diodes which were exhausted, and the cathodes were thereafter treated in the usual manner. It was observed that emissive coatings on rhenium were easily obtained from these alkaline earth carbonates without encountering the difficulties mentioned above which apply in the case of other refractory metals such as molybdenum and tungsten.

With tungsten as an additive, unless special precautions are taken to avoid oxidation of the base metal, for example by means of carbon dioxide given off during decomposition of the carbonates, there will be formed compounds of the alkaline earths such as $BaWO_3$, $BaWO_4$, Ba_3WO_6. These compounds are not electron emissive although they are stable at the high temperatures of activation and at the operating temperatures of thermionic cathodes.

The results obtained with alkaline earth oxides on rhenium confirm the data in the chemical literature concerning the instability, at high temperature and under vacuum, of the oxygen-containing compounds of rhenium with alkaline earth metals, such as barium rhenate $BaReO_4$ and perrhenate $Ba(ReO_4)_2$.

Life tests over a wide range of temperatures confirm the excellent qualities of the emissive coatings thus prepared.

The emission was stable throughout operating tests exceeding 2000 hours, in the course of which there occurred not the least formation of interfacial resistance.

Although rhenium is less strongly reducing than tungsten, the excellent life properties as well as the rapid activation of cathodes according to the invention can be explained on the assumption that the rhenium frees barium from barium oxide according to the reaction:

$$\underset{\text{(solid)}}{n\text{Re}} + \underset{\text{(solid)}}{p\text{BaO}} \rightleftarrows \underset{\text{(volatile)}}{\text{Re}_n\text{O}_p} + \underset{\text{(vapor)}}{p\text{Ba}}$$

This reasoning is of course applicable to other alkaline earth oxides present in the emissive coating.

The reaction last given can occur from left to right as a result of the fact that the equilibrium tends to shift in this direction, the products of the reaction in this direction being both gaseous at the temperature at which the reaction takes place.

The oxygen-containing rhenium compound indicated by the symbol Re_nO_p may be a single oxide or a mixture of the known oxides ReO_2, ReO_3, Re_2O_7, etc., which are volatile at the cathode formation or activation temperature and at the operating temperature of the cathodes, having moreover a thermal dissociation pressure low enough so that the barium vapor formed (and which remains adsorbed in the interior of the emissive coating) will not be reoxidized.

Moreover the volatilization of rhenium oxide does not appear to be troublesome inasmuch as no parasitic electric conductivity appeared in the vacuum tubes of applicant's experiments.

power such as are used in miniature and sub-miniature tubes having directly heated cathodes. The relatively high resistivity of rhenium (21.10^{-6} ohm-cm. at 20° C.) leads to heavier and consequently more rugged filaments than those of tungsten or alloys of nickel presently in use. Rhenium has moreover the advantage that it does not change with age, its recrystallization temperature being much higher than either the operating or formation temperatures of alkaline earth oxide cathodes.

(2) As an activator for liberation of the alkaline earth metals from their oxides at the activation and operating temperatures of thermionic cathodes.

On the basis of this experience, applicant has produced alloys in accordance with the present invention formed of varying proportions of rhenium with a balance of pure nickel.

Applicant has found that the reducing action of rhenium is substantial in alloys containing as little as 0.1% of this element. Applicant has compared, in oxide-coated cathodes, and over the useful lives thereof, the thermionic properties of alloys comprising 1, 5 and 10% of rhenium with a balance of pure nickel with those of rhenium-free alloys. The criterion adopted in this comparison for evaluating various cathodes of the same physical shape is the factor of merit defined in the article of Thomas H. Briggs and C. D. Richards, Jr. in the bulletin of the A. S. T. M. for January 1951.

In the accompanying drawings:

Fig. 1 is a graph representing the variation with time of this factor of merit for diodes having plane circular cathodes 6 mm. in diameter mounted 1.5 mm. from their anodes and operated with 30 volts between anode and cathode.

Fig. 2 is a diagram of a test apparatus useful in testing the alloys of the invention; and

Fig. 3 is a graph useful in explaining the properties of the alloys of the invention.

In Fig. 1, the curves **1**, **1'** and **1''** represent the variation, with time in hours, of the factor of merit (abbreviated f. m. in the figure) for alloys of 1, 5 and 10% of rhenium respectively, the balance in all cases being substantially pure nickel.

