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Watanabe et al.

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[45] **July 1, 1975**

[54] **PROCESS FOR FORMING CARBON COATINGS**

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[30] **Foreign Application Priority Data**

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May 12, 1972	Japan	47-46396

[52] **U.S. Cl.** **427/249**
[51] **Int. Cl.** **C01b 31/00**
[58] **Field of Search** .... 117/46 CB, 46 CC, 130 E, 117/169 R, 71 M, 71 R, 49, 106 R, 106 C

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Primary Examiner—William D. Martin
Assistant Examiner—Janyce A. Bell
Attorney, Agent, or Firm—Craig & Antonelli

[57] **ABSTRACT**

A nickel-phosphorus alloy layer having an amount of 4–12 percent by weight phosphorus is first allowed to adhere to the surface of a substrate and the nickel-phosphorus alloy layer-coated substrate is heated in an atmosphere of a noncombustible hydrocarbon-containing gas to effect thermal decomposition of the gas, thereby depositing carbon onto the surface of said substrate to form a dense carbon coating thereon without causing thermal deformation of the coated substrate or decrease in stiffness of the resulting carbon coating. It is also possible to first subject a nickel-phosphorus alloy layer formed on the surface of a substrate to preliminary oxidation and then heat the substrate in the presence of a hydrocarbon-containing gas to effect thermal decomposition of said gas.

