Feb. 4, 1969 J. W. DENISON, JR 3,425,111

METHOD OF MAKING CATHODES BY NEUTRON BOMBARDMENT

Filed Oct. 8, 1964 Sheet 1 of 2

Fig. 1.

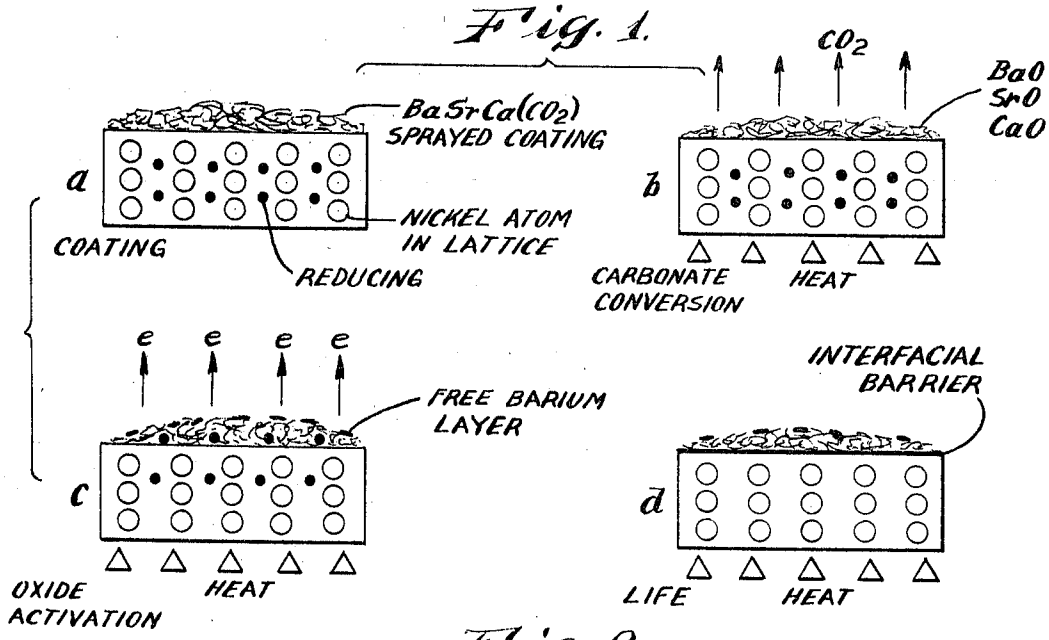
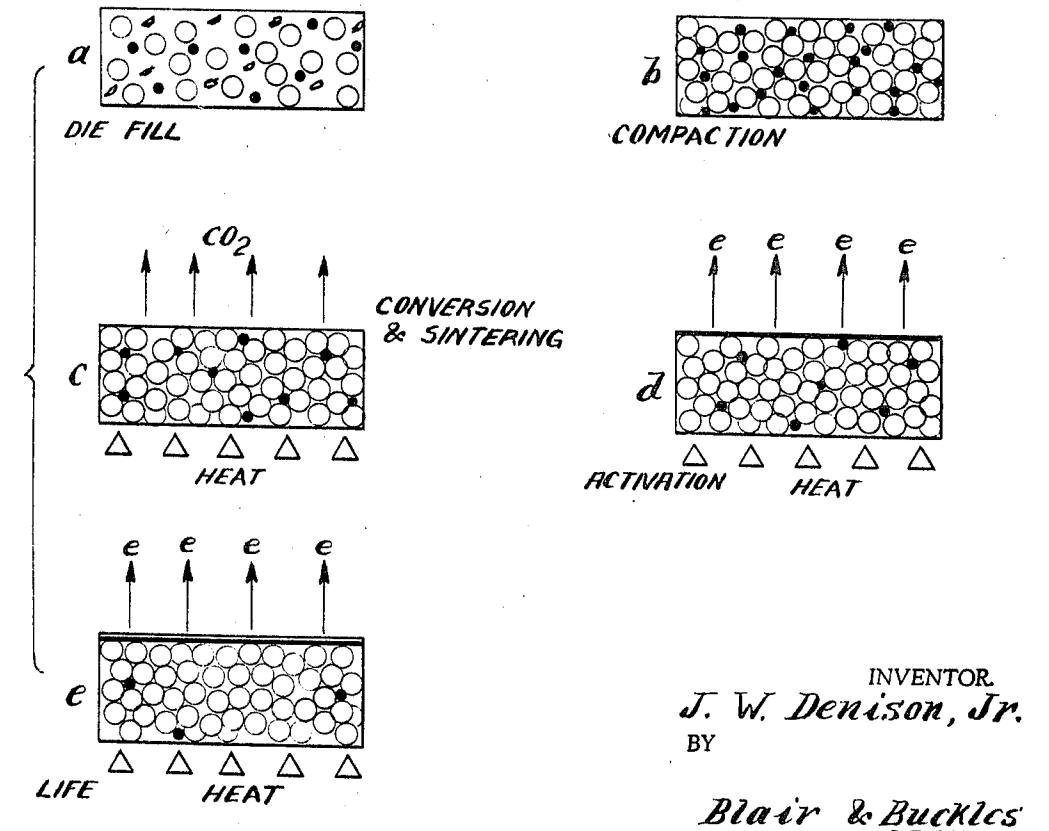


