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METHOD OF CARBONIZING METALS AND ALLOYS

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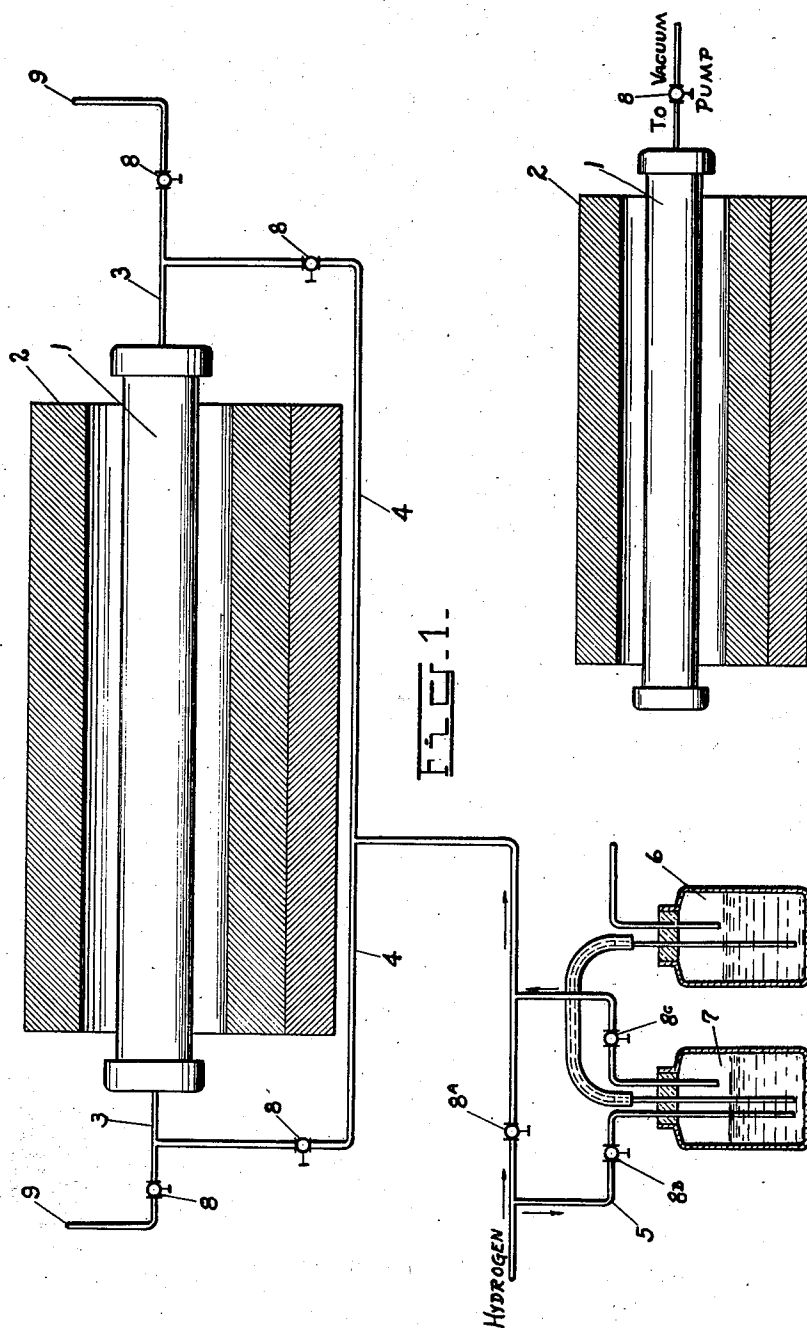


FIG. 2-

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## METHOD OF CARBONIZING METALS AND ALLOYS

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This invention relates to metallurgy and more particularly relates to methods of coating metals and comprises essentially in a method of forming an adherent gas-free carbon coating upon metal surfaces.

In the production of electron discharge devices particularly of the rectifier and oscillator types, the use of high plate and grid voltages result in pronounced heating of the refractory metals comprising these electrodes. In some types this heating effect is sufficient to raise the temperature of these electrodes to bright redness. Under such temperature conditions these electrodes are then capable of themselves emitting electrons which disrupt the operating efficiency of these devices.

