

UNITED STATES PATENT OFFICE

HOWARD M. ELSEY, OF OAKMONT, PENNSYLVANIA, ASSIGNOR TO WESTINGHOUSE ELECTRIC & MANUFACTURING COMPANY, A CORPORATION OF PENNSYLVANIA

PROCESS OF CARBONIZING NICKEL OR OTHER METALS

No Drawing.

Application filed February 4, 1928. Serial No. 252,047.

My invention relates to a process of carbonizing metallic surfaces and more particularly to a process of carbonizing nickel, or other metals, which are used as plates or grids in electron tubes.

An object of my invention is to provide a process of carbonizing metals, and especially nickel, in such manner that a uniformly carbonized surface will be produced.

Another object of my invention is to provide a process of carbonizing metallic surfaces which consists essentially in oxidizing the metallic surface and then subjecting the oxidized metal to the action of a hydrocarbon gas at an elevated temperature, to produce a uniformly carbonized metal.

In electron tubes having thermionically emissive cathodes, particularly cathodes comprising oxides of the alkaline-earth metals, there is a tendency for the cathode material to volatilize and deposit upon the anodes or other electrodes which are not intended to emit electrons during the operation of the tubes. When electron tubes having a considerable power output are employed, the anodes and grids become heated and the result of such deposits is that they fail to perform their expected function, but, instead, become emitters of electrons.

In order to prevent the tendency of the grids or plates from emitting electrons, it has been proposed to carbonize their surfaces. It has been found that the efficiency of anodes and grids carbonized in this manner is greatly increased, as a carbonized surface not only prevents the emission of electrons but also increases the ability of the grids or plates to radiate heat and, consequently, decreases their operating temperature at a given current.

In carbonizing nickel, it has formerly been the practice to pack a large number of nickel sheets in a cold electric furnace that could be made gas-tight. A stream of natural gas was then passed through the furnace, dis-

placing the air. During passage of the natural gas, the temperature of the furnace was gradually raised until the hydrocarbon gas became decomposed or until a reaction took place between the hydrocarbon gas and the nickel.

After the nickel was exposed to the action of the carbon resulting from the decomposition of the hydrocarbon gas, or after reaction took place between the nickel and hydrocarbon gas for about an hour, the furnace was then slowly cooled. The carbonized nickel plates might then be removed from the furnace and formed or shaped, as desired, into plates or grids.

Difficulty, however, has been experienced in producing an evenly carbonized surface by the method just described. Parts of the nickel surface would be uncoated, or, if they were coated, the carbon could be rubbed off very easily, leaving an undesirable bright surface.

The cracking of a hydrocarbon vapor to yield carbon, as one product, is a reaction which can be accelerated by the presence of a suitable catalytic agent, such as an active nickel surface. I am, therefore, of the opinion that much of the trouble was caused by portions of the nickel varying in catalytic activity.

I have made the discovery that the activity of metal surfaces, such as nickel and tungsten, and alloys, such as nichrome, may be rendered uniform by previously oxidizing the metals and then exposing the metals to the carbonizing action of a hydrocarbon vapor, preferably one that does not contain free hydrogen, at a sufficiently high temperature to decompose the hydrocarbon or to effect a reaction between the hydrocarbon vapors and the oxidized metal. If preferred, the hydrocarbon vapors may be diluted with an inert gas, such as nitrogen, argon, or helium, although this is not essential.

In practicing my invention, the nickel, or other metal, is oxidized in any well-known

manner, as by heating the metal and exposing it to a current of air, and is then placed in an air-free furnace through which a hydrocarbon gas, preferably free from uncombined hydrogen, such as petroleum gas or casing-head gasoline, which is sometimes sold under the trade name of "Bu-tane," may be passed; or, if preferred, the process may be made continuous by oxidizing the metal in one furnace and then placing it in the carbonizing furnace while the gas is flowing.

The furnace is maintained at an elevated temperature, such as from approximately 700 to 1000° C., and from about five minutes to an hour is required to decompose the hydrocarbon vapor or so to effect the reaction between the hydrocarbon vapors and the nickel oxide so as to produce a uniformly carbonized surface. During the reaction which takes place, the nickel oxide is reduced by the hydrocarbon to nickel and the carbon is combined with the reduced nickel surface. As a result of the treatment at such high temperatures, the surface of the nickel plates becomes carbonized in a very permanent form, possibly by the formation of a carbide of the nickel, or by forming a solid solution of carbon in the nickel. After the carbon has been formed upon the nickel surface, it is heated in vacua to remove any occluded gases or other volatile material. The nickel or other metal may then be formed or shaped into grids or plates, or utilized for other purposes.