70 Claims, 11 Drawing Figures

FIG. 1

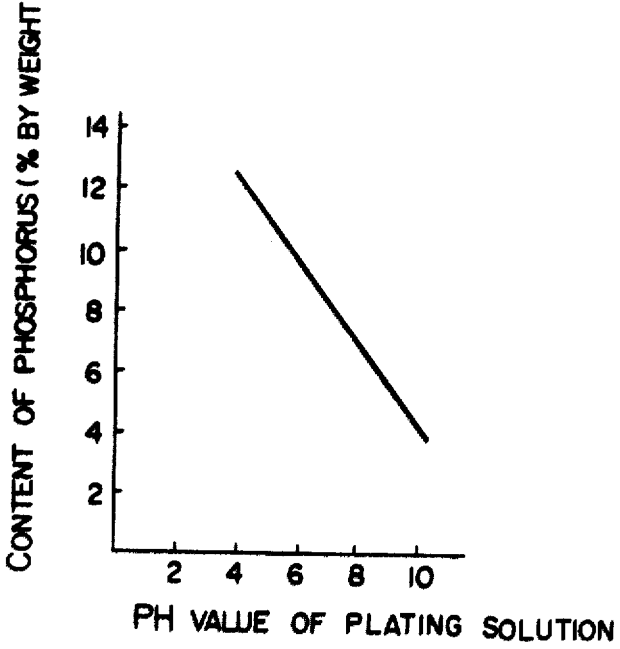

CONTENT OF PHOSPHORUS (% BY WEIGHT)
14
12
10
8
6
4
2
2
4
6
8
10
PH VALUE OF PLATING SOLUTION

FIG. 2

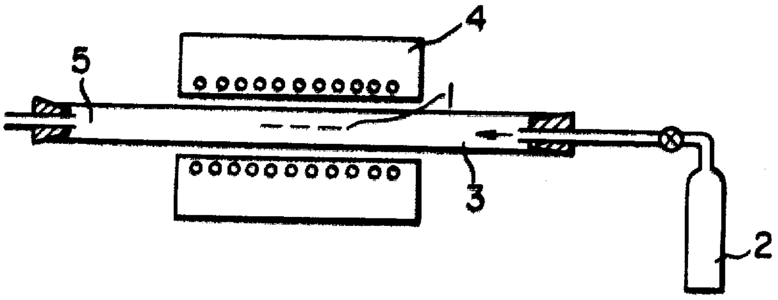

4
5
1
3
2

FIG. 3

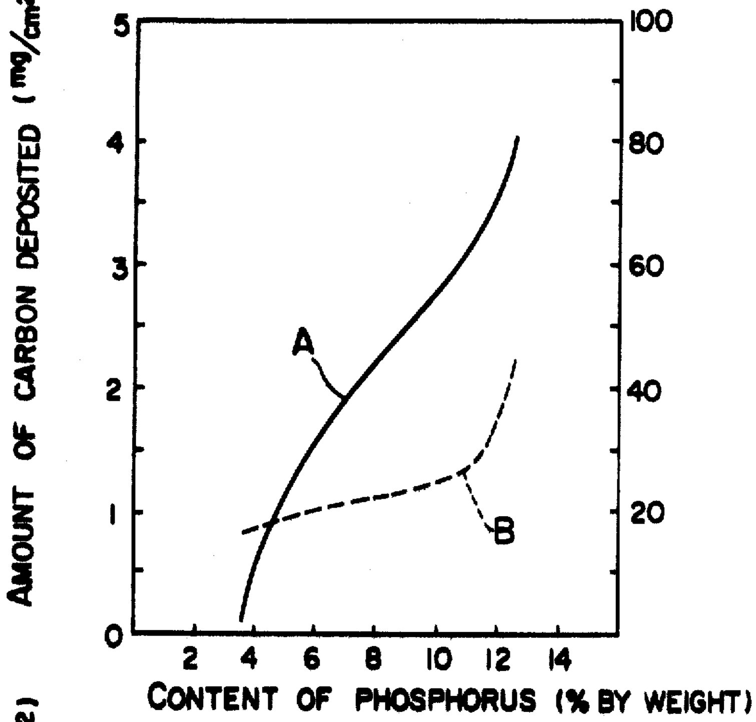

AMOUNT OF CARBON DEPOSITED (mg/cm²)
5
4
3
2
1
0
100
80
60
40
20
A
B
2
4
6
8
10
12
14
CONTENT OF PHOSPHORUS (% BY WEIGHT)

FIG. 6

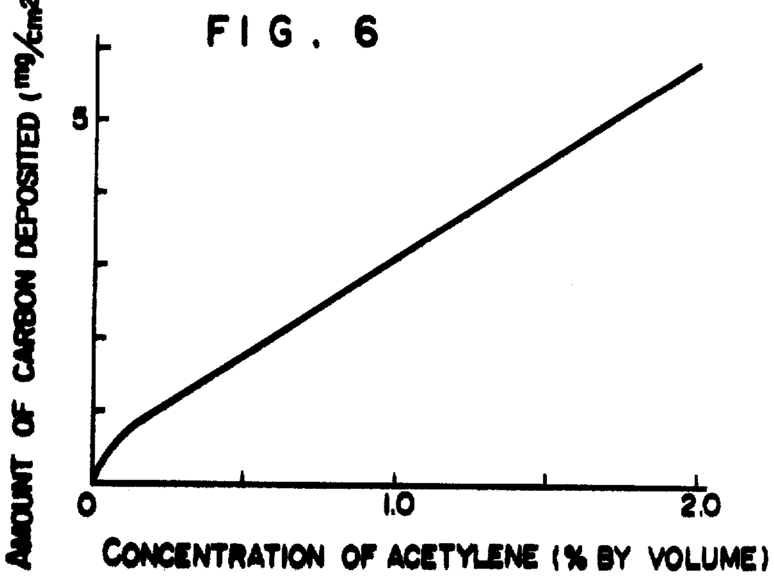

AMOUNT OF CARBON DEPOSITED (mg/cm²)
5
0
1.0
2.0
CONCENTRATION OF ACETYLENE (% BY VOLUME)

