Patented Mar. 5, 1940 2,192,491

UNITED STATES PATENT OFFICE

2,192,491

CATHODE FOR ELECTRON DISCHARGE DEVICES

Emil Gideon Widell, Bloomfield, N. J., assignor, by mesne assignments, to Radio Corporation of America, New York, N. Y., a corporation of Delaware

No Drawing. Application February 1, 1939, Serial No. 254,045

8 Claims. (Cl. 250—27.5)

My invention relates to cathodes for electron discharge devices, particularly to cathodes of the type in which a base metal carries the electron emissive coating, usually of alkaline earth metal bodies. This application is a continuation in part of my copending application, Serial No. 227,068, filed August 27, 1938.

In amplifiers with high amplification factors electron emission from the grids and anodes of the tubes should be reduced to a minimum, since this emission causes considerable background noises and reduces efficiency. The usual oxide coated cathode is a sleeve or wire of commercial nickel or nickel-cobalt alloy coated with active oxides such as barium-strontium oxides. These commercial nickels and nickel-cobalt alloys contain as a deoxidizer some other metal, such as silicon, manganese or magnesium, which is not only a deoxidizer, but is also a good enough reducing agent for the oxides of the coating to cause liberation of the active metal at the usual operating temperature of the cathode. The liberated metal deposits on the electrodes in the tube and emits electrons that cause objectionable noise, reverse currents, grid emission and low efficiency. To avoid these objectionable features of commercial nickel and nickel-cobalt alloys, use has been made of seamless cathode sleeves of electrolytic nickel, but the softness and high cost of manufacture of the seamless sleeve makes it uncommercial.

An object of my invention is to provide an oxide coated cathode with a core of substantially pure nickel or nickel cobalt alloy which is free from the usual metallic deoxidizer and reducing agents and which is mechanically strong and resistive to bending when hot or cold yet easy and inexpensive to manufacture.

According to my invention nickel is refined and purified in the usual way, such as depositing it in large sheets upon a nickel anode in an electrolytic bath to obtain what is known commercially as pure electrolytic nickel which contains from .3% to .8% cobalt and no more than traces of other materials. This electrolytic sheet metal is not suitable for cathode sleeves because it is non-uniform in texture and cannot be rolled without pulling holes in the sheet.

The electrolytic nickel may be melted and molded into ingots, but can be rolled into smooth sheets only with great difficulty. A molded ingot of electrolytic nickel is too hard to work and sheets of the metal are too brittle to be made into tubular sleeves commonly used for indirectly heated cathodes. To make the ingots workable and the sheets sufficiently malleable to be easily formed into cathode sleeves, I add, according to my invention, a material that will ductilize the nickel but will not appear in the finished cathode sleeve as a strong reducing agent for the alkaline earth metal oxides of the coating. I have found that carbon added to the melt makes the ingots workable and the sheets sufficiently malleable to make the manufacture of cathode sleeves easy, but unlike the metal deoxidizers, such as manganese, magnesium or silicon, which remain in the nickel to spoil the cathode with their reducing properties, the carbon added according to my invention deoxidizes the nickel, leaving it free of reducing agents and the ingots workable and the sheets malleable. The quantity of carbon added may be easily controlled in the melt to completely deoxidize the nickel and to leave the finished sheet after drawing and annealing, free of oxygen, deoxidizers, and objectionable products of reaction. The carbon combines with the oxygen to produce gas, probably carbon monoxide, which leaves the melt during firing. The quantity of carbon is so chosen that most of the carbon remaining in the ingots after melting is removed by the rolls and annealing fires.

Electrolytic nickel when deoxidized according to my invention and cast into relatively long ingots may be easily rolled into thin sheets from which long strips may be cut and made into locked seamed cathode sleeves.

While cathodes made from pure electrolytic nickel, deoxidized and rolled according to my invention, are good bases for the usual barium-strontium oxide cathode coatings, and are strong enough for cathodes of standard lengths, long lengths of the cathodes may bow or buckle when roughly handled and sag when hot. In the tube type commercially known as the 25L6G with a cathode of commercial Grade A nickel, bracing means at the center of the cathode is used. Of the metals which can be alloyed with the nickel to increase its hot strength and stiffness without disturbing its malleability and which can be deoxidized without residues that will reduce the emitting oxides or deleteriously effect emission, I have found that cobalt is best for the purpose.