By my improved method, the nickel is uniformly carbonized and is much superior for use as grids or plates in electron tubes than electrodes made of metal alone or metal carbonized by previous methods.

The thickness of the layer of carbonized metal which is formed may be controlled by mixing the hydrocarbon vapors with an inert gas, such as nitrogen. When an inert gas is mixed with the hydrocarbon vapors, the carbon does not penetrate so deeply into the metal during the same period of time, but a uniformly carbonized surface is produced and the carbon burns in, or alloys with, the metal without obtaining a large excess of carbon, which, being out of contact with the nickel, cannot enter into solution or reaction with it.

While it cannot be stated definitely that free hydrogen in hydrocarbon gases has a deleterious effect in producing a uniformly carbonized metal, experiments indicate that this is true. I prefer, therefore, to use a hydrocarbon gas free from uncombined hydrogen, although gases containing some free hydrogen, such as natural gas, have given very good results.

While I have described a specific process and product, it will be understood that various modifications may be made without departing from the spirit of my invention. For

example, other hydrocarbon gases, such as butane, ethylene, or ethane, may be substituted for the casing-head gasoline, and other inert gases, such as argon or helium, may be utilized instead of nitrogen. I desire, therefore, that only such limitations shall be placed upon my invention as are imposed by the prior art or the appended claims.

I claim as my invention:

1. The process of producing a uniformly carbonized nickel surface which comprises oxidizing a sheet of nickel and subjecting the oxidized nickel, at an elevated temperature, to the action of a hydrocarbon gas.

2. The process of producing uniformly carbonized nickel which comprises oxidizing the nickel and subjecting the oxidized nickel, at an elevated temperature, to the action of a hydrocarbon compound which is a gas at ordinary temperatures for a sufficient length of time to reduce the nickel oxide and to uniformly carbonize the nickel.

3. The process of producing a uniformly carbonized metal substantially free from oxides containing a major proportion of nickel which consists in uniformly oxidizing the metal, placing the uniformly oxidized metal in a furnace, and passing a reducing atmosphere containing a hydrocarbon compound which is a gas at ordinary temperatures through the furnace, the furnace being maintained at a sufficient temperature and the metal being exposed to the gas for a sufficient length of time to cause the hydrocarbon gas to reduce the metal oxide and carbonize the reduced metal.

4. The process of producing uniformly carbonized nickel which comprises oxidizing the nickel, placing the oxidized nickel in a furnace and passing the vapors of casing-head gasoline through the furnace, the furnace being maintained at a sufficient temperature to cause the vapors of the casing-head gasoline to reduce the nickel oxide and to form a carbonized metal.

5. The process of producing uniformly carbonized nickel which comprises oxidizing the nickel, placing the oxidized nickel in a furnace through which a hydrocarbon gas is flowing, the furnace being maintained as a sufficient temperature to carbonize the metal.

6. The process of producing a uniformly carbonized alloy containing a major proportion of nickel which comprises uniformly oxidizing the metal and then exposing the uniformly oxidized metal to a reducing atmosphere containing a hydrocarbon gas for a sufficient length of time to reduce the oxide and produce a uniformly carbonized surface.

7. A process of producing a uniformly carbonized metal free from oxides for electron discharge devices which comprises uniformly oxidizing the surface of metal selected from a group consisting of nickel, tungsten, and

alloys of nickel containing a major proportion of nickel, and then heating the metal in a reducing atmosphere containing normally gaseous hydrocarbon to reduce the oxide and carbonize the metal.

5 8. A process of producing a uniformly carbonized metal free from oxides for electron discharge devices which comprises uniformly oxidizing the surface of metal selected from
10 a group consisting of nickel, tungsten, and alloys of nickel containing a major proportion of nickel, and then heating the metal at temperatures of about 700° C. to 1000° C. in
15 a reducing atmosphere containing normally gaseous hydrocarbon to reduce the oxide and carbonize the metal.

In testimony whereof, I have hereunto subscribed my name this first day of February, 1928.

HOWARD M. ELSEY.