One of the methods devised to overcome this heating effect is to cover the metal surface of these electrodes with a material which will more readily radiate and dissipate the heat energy of the device than the bright metallic surface heretofore employed. Black coatings have been found to serve this purpose admirably, and many methods have been developed wherein black carbonaceous coatings have been applied to these surfaces.

It has been found, however, that although such blackening by coating with carbonaceous material is effective in reducing and even eliminating back emission due to incandescing the metal electrodes, the majority of such coatings have introduced an additional factor in that unless highly purified carbon is employed therein the contained impurities are broken down under the influence of the electron bombardment and the resultant liberated impurities either produce back emission effects or are volatilized and destroy the emissive qualities of the filament.

Such carbonaceous coatings have also been difficult to cause to adhere to the metal surfaces, and are usually hard to free of adsorbed and absorbed gaseous impurities.

One of the objects of this invention is to provide a method of coating metal surfaces with substantially pure carbon.

Another object of this invention is to provide a method whereby a closely adherent

substantially pure carbon coating may be obtained on metal surfaces.

Another object of this invention is to provide a gas-free closely adherent substantially pure carbon coating upon the metal surfaces of the plate (anode), grid, and supports of electron discharge devices.

Another object of this invention is to provide an electrode suitable for use in electron discharge devices which is substantially free of deleterious surface impurities decomposable under the influence of electron bombardment, and which is coated with a closely adherent heat radiating carbon layer, substantially integral with but only superficially attached thereto.

Other objects and advantages will be apparent as the method is more fully disclosed.

My invention substantially is comprised of two operations, each containing two steps.

1. Deoxidizing and carbonizing.

2. Degasifying and surface cementing.

The carbonizing step in the first operation is dependent upon obtaining an oxide-free metal surface to deposit the carbon upon. I have also found that the subsequent degasifying and surface cementing step is dependent upon this procedure as it is essential that these metal parts be free of oxygen carrying compounds.

This surface deoxidizing is obtained by means of heating the metal body in a reducing gas (hydrogen) prior to carbonizing, thereafter the metal surface is carbonized by introducing into the reducing gas a proportion of a hydrocarbon of the paraffin series and heating the deoxidized metal to a temperature sufficient to effect decomposition or dissociation of the hydrocarbon vapor. The two steps in this operation are made in a continuous or consecutive manner without intervening exposure to any other gases. The deposited carbon thereupon is formed in a dense coherent layer on the surface of the clean metal body. Upon cooling to room temperature this coating is treated by the second operation of my process to effect consolidation and firm cementation of the carbon upon the surface of the metal body.

In the second operation the coated surface

and the metal body are mutually degasified and cemented together by a second heating in a high vacuo for a prolonged time interval.

The temperature of heating is not sufficient to cause any more than superficial formation of metallic carbides but provides a means whereby these carbonized metals may be latterly exposed to atmospheric contamination without the formation of surface oxides which are decomposable under the influence of electronic bombardment, and normally inherent on most metal surfaces. The removal of this oxide film is essential in order to prevent the destruction of the activating constituent of the hot cathode in an electron-emitting device by interaction with the liberated oxygen of the electronically decomposed surface oxides.

In this manner I obtain, by the practice of my invention, a carbon coated metal body suitable for use in electron discharge devices which has a coating that is not only adherent sufficiently to prevent the formation of oxide films thereon but of a sufficient thickness to substantially serve as a heat radiating surface, and moreover is of a degree of purity such that the back emission of electrons due to the unavoidable heating effect produced during the operation of the electron discharge device is restrained and in most cases inhibited.

In the practice of my invention I preferably employ the formed and finished plate, grid and support material, although I have found that the coating I obtain by my process is sufficiently adherent when applied to sheets so that the plate or anodes may be stamped or formed therefrom subsequent to the carbonizing step. The stamped or formed electrodes may then be put through a degasifying or vacuum treating operation as described above.

In the practice of my invention I have employed various members of the hydrocarbons of the paraffin series, some of which are gaseous at room temperatures, such as methane, and others of which have higher boiling points but high vapor pressures and which may be carried over the heated metal surface by saturating an inert or reducing gas with the vapor of the hydrocarbon liquid at room temperatures.