Fig. 2.



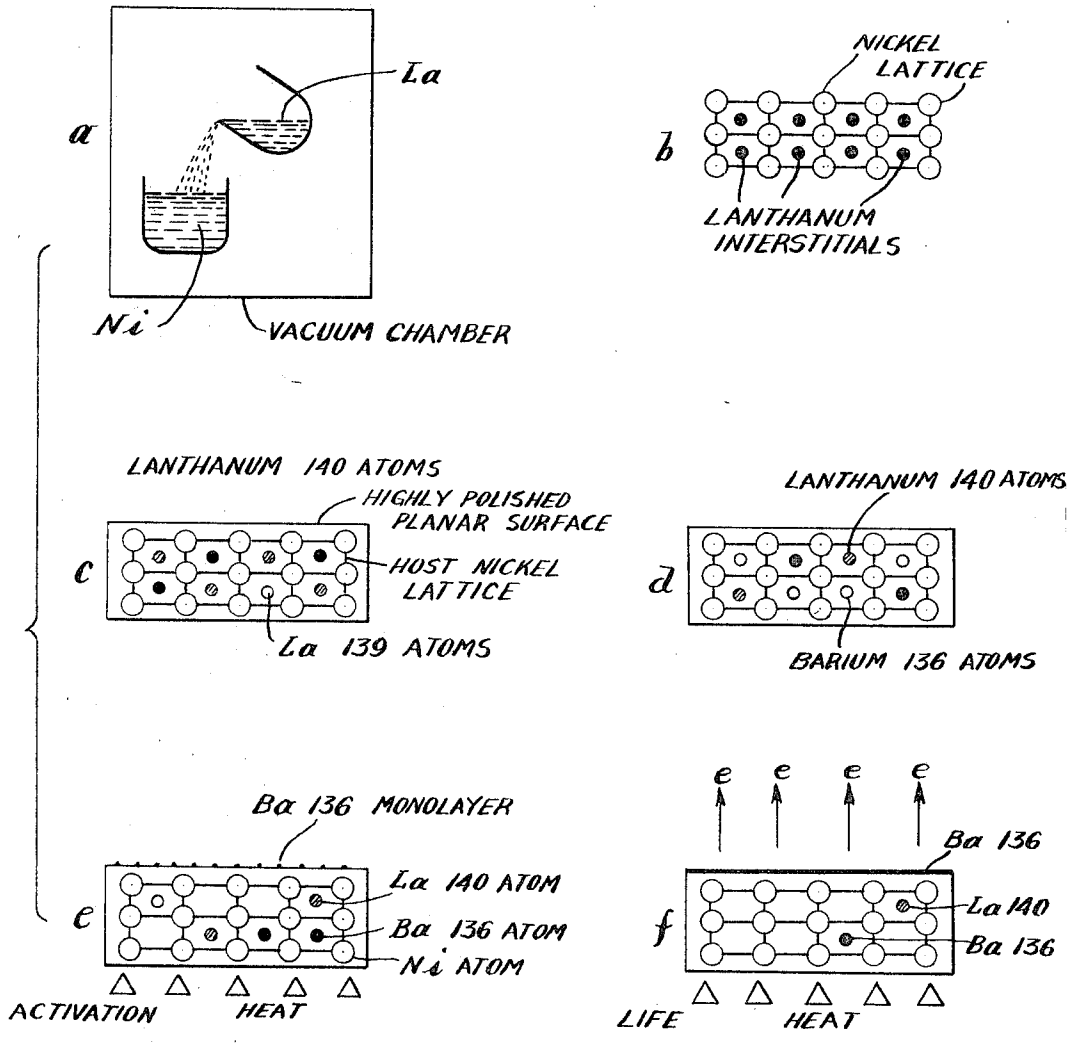
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Fig. 3.