I have found that any desired amount of electrolytic or chemically pure cobalt may be alloyed with the nickel up to 30 or 40% by weight of the alloy, depending on the stiffness desired, without making the sheet too hard to work or too stiff to form into small diameter cathode sleeves. The less expensive commercial cobalt, such as so-called rondells or pellets, may be added in desired

amounts up to about 20% by weight of the alloy without making the sheet too hard to work. The impurities in commercial cobalt, comprising oxygen, carbon, lime and sulphur usually in amounts less than 2% of the cobalt, appear to introduce hardening agents into the alloy which limit the amount of commercial cobalt permissible in the alloy although the lime slags off in the melt and most of the sulphur goes off as gas, probably hydrogen sulphide, from the melt. Cathode sleeves .045" in diameter and 27 mm. in length formed from my nickel cobalt alloy sheets .002" in thickness have sufficient stiffness when containing 9% to 5% cobalt to stand up well under severe mechanical shock when cold or when heated to emission temperature. 17% cobalt in the alloy was found sufficient to stiffen the relatively long cathode sleeves in the tube type commercially known as 25L6G where the sleeve is flattened .100" diameter tubing supported at its ends in insulators about 40 mm. apart.

Stiffness or resistivity to bending, commonly measured is terms of modulus of elasticity of tension, or Youngs modulus, is a function of the percent of cobalt alloyed with the nickel. Up to 20% added commercial cobalt the modulus of elasticity steadily increases with little decrease in malleability. The addition of cobalt to give the finished sleeve high strength without materially increasing the difficulty of rolling and working is desirable in high speed manufacturing processes where the sleeves must be made by machines from strip material. The cobalt is conveniently alloyed with the nickel by melting rondells or pieces of commercially pure cobalt with pieces of electrolytic nickel in a magnesium oxide lined crucible. The melt is then deoxidized by adding carbon.

The amount of carbon added to the melt depends upon its oxygen content and the working procedure, which varies with rolling and annealing temperature, the number of passes, and final thickness and strength. I have found that by adding between .20% and .50% carbon to the melt the ingots formed are workable and easily rolled to sheets of uniform thickness and texture as thin as .002". Preferably the melt is raised to a temperature of 1500° C. and pieces of carbon are added one at a time. The molten nickel receives the first few pieces with violent bubbling and sparking, indicating reaction between the carbon and oxygen. The carbon monoxide vapors burn and pass off. As more carbon is added the violence of reaction diminishes indicating diminution in the contained oxygen. When the addition of carbon produces no further visible reaction on the surface of the melt, sufficient carbon has been added for complete deoxidation of the nickel. Then sufficient additional carbon is added to carry the nickel through the rolls and annealing fires before all the carbon is lost.

To accurately control the total amount of carbon added to the melt it has been found convenient to make up sticks or rods of a carbon-nickel alloy containing about 3% carbon and 97% nickel from which pieces may be cut off and dropped into the melt. The carbon-nickel alloy, called the master alloy, is made by melting nickel in a graphite crucible and poured into molds in stick form about ¾" in diameter and 1' long.

I have found that carbon in the nickel-cobalt alloy ingot in excess of 1.0% makes the ingot too hard to work and that carbon in excess of .1% in the finished sheet reduces too much of the alkaline earth metal oxides of the cathode coating, permitting the active metal to vaporize. After adding .30% carbon to the melt, from .10 to .15% carbon is retained in the molded ingots and after rolling and annealing to a thickness of .002" the carbon content is reduced to between .03 and .05%. This amount of carbon is insufficient to exert a strong reducing action on the oxide coating of the cathode. This slight residue of carbon in the finished sheet permits easy processing of the metal in the melt and during rolling and annealing, insuring uniform sheets of nickel cobalt in manufacture. The slight excess of carbon insures a complete deoxidation of the nickel cobalt in the melt and in the rolls which is preferred to an insufficiency of carbon and a trace of oxygen.

Typical sheet nickel-cobalt alloy prepared according to my invention with pure cobalt comprises, by spectroscopic analysis, .03 to .04% carbon, .05 to .075% iron, and a trace of silicon, magnesium and copper. These traces comprise probably less than .005% of the total and may be introduced from the surfaces of the crucible or rolls. No manganese was found. The facility with which the nickel cobalt may be completely deoxidized, rolled and annealed, leaving the finished sheet of substantially pure metal, makes the carbon particularly desirable compared to the common metallic deoxidizers such as silicon, manganese and magnesium. These metals invariably leave residues in the finished sheet that produce excessive reduction of the oxide coatings of the cathode.