FIG. 4

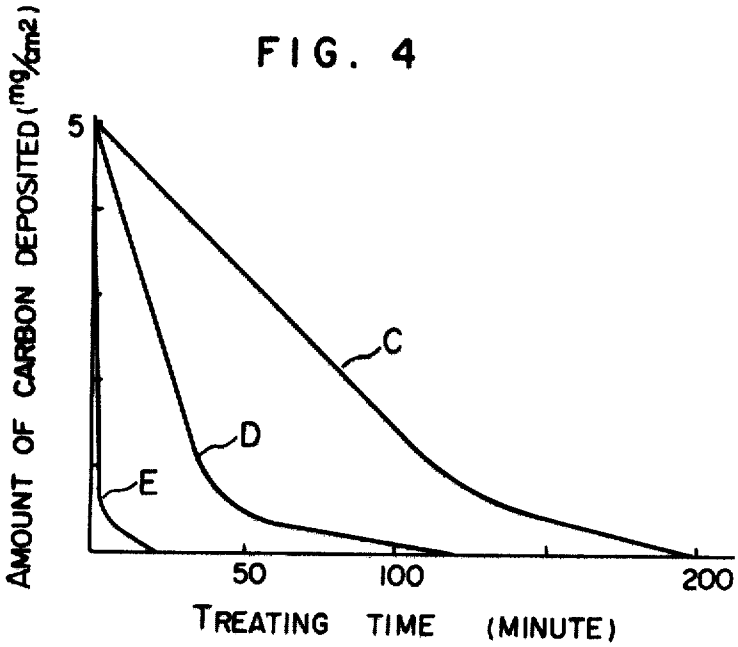

AMOUNT OF CARBON DEPOSITED (mg/cm^2)
5
C
D
E
50
100
200
TREATING TIME (MINUTE)

FIG. 5

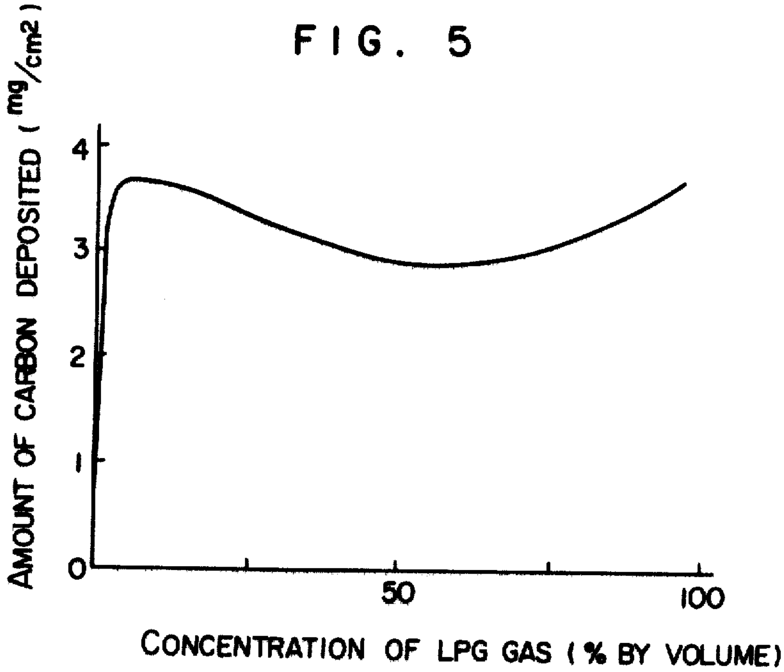

AMOUNT OF CARBON DEPOSITED (mg/cm^2)
4
3
2
1
0
50
100
CONCENTRATION OF LPG GAS (% BY VOLUME)

FIG. 7

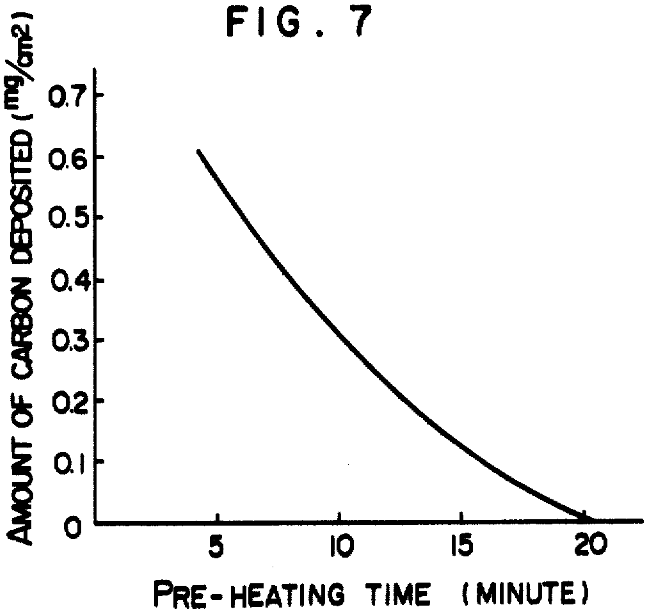

AMOUNT OF CARBON DEPOSITED ($^{mg}/_{cm^2}$)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
PRE-HEATING TIME (MINUTE)