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METHOD OF MAKING CATHODES BY NEUTRON BOMBARDMENT

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Int. Cl. H01j 9/00, 9/04; G21g 1/00

ABSTRACT OF THE DISCLOSURE

A method is disclosed for producing improved electron emissive cathodes for use in vacuum tubes and other electronic applications. The method of the invention employs nuclide reactions through neutron bombardment to transmute atoms of rare earth metals within a host metal base into a pure metal matrix of low work function, without the presence of oxygen. The irradiated base and matrix is then heated in a vacuum to cause the rare metal atoms within the matrix to migrate to the host surface where they form a monatomic layer of the low work function pure metal. The method is applicable to a variety of base metals and rare earths transmutable into pure metals having the desired work function characteristics. A detailed process is disclosed as a preferred embodiment using nickel as the host metal and lanthanum as a dopant which is transmuted into barium atoms in a matrix within the nickel.

This invention relates to electron emissive cathodes for vacuum tubes, and particularly to methods for making such cathodes having superior operating characteristics and longer active life. The improved cathodes of the invention are particularly well suited for incorporation in small vacuum tubes designed for microwave radio frequency applications, although the advantages of the invention may be realized also in other forms of vacuum tubes.

Cathodes are surfaces which emit electrons under the influence of an activating energy, such as heat, and generally in the presence of an electric field which attracts the electrons thus released in a desired path through a vacuum, usually toward an anode. The performance of vacuum tubes at ultra high frequencies, and in the microwave spectrum particularly, is directly related to cathode operation. Some of the inherent problems in vacuum tube technology are to design cathodes for high current density, maximum efficiency, low noise operation, long life, minimum degradation, and yet capable of meeting severe stress requirements—both electrical and mechanical.

The primary objective of this invention is to produce cathodes having all of the above mentioned characteristics.

A more particular object is to produce such cathodes having an unusually long life, and with minimum degradation during continued operation.

A further object is to provide a method for producing such cathodes which is simple of operation and yields uniformly consistent results.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

FIGURE 1 represents a prior art method of cathode formation by sprayed oxide coating. The successive sketches *a* through *d* relate the thermal history of such an oxide coated cathode from initial piece part manufacture to life end point, showing the chemical reactions involved in the production of electrons.

FIGURE 2 represents another form of prior art cathode, generally known as a "dispenser cathode," and the successive sketches *a* through *e* relate the chemical reactions in the thermal history of such a cathode.

FIGURE 3 represents the steps involved in the formation of improved cathodes by nuclear transformation, in accordance with my invention.

GENERAL DISCUSSION

Any cathode design is a compromise of factors and parameters. For example, a high cathode temperature allows copius quantities of electrons to be emitted; a cathode temperature as low as possible increases tube reliability by relieving heater requirements. Tube failure rates are vastly improved if heater energy can be reduced. In addition, total tube life and emission performance are determined by the chemical thermodynamics of the cathode structure and end-point reactions that cause thermionic emission density reduction.

The cathodes in which I am here interested, and which are the subject of this invention, are composed of a pure nickel base support with means for providing and maintaining a thin layer of pure barium or lithium coating on the emitting surface.

Prior cathode techniques have included the coating of a barium oxide, as by spraying, on the surface of a nickel base. When heat was applied to the base the inherent impurities in the nickel, which might include minute quantities of titanium, zirconium, magnesium, aluminum, or silicon, would react with the surface oxide coating to reduce a portion of the barium oxide to pure metallic barium. The chemical reaction interplay during such cathode operation is of considerable interest. One of the important reactions related to tube life and performance is the formation of a dielectric interface layer at the boundary of oxide deposit and nickel base metal.