The particular hydrocarbon of the paraffin series which I prefer to employ in the carbonizing step is commonly known as "petroleum ether", which may be purchased on the market.

Petroleum ether is a composite hydrocarbon having a high vapor pressure and a boiling point ranging from 30° C. to 80° C., and may be introduced into the carbonizing process as a vapor by bubbling the hydrogen through the liquid petroleum ether in a manner shown and described in my specific description.

I have determined that the paraffin series

of hydrocarbons decompose at temperatures lying between 775° C. and 825° C. yielding a very pure carbon as a decomposition product. With the refractory metal bodies commonly employed in the forming of anodes, grids and grid and plate supports in electron discharge devices, such as iron, nickel, or refractory alloys of these metals with copper, chromium, manganese, etc., the carbon deposited at this temperature forms a closely adherent film, which film is very difficult to remove even by abrasion methods, particularly when the metal body has been previously freed of the surface adherent oxide layer and which film may subsequently be caused to uniformly adhere to the surface and prevent the formation of surface oxide compounds by suitable treatment in vacuo.

As a specific embodiment of my process I will describe the procedure employed in coating nickel with an adherent gas-free carbon layer.

In the accompanying drawing, Fig. 1 is a cross sectional schematic diagram of the apparatus employed in the first or deoxidizing and carbonizing step of my process; and,

Fig. 2 is a cross sectional schematic diagram of the apparatus employed in the second or degasification and cementation step of my process.

In Fig. 1, the carbonizing tube 1 which may be silica, iron, or any heat resistant alloy is mounted in a furnace 2 which may be heated electrically or by gas as desired. Suitable connections such as 3 should be provided for passing the carbonizing gas through the carbonizing tube 1, and where there is considerable length to the tube 1, suitable piping 4 for reversing the gas flow, I prefer to provide a shunting means, such as indicated at 5, of passing the hydrogen through the petroleum ether without interrupting the flow of gas through the carbonizing chamber and carrying the resulting gas mixture to the carbonizing tube 1. I also provide a method, such as indicated at 6, of effecting a refilling of the chamber 7 with petroleum ether as the supply therein becomes exhausted. Suitable valves 8 are provided where indicated to provide a way of controlling the process. In Fig. 2 the evacuating chamber 1 enclosed within furnace 2 only are shown.

In the practice of my invention the nickel objects to be coated with the carbon (such as plates, grids and grid and plate support wires) are loosely placed in suitable containers, such as perforated iron or steel containers, and placed in position in the carbonizing chamber 1. The hydrogen is then passed through the chamber at a rate sufficient to give a small flame at the gas outlets 9 at the opposite ends of the carbonizing chamber 1. When the air has thoroughly been displaced, the chamber 1 may be heated to the carbonizing temperature. Furnace 2 should

preferably be of the wire wound resistance type electric furnace although the temperature is sufficiently low to permit the use of gas fired furnaces if desired.

5 Dissociation of the petroleum ether when passed over heated nickel and nickel base alloys occurs between 700° C. to 900° C. but most satisfactory results with nickel are obtained at temperatures between 775° C. to 825° C.

10 When the furnace temperature has reached approximately 775° C. the flow of the hydrogen is diverted through the petroleum ether by closing valve 8a and opening valves 8b and 8c, and the carbonizing continued within the indicated temperature range for a period of time sufficient to effect complete surface coating. By regulating the gas flow with respect to the diameter of the carbonizing tube, length of heating zone and surface area to be carbonized a uniform time interval may be established.

25 In practice I have observed the following schedules in the carbonizing of nickel surfaces:—

| Diameter of tube | Length heating zone | Surface area carbonized | Gas flow            |
|------------------|---------------------|-------------------------|---------------------|
| Inches           | Inches              | Square inches           | Cubic feet per hour |
| 2                | 18                  | 200                     | 0.5                 |
| 4                | 60                  | 2,200                   | 2.0                 |
| 8                | 60                  | 11,000                  | 4.0                 |

30 Under these conditions the time interval is approximately one hour.

I have found in the practice of this carbonizing method that the direction of the gas flow through the carbonizing chamber should be reversed at frequent intervals. I prefer to reverse the gas flow at 10 minute intervals, in order to equalize, if possible, the carbonizing effect at both ends of the carbonizing chamber.