FIG. 8

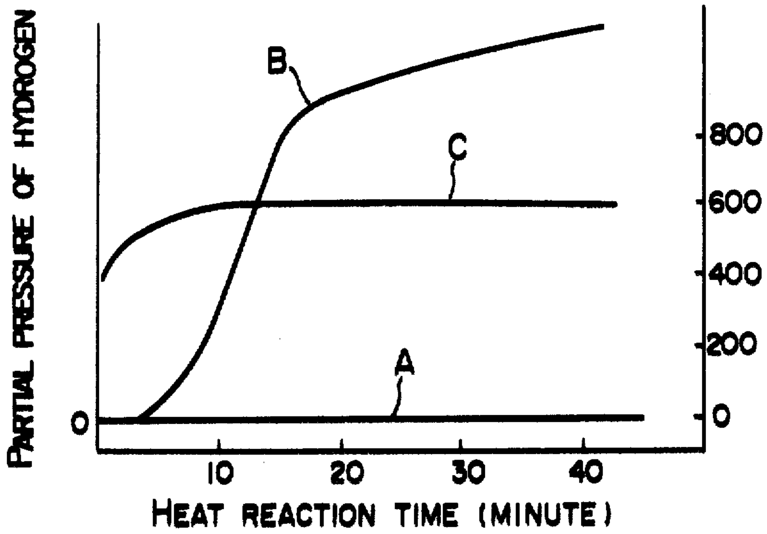

PARTIAL PRESSURE OF HYDROGEN
B
C
A
0
800
600
400
200
0
10
20
30
40
HEAT REACTION TIME (MINUTE)