X-ray diffraction technique has been used to identify the compounds present and estimate their thickness. They are formed by solid-state reaction between the coating and base metal constituents. Some of the interface compounds formed as a function of time, temperature, and diffusion coefficient are as follows:

Si—Barium orthosilicate Ba_2SiO_4
Al—Barium aluminate $BaAl_2O_4$
Ti—Barium titanate $BaTiO_3$
Mg—Magnesium oxide MgO
Zr—Barium zirconate $BaZrO_3$

Although these elements are vitally necessary for production of free barium, under most conditions of tube operation they continue to react, following their reducing role, to form the compound known as interface. Since these compounds are dielectric, they impose an impedance into the tube circuitry with deleterious effect. In addition, it has been speculated that the interface layer may actually limit the thermionic emission of a cathode through ohmic resistance or potential barrier. In high frequency close-spaced tubes a major fraction of an applied voltage pulse may be lost in the interface layer.

Cathode sparking is undoubtedly related to the presence of an interface. The presence of high resistance interface layer will limit the maximum available pulse emission current where sparking occurs either by joule heating of the layer locally, or by dielectric breakdown where energy is absorbed. Interface impedance can cause a drastic drop in transconductance (*gm*), and substantially shorten effective life of a tube.

Therefore, elimination of interface is an important objective of my invention, resulting in improved emission, improved transconductance (*gm*), decreased internal shorts, and other factors leading to improved reliability.

PRIOR ART METHODS

Referring now to FIGURE 1 of the drawings, the steps and reactions involved in making and operating oxide coated cathodes will be briefly described. As shown at

FIGURE 1*a*, the nickel base metal contains small quantities of reducing impurities interspersed in the interstices between nickel atoms in their normal lattice. A coating of barium strontium calcium carbonate, BaSrCa (CO_3), is first sprayed on one surface of the nickel base. Heat is then applied in step *b* to the opposite surface of the base to effect carbonate conversion. Carbon dioxide is driven off, leaving a coating composed of barium oxide; strontium oxide and calcium oxide. In step *c* further application of heat in a vacuum produces diffusion of the reducing agents to the surface of the nickel where they react with the oxide to produce free barium, strontium and calcium. The free barium in turn emits electrons. However, with continued application of heat during normal operation of the cathode, the reducing agents continue to react with the coated surface to form a troublesome interfacial barrier of dielectric material, as shown in FIGURE 1*d*, which increases in thickness with time and thereby reduces the useful effective life of the cathode.

One approach to a partial solution of this problem in the prior art has been the development of "dispenser cathodes" which are made of pressed and sintered powders formed into a pellet composed of a nickel matrix containing the carbonates and a small amount of reducing agent to accelerate the production of barium metal. In general, these mixtures are pressed into pellets at pressures of from 50 to 100 tons per square inch, sintered at elevated temperature in a hydrogen atmosphere at about 600° C. for about fifteen minutes. The pellets may then be attached to a much thicker base layer of nickel powder which also has been enriched with an activator such as zirconium hydride.

Dispenser cathodes are widely used and indeed display superior characteristics for electron emission, heavy ion bombardment resistance, improved interface reduction, and surface roughness. It has been demonstrated that surface work function is radically reduced. However, the same chemical processes as those described above are involved in the production of free alkali metal in the matrix of the cathode body. The improvement centers about the electrical conductivity engendered by a sintered nickel particle matrix where high conductive metal carries hot electrons to a monolayer of low work-function metal.

The difference between a dispenser cathode and oxide coated cathode is obvious when one considers the oxide layer to be a semiconductor. Photomicrographs display islands of oxide in a matrix of conductive nickel.

Other advantages such as reduced surface roughness and heavy ion bombardment resistance are incurred by the methods of formation where dense, planar surfaces are produced by pressing at high pressure (100 tons in.^{2}) or electrophoresis of finely divided particles.