45 At the conclusion of the carbonizing process the furnace is turned off and the chamber and contents allowed to cool to temperatures below 300° C., periodically reversing the hydrocarbon saturated gas flow until after the temperature has been lowered to 500° C. Thereafter until cooled to room temperature the hydrocarbon gas may be shut off and an atmosphere of pure hydrogen passed through the chamber.

55 The cooled carbonized metal parts are then cleaned of the excess loosely adherent carbon by brushing or by tumbling in sawdust, and are ready for the second step in my process.

60 The second step comprises a high temperature vacuum treatment for the purpose of removing adsorbed or absorbed gases and to cause the complete cementation of the deposited carbon to the surface of the metal body. The apparatus employed as indicated

in the accompanying drawing (Fig. 2) is similar to that used in the carbonizing procedure with the exception that instead of gas flowing through the chamber 1, the chamber is hermetically sealed and connected in any suitable manner to an exhaust system as indicated, wherein a vacuum approximating 0.25 mm. of mercury may be obtained within the chamber. Valve 8 is placed in between the evacuating means and the chamber to facilitate handling.

The carbonized metal parts, after cleaning off the excess carbon deposit, are placed in the chamber and heated by any suitable means to between 850° C. to 950° C. for from one to one and one-half hours or until a gas pressure of not more than 0.25 mm. has been maintained for a prolonged period of time. The heating of the metal parts during the degasification process should proceed from room temperatures to the maximum temperature with regular increases in the temperature gradient while evacuating the liberated gases continuously as liberated.

The degasified carbonized parts should then be cooled to room temperature before exposure to the air and until used in the construction of electron discharge devices should be protected from undue exposure to absorption of atmospheric gases as the carbon is now in a highly active absorptive state.

The carbon coating will be found to protect the surface of the metal from undue formation of surface metal oxides during both the vacuum treatment and subsequent exposure to air prior to incorporation within the electron discharge device.

Nickel parts so treated and carbonized substantially as described will be found to have thereon a closely adherent carbon coating which moreover is substantially free of electronically decomposable intermetallic compounds which would deleteriously affect the operating efficiency of the hot cathode of an electron discharge device, and moreover will be found to be substantially free from deleterious and difficultly evacuated gases. It is believed that the temperatures employed are not sufficient to effect appreciable formation of metallic carbide formation except in so far as is necessary to cause adherence of the deposited carbon to the surface of the metal body.

When these metal parts are incorporated within an electron discharge device they will be found to more efficiently radiate the heat energy than heretofore obtained by other methods of applying the carbon coating and thereby reducing and substantially eliminating that source of "back-emission" trouble which the uncoated electrode material normally would develop. In addition thereto, the high degree of purity obtained in the carbon deposit substantially eliminates that

source of "back-emission" which has been encountered in prior processes from the electronically decomposable compounds inadvertently included therein.

5 Having broadly outlined the scope of my invention and specifically described the same as regards to nickel, it is obvious that many departures from the specific process may be made without departing from the nature of  
10 the same. By the process as described with nickel and within the temperature and times specified, I have been able to successfully carbonize iron, various nickel alloys with manganese, iron, chromium, copper, etc. More  
15 refractory metals, such as molybdenum and tungsten would require substantially higher temperatures to produce the same effect as is at present obtained with nickel, iron or the alloys of these metals with other metals.

20 Such variations are anticipated as should fall within the scope of the following claims.

What is claimed is:

1. The method of producing adherent carbon coatings on metal surfaces which comprises heating a metal first in an atmosphere  
25 of a gas reducing with respect to the oxygen compounds of the metal thereafter introducing into said gas atmosphere without intervening exposure of the metal to other gases  
30 a proportion of the vapor of a hydrocarbon of the paraffin series, and continuing the heating of the metal body, the temperature of heating approximately the decomposition temperature of the hydrocarbon vapor employed.  
35

2. The method of forming an adherent carbon coating on nickel surfaces comprising heating the nickel to approximately 800° C. in an atmosphere of hydrogen subsequently  
40 introducing into the hydrogen atmosphere a proportion of the vapor of a hydrocarbon of the paraffin series and continuing the heating until a sufficient depth of carbon coating has been obtained.