FIG. 9

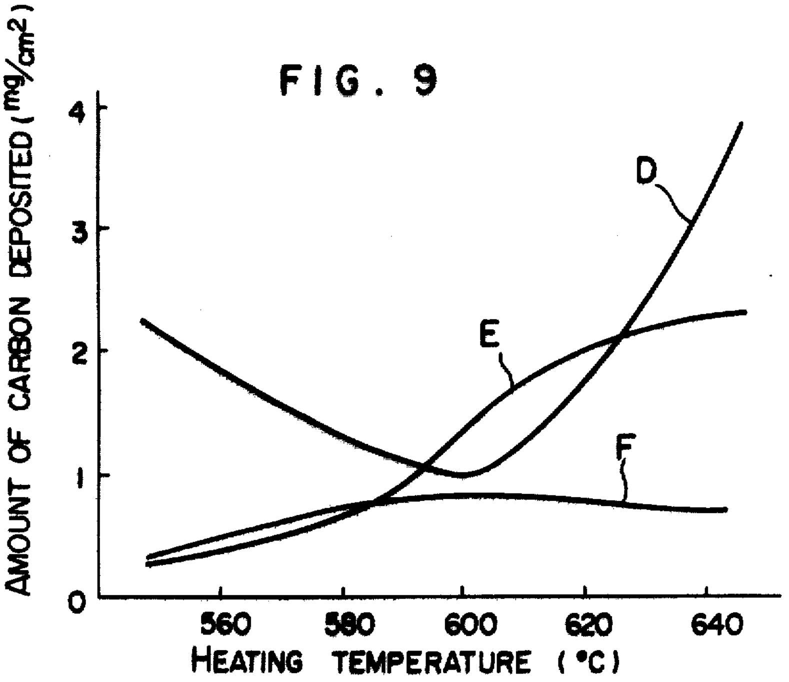

AMOUNT OF CARBON DEPOSITED ($^{mg}/_{cm^2}$)
4
3
2
1
0
560
580
600
620
640
HEATING TEMPERATURE (°C)
D
E
F

FIG. 10

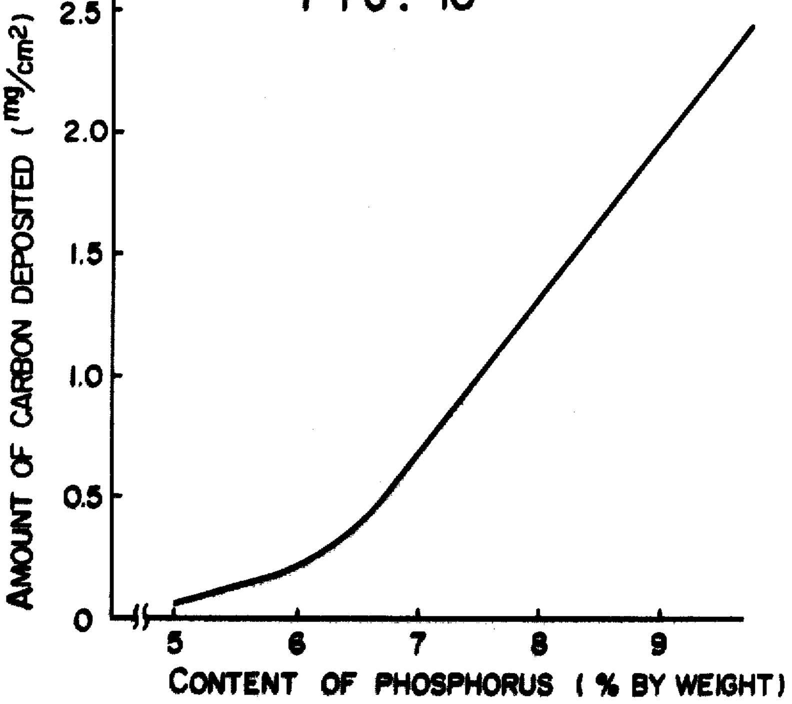
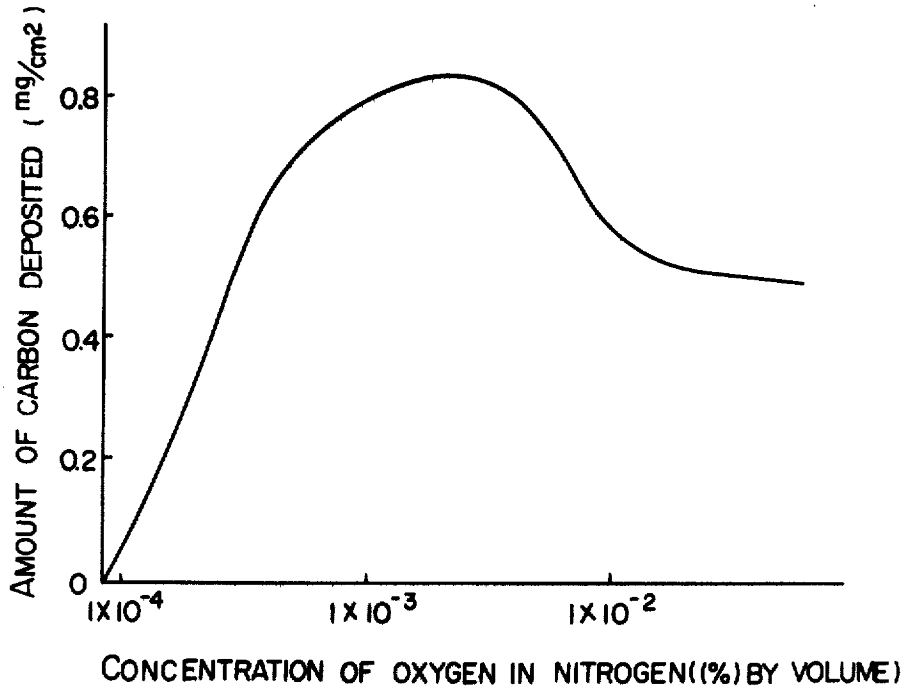

AMOUNT OF CARBON DEPOSITED ($^{mg}/_{cm^2}$)
2.5
2.0
1.5
1.0
0.5
0
5
6
7
8
9
CONTENT OF PHOSPHORUS (% BY WEIGHT)

FIG. 11


AMOUNT OF CARBON DEPOSITED (mg/cm2)
0.8
0.6
0.4
0.2
0
1X10-4
1X10-3
1X10-2
CONCENTRATION OF OXYGEN IN NITROGEN((%) BY VOLUME)

PROCESS FOR FORMING CARBON COATINGS

This invention relates to a process for forming a graphitic carbon coating at relatively low temperatures on the surface of an object composed of a metal or other material. More particularly, the invention pertains to a novel and efficient process for forming a carbon coating at a relatively low temperature below 700°C on the surface of an object (hereinafter referred to as "substrate") composed of such metal, for example, as an iron sheet or other substance in such a state that the carbon coating formed has a predetermined thickness, is high in density, and is firmly stuck to the surface of the substrate.