Referring now to FIGURE 2 of the drawings, the prior art method of producing dispenser cathodes, such as BNL, or phormat cathodes, will be briefly described. The first step *a* is to fill a die with loose powder composed of nickel, barium carbonate, and a suitable reducing agent such as titanium or zirconium hydride. Next, *b*, the powders are compacted by subjection to pressures of from 50 to 100 tons 1 sq. in. In step *c* heat at approximately 800° C. is applied to sinter the compacted pellet for approximately 15 minutes. This releases carbon dioxide from the barium carbonate, converting it to barium oxide. The nickel particles join by point to point diffusion into a nickel matrix. During activation, step *d*, with further application of heat in a vacuum, the reducing agent reacts with the barium oxide to form free barium which diffuses to the surface and spreads, whereupon it is oxidized then recoated with more barium. During the normal operation of such matrix dispenser cathodes, interface dielectric deposit develops over the individual grains at the surface, as shown in FIGURE 2*e*, causing depletion and impedance effects which limit the useful life of the cathode.

THE INVENTION

When all of the parameters of cathode construction processing and high vacuum chemistry, of activation and life, surface condition, emission density, interelectrode spacing, heavy ion bombardment, and life requirements are considered it become evident that a new technology is needed to eliminate interface problems. I have devised such a technique which not only prevents interface but also offers other advantages, all interrelated to improvement needs. In general, I achieve these desired results by eliminating the need for and use of reducing agents in my matrix cathodes, and by employing nuclear bombardment to transmute atoms of rare metals within a host metal base into a pure element matrix of low work function material without the presence of oxygen.

For several years an increasing interest has developed throughout many industries in possibilities for process improvement or analytical determination by neutron bombardment. Some industries have seen product improvement when the object is subjected to neutron flux. Some polymers cross-link with property improvement. Solid-state circuitry has been formed by conversion of silicon atoms in a lattice to phosphorus, creating pn pn junctions. Neutron activation analysis has become a standard laboratory analytical technique. I have discovered that electron emissive cathodes may be produced by utilizing nuclide transformation reactions to produce low work function materials in the matrix of a metal suitably chosen for electron emissive functions.

Referring now to FIGURE 3 of the drawings, the successive steps of my process for making improved electron emissive cathodes will be described in greater detail. I start with spectroscopically pure nickel which is melted in a vacuum. To this is added a small amount of the element lanthanum as a dopant. Upon cooling this melt, still in a vacuum, an alloy of uniformly dispersed lanthanum in the host metal, nickel, is formed, FIGURE 3*b*.

Pieces of this cathode alloy are then formed into planar surfaces by precision rolling to any desired thickness, and cut to any desired shape, as for example a disc button. The emissive surface may be ground and electropolished to very precise dimensional tolerances, and the cathode is then ready to mount in a vacuum tube body. Since no chemical conversion is needed, as in the prior art techniques, the only processing required is to effect high temperature sealing of the electrodes to the vacuum tube body, and to remove gases from the tube envelope.

Following the sealing of the cathode and other electrodes into the tube body, the tube is completed except for transformation of the lanthanum dopant to barium. This is accomplished by subjecting the cathode, within the sealed tube, to intense bombardment by a concentrated beam of neutrons. The nuclide transformation reactions which take place are illustrated in FIGURES 3*c* and *d*. The thermal neutron flux transmutes lanthanum 139 atoms into lanthanum 140 atoms. Then, following radioactive decay (40 hour half-life) the lanthanum 140 atoms decay to barium 136 atoms.

When heat is now applied to the cathode disc, FIGURE 3*e*, the barium 136 atoms diffuse through the nickel lattice down the thermal gradient to the polished surface where they assume a monolayer position. The first monatomic layer of barium to form on the emitter surface is oxidized by residual ambient oxygen within the tube to form a tightly bonded molecular layer of barium oxide adhered to the surface by Van der Waal forces. Additional diffusion of barium atoms to the surface forms a second monatomic layer of pure barium on the surface of the oxide layer, thereby forming a Ba-BaO-Ni cathode having excellent surface uniformity, both as to smoothness and distribution of metallic barium.

The barium surface is resistant to heavy ion bombardment by virtue of its thinness and ionic bonding to the polished nickel surface. The bonding occurs due to intimate contact following diffusion and migration. The con-

tact is much enhanced by migration forces causing flow. Adherence is related to the 7th power of distance between nuclei. The close spacing of nuclei obtained by my process cannot be obtained by spraying, pressing or electrophoresis, as employed heretofore.