45 3. The process of forming an adherent carbon coating on the surface of refractory metals, the oxides of which are reducible by hydrogen, which comprises heating a metal body to approximately 800° C. in an atmosphere  
50 of pure dry hydrogen to effect reduction and removal of the oxygen compounds of the same, and thereafter introducing into the hydrogen atmosphere the vapor of a hydrocarbon of the paraffin series and continuing  
55 the heating at the same temperature until surface carbonization has become effected.

4. The process of forming an adherent carbon coating on the surface of a nickel containing metal, which comprises heating a  
60 nickel containing metal in an atmosphere of pure dry hydrogen to temperatures approximating 800° C. to effect substantial removal of the oxygen containing compounds therein and thereon and thereafter introducing into  
65 the hydrogen atmosphere the vapor of a hydrocarbon of the paraffin series, and continuing the heating at the same temperature until surface carbonization has become effected.

drocarbon of the paraffin series, and continuing the heating at the same temperature until surface carbonization has become effected.

5. The process of forming an adherent carbon coating on a nickel surface which comprises heating the metal body in an atmosphere of pure dry hydrogen to temperatures approximating 800° C. to effect substantial removal of the surface oxides and thereafter  
70 introducing into the hydrogen atmosphere the vapor of petroleum ether, and continuing the heating at the same temperature until surface carbonization has become effected.  
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6. The process of treating electrodes for use in electron discharge devices which comprises heating electrodes in a pure dry hydrogen atmosphere to effect reduction and removal of oxygen containing compounds therein and thereon and thereafter carbonizing the cleaned metal surface by heating the  
80 electrodes in an atmosphere containing a proportion of a hydrocarbon of the paraffin series to the decomposition temperature of the same, without intervening exposure to atmospheric gases.  
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7. The process of treating nickel electrodes for use in electron discharge devices which comprises heating nickel electrodes in a pure dry hydrogen atmosphere to temperatures approximating 800° C., and thereafter  
90 introducing into the hydrogen atmosphere a proportion of the vapor of a hydrocarbon of the paraffin series and continuing the heating at approximately the same temperature for a sufficient interval of time to effect surface carbonizing of the nickel electrode.  
95

8. The process of treating electrodes for use in electron discharge devices which comprises deoxidizing the electrodes by heating in a pure dry hydrogen atmosphere, carbonizing the cleaned surface by heating in a  
100 vapor of a hydrocarbon of the paraffin series without intervening exposure to atmospheric gases and thereafter effecting cementation of the carbon coating to the metal base and substantial degasification of the carbonized electrodes by heating the same in a high vacuum prior to utilizing the electrodes as incorporated parts of an electron discharge device.  
105

9. The process of treating nickel electrodes for use in electron discharge devices which comprises deoxidizing the nickel electrodes by heating in pure dry hydrogen at temperatures approximating 800° C., carbonizing the deoxidized surface by introducing into the  
110 hydrogen atmosphere a proportion of a vapor of a hydrocarbon of the paraffin series and continuing the heating without intervening exposure to atmospheric gases, and thereafter degasifying and cementing the carbon coating to the metal surface of the electrodes by heating them to approximately 900° C. in a vacuum of the order of .25 mm. of mercury prior to incorporating the electrodes into the electron discharge device.  
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10. As an article of manufacture, deoxidized nickel coated with a substantially pure adherent carbon film.

11. As an article of manufacture, deoxidized nickel coated with an adherent substantially pure degasified carbon film.

12. As an article of manufacture, an electrode for electron discharge devices composed of deoxidized nickel coated with an adherent substantially pure carbon film.

13. As an article of manufacture, an electrode for electron discharge devices composed of deoxidized nickel coated with an adherent gas-free substantially pure carbon film.

In testimony whereof, I have hereunto subscribed my name this 23rd day of May 1928.

CHARLES V. IREDELL.