For minimum grid emission the cathode core should contain no more than traces of the metals which reduce the alkaline earth oxide coatings on the cathodes. Some of the stronger reducing agents for the oxides are zirconium, magnesium, silicon, aluminum and titanium. Metals which often appear in nickel and nickel cobalt alloys, but which do not act as reducing agents for the alkaline earth oxides include such metals as iron and copper. Iron does not appear to have any direct ill effects on my cathode except to change the thermal efficiency of the cathode, and copper may be present in considerable quantities without effecting the desirable properties of the cathode, its amount being limited apparently by the impurities carried in with copper and by the low vaporization temperature of the copper.

The wrought substantially pure nickel cobalt sheet prepared according to my invention may be cut into ribbons for use as filamentary cathodes or cut into strips and fed into a cathode sleeve making machine which rolls short sections of the strip into cylinders and closes the cylinder with a seam along one side in the manner disclosed in the Haslauer Patent 2,029,482, February 4, 1936. The ribbons or cylinders are coated with active metal compounds such as barium-strontium carbonates and mounted in electron or gas discharge devices. After decomposition of the carbonate and removal of the carbonaceous gases the tube is sealed off and the remaining oxides activated for a few seconds by heating the cathode to a high temperature to reduce the requisite amount of the oxides for good electron activity.

The purity of my improved cathode material and freedom from vaporized metallic barium on the electrodes from the barium-strontium oxide cathode coating is indicated by the absence of reverse or grid emission. The tube type commercially known as the 42 with a cathode of

nickel-cobalt alloy deoxidized with carbon according to my invention and coated with barium-strontium oxides showed, with rated potentials on all electrodes, zero grid emission after forty-eight hours of operation. The same tube with the conventional cathode of commercial Grade A nickel showed the grid emission to steadily increase from 1.5 microamperes to 15.5 microamperes during the first three and one-half hours of operation. Deposited barium on grids not only causes emission of electrons from the grids but makes contact potential unsteady, changes grid bias and renders tube operation unstable and inefficient. Grid emission can be quite serious in producing noise in some applications of high-transconductance tubes. Furthermore, grid emission, if large resistances are placed in the grid circuit, may cause the tubes to "run away" due to loss of negative grid bias.

The strength of my improved cathode core may be easily controlled by the addition of cobalt to adapt the core to a cathode of any desired cross section and length.

I claim:

1. A cathode comprising substantially pure nickel-cobalt alloy with .02 to .05% carbon, and a coating of alkaline earth oxides on the nickel, the alloy being free of materials which will reduce said oxides.

2. A cathode comprising a seamed tubular sleeve of an alloy of nickel and cobalt, the alloy being free of strong reducing agents and containing between .02 and .05% carbon, and no more than a trace of silicon and magnesium, and a coating of alkaline earth metal oxides on said sleeve.

3. A cathode for an electron discharge device comprising tubular metal sleeve of chemically pure alloy of nickel and cobalt, the sleeve being formed from sheet alloy and closed along one side with a seam, a coating of alkaline earths metal oxides on the sleeve, the nickel containing between .02 and .05% carbon and free of reducing agents for said oxides.

4. A cathode comprising a sheet of wrought completely deoxidized nickel cobalt alloy with .02 to .05% carbon, and free of reducing agents for alkaline earth oxides, and a coating of alkaline earth metal oxide on said cathode.

5. A cathode comprising a core of alloyed nickel and cobalt, the cobalt comprising up to 40% by weight of the alloy, the alloy being free of strong reducing agents and containing between .02 and .05% carbon, and a coating of alkaline earth metal oxides on said core.

6. An alloy consisting principally of nickel, cobalt up to 20%, and carbon less than .05%, said alloy being free of strong reducing agents for alkaline earth metal oxides.

7. A nickel base alloy consisting by weight of cobalt from 1 to 10%, carbon .02 to .05%, and the balance nickel.

8. A cathode core of nickel and cobalt, the cobalt being alloyed with the nickel and comprising up to 10% of the alloy, the alloy being free of strong reducing agents and containing between .02 and .05% carbon.

EMIL GIDEON WIDELL.