There are two reactions that occur during and after neutron bombardment:

(1) $La^{139} + (np) \longrightarrow Ba^{139}$ 83 min. half life

(2) $La^{139} + (n\alpha) \longrightarrow CS^{136}$ 13 day half $\downarrow Ba^{136}$

While the electron emission capabilities of barium and thorium have long been recognized, I have discovered that the element lithium possesses properties that are superior in many aspects to those possessed by the alkaline earth metals currently used in electron tubes. For example, lithium has a lower bulk metal work function than barium. Also, the temperature at which the vapor pressure is 1×10^{-5} torr is higher for lithium than for barium. I have also discovered that my above described process for activating cathodes through nuclear bombardment may be employed to produce lithium cathodes which are more efficient emitters than those made by transmutation of lanthanum into barium.

In making lithium cathodes by my nuclear transformation process I employ a generous doping of the naturally occurring boron element, B^{10}, which is incorporated in a host lattice of a metal such as nickel in the same manner that lanthanum was alloyed with nickel as described hereinabove with reference to FIGURE 3 of the drawings. I prefer to use as much as 20% by weight of boron in nickel alloy. This metal is then formed mechanically in the manner described above and mounted in a vacuum tube envelope which is outgassed and sealed in the usual manner, as described above with reference to FIGURE 3. The assembled and sealed tube is now ready to have its cathode activated by intensive nuclear bombardment, which causes the following nuclear reaction to take place in the nickel boron alloy of the cathode:

$$B^{10}+(n)\rightarrow Li^{7}+(\alpha)$$

The boron[10] nucleus receives a neutron whereupon it becomes unstable, emits an alpha particle and is thus transmuted to elemental lithium. The activation mechanism is similar to that described above for my La→Ba cathode; lithium diffuses to the surface in accordance with Fick's Law of Diffusion to form a low work function monolayer.

Boron has a very advantageous vapor pressure—it approaches the evaporation characteristics of molybdenum. Therefore, very favorable conditions are present during high temperature sealing and outgassing. Interelectrode leakage and other processing occurrences related to usual evaporation is minimized.

Thus, for example, a cathode constructed from a disc shaped pellet of nickel and boron containing 20% boron by weight and having a diameter of .03 cm. and a thickness of .01 cm. will have approximately 10,000 monolayer capability for lithium film formation during its lifetime. This result may be better understood from the following calculation:

Pellet surface area $=\pi/4(.03)^2=7\times10^{-4}$ cm.^{2}

Pellet volume $=(7\times10^{-4})\times(10^{-2})=7\times10^{-6}$ cm.^{3}

Available reactor flux $=10^{15}$ neutrons/cm.^{2}/sec.

Weight of pellet $=(7\times10^{-6}$ cc.) (8.9 gm./cc.)
$=63\mu$g. Ni

Number of nickel atoms in pellet
$$=(63\times10^{-6}\text{ g.})\times\left(\frac{6.02\times10^{23}}{58\text{ gm.}}\text{ atoms}\right)$$
$=6.6\times10^{17}$ atoms/pellet

Number of boron atoms in pellet
$=\frac{6.6}{5}\times10^{17}$ atoms/pellet
$=1.3\times10^{17}$ atoms/pellet
or
2×10^{22} atoms/cc. concentration

Since atomic abundance of B^{10} in natural boron is 19%, the number of B^{10} atoms in the pellet$=\frac{2}{5}\times10^{22}$ atoms/cc.

The number of boron atoms in the front surface slab is: $\frac{2}{5}\times10^{22}$ (.01 cm. thick)$=\frac{2}{5}\times10^{20}$ atoms on surface.

The nuclear reaction is: $5B^{10}+{}_0N^1\rightarrow{}_3Li^7+{}_2He^4$.

The cross section presented by this reaction in the surface slab is:

$$(3890\times10^{-24}\text{ borons})\ (\tfrac{2}{5}\times10^{20})=.\tfrac{8}{5}$$
$$\approx.1$$

This means that one neutron in ten passing through the slab is captured by a boron[10] atom.