Curve **2** similarly represents the variation with time of the factor of merit for an alloy of the prior art comprising 4% of tungsten, from 0.01 to 0.06% magnesium, 0.05% silcon, 0.02% titanium, 0.1% iron, 0.12% manganese, 0.1% copper, 0.08% carbon, and the balance nickel. This alloy is commercially known as "Cathalloy A31."

Curve **3** represents the variation with time of the factor of merit for an "active" nickel of the prior art including 0.21% silicon, this alloy being commercially known as "Supernickimphy No. 2."

The composition by weight percents of the various alloys whose factors of merit are plotted in Fig. 1 is given in the accompanying table:

Alloy	Composition in Percent by Weight											
	P	S	Si	Mg	Fe	Mn	Cu	Ti	C	W	Re	Ni
"Supernickimphy" No. 2	------	0.004	0.21	0.03	0.04	tr.	------	------	0.07	------	------	balance.
"Cathalloy A31"	------	------	0.05	0.01 to 0.06	0.10	0.12	0.10	0.02	0.08	3.75 to 4.25	------	Do.
NiRe 1	0.01	0.003	tr.	------	0.06	tr.	------	------	0.03	------	1	Do.
NiRe 5	0.01	0.003	tr.	------	0.06	tr.	------	------	0.03	------	5	Do.
NiRe 10	0.01	0.003	tr.	------	0.06	tr.	------	------	0.03	------	10	Do.

tr. = traces.

In summary the results of applicant's tests indicate value in the use of rhenium:

(1) As a support for the alkaline earth oxides, this support being either in the form of a coating on another metallic support or in the form of the base metal or core of the cathode structure itself. One such application is to directly heated cathodes, particularly those of low

The improvement in thermionic properties achieved with the alloys of the invention having 1, 5 and 10% of rhenium is seen in Fig. 1 to be substantial with respect to the alloy of 4% tungsten (curve 2) and even greater with respect to the active nickel alloy including silicon (curve 3).

Rhenium is thus seen to be an additive element for use

with nickel which is particularly effective in the formation of oxide-coated cathodes, the resulting alloy being easy to manufacture and of long life. This is demonstrated by applicant's data which shows that alloys containing rhenium and nickel alone give better results than those in which other reducing agents are added to complement the action of tungsten.

The preparation of these rhenium-containing alloys and the chemical control thereof are much more easy and dependable since rhenium, being a refractory metal with low reducing power, is not subject to volatilization as is magnesium, nor subject to oxidation as are aluminum, silicon, titanium and zirconium in the course of the necessary heat treatments.

Chemical proportioning of rhenium permits achievement in the resultant cathode structure of the desired proportion of effectively activated metal, without the necessity of electronic control.

Applicant has moreover observed that prolonged heating at the operating temperatures of thermionic cathodes does not involve grain growth in nickel-rhenium alloys. Applicant has further observed that the addition of rhenium to nickel, in particular for proportions of rhenium of at least 5% and strikingly for proportions between 10 and at least 30%, substantially improves the mechanical properties of the resulting alloy at high temperature. The manufacture of nickel-rhenium alloys presents no problems. These alloys are highly ductile, and it is possible to obtain filaments 25 microns in diameter.

For measurement of these improved mechanical properties applicants have used the apparatus schematically indicated in Fig. 2. In Fig. 2 **4** represents a bell jar through which are passed streams of nitrogen and hydrogen. A clamp **5** of molybdenum supports at one end a test piece **10** of the alloy under investigation. At **6** is shown a knife-edged support of alumina. A molybdenum blade **7** carries at its end a nickel contact **8**. A battery **9** and an indicator lamp **14** are mounted in series with the clamp **5** and contact **8**.

The alloy under test in the form of the test blade **10** may for example take the form of a sheet $\frac{1}{10}$ of a millimeter in thickness and 3 millimeters wide by 30 millimeters long. The test piece is clamped at one end in the clamp **5**, and the free end of the test piece overlies the contact **8**, the mid-point being supported at the knife edge **6**. The distance between this knife edge and the contact **8** is 15 millimeters for the test piece dimensions given.

A weight **11**, which in applicant's experiments was of 890 milligrams, is applied to the free end of the test piece and the apparatus is so established that with the whole system at room temperature and with the weight **11** in place there exists a spacing of 1 millimeter between the contact **8** and the free end of the test piece.

A furnace comprising a Nichrome resistor **12** wound inside a quartz tube **13** makes it possible to heat the test piece. By plotting the rise in temperature of the furnace against time for a given voltage applied to the ends of the resistance wire **12**, it is possible, at least over the rising portion of the resulting curve, to correlate the interior temperature of the furnace with heating times from a cold start. Note is then taken of the temperature reached at the time when the end of the test piece comes into contact with the contact **8**. This temperature is then derived from the time elapsing between the start of the heating step and the moment when the test lamp **14** is lighted.

When cold, the bend of the test piece is $\frac{1}{100}$ of a millimeter. When hot and at the instant of lighting of the lamp, it amounts to 1 millimeter. On the assumption that the region of elasticity is not departed from, one may conclude that the time of lighting of the lamp corresponds to a decline of the modulus of elasticity E such that

$$\frac{E_{\text{final}}}{E_{\text{initial}}} = \frac{1}{100}$$

In Fig. 3, the crosses represent for the various alloys of the table and for pure nickel the temperatures reached by the furnace at the moment when the lamp is lighted in the course of a number of tests. The circles represent the average of these "final" temperatures or temperatures of collapse for the various alloys and pure nickel respectively. It is to be observed that the nickel-rhenium alloy having 10 percent of rhenium exhibits a collapsing temperature of 915° C. which is some 75° C. above the corresponding temperatures of the prior art alloys whose collapsing temperatures are approximately 840° C.

From a mechanical point of view this result is of great significance for cathodes of electron tubes which are subjected in use to vibration or to shock or acceleration. When the mechanical conditions of utilization of the cathodes are particularly severe, the content of rhenium in the nickel-rhenium alloy may be as much as 30 percent.

In summary, alloys of nickel with rhenium exhibit the desired properties for a cathode core or base metal and possess the following advantages with respect to presently known alloys:

(1) Ease of preparation, particularly with respect to control by chemical analysis.

(2) Stability at the temperatures of manufacture and use, i. e. absence of risk of oxidation of the active element, or of loss thereof through evaporation.

(3) Effective reduction of the alkaline earth oxides, which contributes to an easy activation of the cathodes.

(4) Speed of diffusion sufficient to insure a continuous and dependable reduction of the alkaline earth oxides throughout a long useful life for the cathodes, without appearance of interface layers due to volatility of the reaction products.

The third and fourth of these enumerated advantages are established by the high values rapidly reached for the factor of merit. This denotes easy activation (item 3) and maintenance of this high factor of merit throughout a long useful life (item 4).

(5) Improvement in mechanical properties, particularly resistance to flexure at high operating temperatures.

(6) Raised fusion and recrystallization temperatures.

(7) Susceptibility to complete out-gasing during the processing of the cathodes, no gases being retained in chemically combined form with the components of the alloy.

(8) Reduction in thermal conductivity—a generally advantageous factor for both filaments and indirectly heated cathodes.

(9) Increase in electrical resistivity—a factor of particular benefit in the case of directly heated cathode filaments since it makes possible filaments of larger cross section.

The nickel-rhenium alloys described herein are particularly advantageous when the nickel used is of high purity, such as that sold under the name "Nickel Mond." It is to be understood however that the invention also comprises cathode alloys in which the nickel includes the usual proportion of reducing metals, in particular from 0.01 to 0.2% of silicon and from 0.01 to 0.15% of magnesium.

I claim:

1. An electrically conductive core for a thermionically active cathode having an alkaline earth oxide coating comprising an alloy consisting essentially of from 1 to 30% by weight of rhenium and the balance all nickel.

2. An electrically conductive core for thermionic cathodes with alkaline earth oxide coatings having a factor of merit greater than 1.3 and a collapsing temperature between 840° and 915° C. comprising an alloy

consisting essentially of from 1 to 10 percent by weight of rhenium and the balance all nickel.

3. An electrically conductive core for thermionic cathodes with alkaline earth oxide coatings having a collapsing temperature in excess of 900° C. comprising an alloy consisting essentially of from 10 to 30 percent by weight of rhenium and the balance all nickel.

References Cited in the file of this patent

UNITED STATES PATENTS

1,806,410	Noddack et al.	May 19, 1931
1,829,756	Noddack et al.	Nov. 3, 1931
2,308,389	Reyling	Jan. 12, 1943
2,323,173	Widell	June 29, 1943
2,391,458	Hensel	Dec. 25, 1945
2,778,970	Widell	Jan. 22, 1957

FOREIGN PATENTS

746,015	Germany	May 12, 1943
351,216	Great Britain	June 4, 1930

OTHER REFERENCES

Materials and Methods (Rhenium Metal—Its Properties and Future, Kates), March 1954, pages 88–91.