Therefore:

$(7\times10^{-4}$ cm.^{2} area) (.1 capture) factor
$\times(10^{15}$n/cm.^{2}/sec. neutron flux)
$=10''$ lithium atoms formed in the pellet per second

$$\frac{10''}{\text{sec.}}\times3.6\times10^{3}\frac{\text{sec.}}{\text{hr.}}4\times\frac{10^{14}\text{ Li atom}}{\text{hr.}}$$

The monolayer formed consists of about 5×10^{10} atoms. Therefore, I get approximately 10,000 monolayer capability for lithium film formation from the bulk of the pellet.

Since no reducing elements are present or needed in my process, the development of interface cannot occur. The materials of reaction which cause interface are not present in my cathode matrix. Cathode life is limited only by supply of barium or lithium in the nickel lattice reservoir. While there has not yet been sufficient time for protracted life testing, I believe that the emitter surface which my process produces will prove very stable over a long life, with very little replenishment needed. An equilibrium condition prevails where as many atoms of a constituent return to the host lattice as are lost by thermal evaporation or migration into the free metal surface. Because lanthanum and boron possess a vapor pressure equivalent to that of nickel, iron or cobalt, sublimation which normally is incurred during conversion and operation of the prior art cathodes cannot occur in vacuum tubes incorporating my invention. Interelectrode leakage and secondary emission are also minimized by my construction.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above process and in the article set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties, and the relation of elements, which are exemplified in the foregoing detailed disclosure, and the scope of the invention will be indicated in the claims.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention which, as a matter of language, might be said to fall therebetween.

Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

I claim:

1. The method of forming electron emissive cathodes comprising the steps of:

(A) adding, as a dopant to a melt of vacuum melted pure nickel, a minute quantity of a nuclide of a rare earth element transmutable into a pure metallic element having a low work function and high electron emissivity,

(B) cooling the melted mixture to a solid state,

(C) bombarding the alloy metal with a concentrated beam of neutrons, whereby the nuclide atoms are transmuted to the pure metallic low work function element, and

(D) applying heat to the irradiated metal alloy in a vacuum, whereby the transmuted atoms are diffused from the interstices thereof and migrate to the surface.

2. The method of claim **1** in which the dopant in step A is a nuclide of boron which is transmuted by step C into pure lithium.

3. The method of claim **2** in which the dopant is naturally occurring boron B^{10}.

4. The method of claim **3** wherein the alloy mixture of which the unradiated cathode is composed comprises approximately 20% by weight of boron and 80% by weight of nickel.

5. The method of claim **3** in which the formed alloy cathode is sealed into a vacuum tube containing at least one other electrode before the step of neutron bombardment.

6. The method of claim **1** in which the starting material is spectroscopically pure nickel.

7. The method of forming electron emissive cathodes comprising the steps of:

(A) adding a minute quantity of the element lanthanum as a dopant to a melt of vacuum melted pure nickel,

(B) cooling the melted mixture to a solid state,

(C) rolling and polishing at least one surface of the metal alloy thus formed into a smooth surface, and

(D) bombarding the alloy metal with a concentrated beam of neutrons, whereby the lanthanum 139 atoms are transmuted to lanthanum 140 atoms,

(E) allowing the lanthanum 140 atoms to undergo radioactive decay whereby they are transmuted to atoms of barium 139, and

(F) applying heat to the metal alloy in a vacuum, whereby the barium atoms are diffused from the interstices thereof and migrate to said polished surface.

8. The method of claim **7** in which the formed metal cathode is sealed into a vacuum tube containing at least one other electrode before the step of neutron bombardment.

9. The method of claim **7** in which the starting material is spectroscopically pure nickel.

10. The method of forming electron emissive cathodes comprising the steps of:

(A) adding naturally occurring boron nuclide B^{10} as a dopant to a melt of pure nickel,

(B) cooling the melted mixture to a solid state,

(C) rolling and polishing at least one surface of the metal alloy thus formed into a smooth surface,

(D) bombarding the alloy metal with a concentrated beam of neutrons, whereby the boron nuclide atoms are transmuted to lithium nuclide Li^7, and

(E) applying heat to the metal alloy in a vacuum, whereby the lithium atoms are diffused from the interstices thereof and migrate to said polished surface.

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