Carbon has not only exellent corrosion resistance to chemical agents but also good physical properties such as heat radiation ability. Carbon is also low in secondary-electron emission, and hence in the field of electronic appliances and parts thereof, those appliances or parts are frequently used after being coated on the surface thereof with carbon with the view of preventing said surface from secondary-electron emission. A process for coating the surface of substrates with carbon is roughly divided into three methods, i.e. spreading, evaporating or spattering, and decomposing. The spreading method, i.e. the first one of the above-mentioned three methods, is to spread or spray a carbon-containing paint on a substrate. This method is very simple, but involves such problem as uniformity in thickness of the spread coatings or reproducibility. The said method has also such drawback that because of weak adhesion between the substrate and the spread carbon layer, in the spread substrate obtained by this method the carbon layer easily peels off from the substrate when said substrate is heat-treated. This method is not a practical means to obtain a uniform and dense carbon layer on the surface of substrate. As the second method, there is a vacuum evaporation coating. According to this method, a dense and strongly adhesive carbon coating can be obtained. In order to evaporate and deposit carbon in vacuo, it is necessary to maintain the temperature of carbon necessary therefor at a high temperature of at least 2,500°C. In the case where treatment of a large number of substrates relatively large in size is intended to be carried out economically, application of this method thereto is extremely difficult. Moreover, it is almost impossible to deposit carbon to form a carbon coating having a uniform thickness on a substrate of complicated shape, because carbon shows its directional qualities when it evaporates. In either method, there are problems as to uniformity and adhesivity of the carbon coating to be formed on the surface of substrate, and also there is such drawback that the carbon coating formed on the surface of substrate is apt to peel off therefrom. Such condition as to adhesivity is required also even under such severe conditions where organic compound type binders cannot be used, when a substrate, for example, is a part of electron tube, because the part is used in vacuo. For example, in case an anode of receiving tube is coated with carbon with the view of maximizing heat radiation, the anode is heated in vacuo at any temperatures between about 600° and about 900°C, and the heating is repeated. For instance, when a shadow mask for color picture tube of television is coated with carbon with the view of preventing secondary-electron emission, the condition under which the shadow mask is used is such that the use of inorganic type binders having characteristics to promote secondary-electron emission is absolutely not permissible, and also there is required such adhesive strength of the carbon coating that said coating is not substantially worn by combustion even when heated in air at a temperature of about 400° to 500°C for 1 to 2 hours, and even when the coating has a thickness of about 1 micron or thicker, said coating will not peel off from the said mask due to slight contact or compact during handling thereof in the assembling operation. Further, when a carbon-coated substrate is used particularly in an electron tube within which is applied a high voltage, it is an extremely important requirement for the carbon coating formed on the substrate that not only the carbon coating is firmly stuck to the surface of said substrate but also carbon particles themselves in said carbon coating adhere to one another, because if a carbon coating forms carbon dusts that float within the tube, the dusts eventually cause spark to give serious damages or serious troubles in the circuit of the electron tube. In order to cope with such requirement, graphitic carbon (hereinafter referred to as "graphite") is desirably used in forming a carbon coating for use in such application. Furthermore, in the case of a corrosion resisting carbon coating formed on a boat for use in the liquid place method of GaAs production, for example, a graphite coating is preferably used so that the coating may not peel off from the boat due to mechanical rubbing during operation at an elevated temperature.

Thus, it is apparent that a graphite coating deposited on a substrate by thermal decomposition of a graphitic carbon-containing reaction gas is most preferable as the graphite coating as mentioned above, which does not substantially subject to loss in weight even when heated in vacuo and/or scrubbed mechanically or heated in air at a temperature of about 400° to about 500°C, and which does not also peel off from a substrate even placed in such state that neither organic nor inorganic binders can be used, and which does not produce carbon dusts.

As the third method, there is a method in which a carbon-containing gas is allowed to react under heating to deposit carbon, thereby coating a substrate with the depositing carbon. According to this method, the carbon coating formed on the substrate strongly sticks to the substrate and is high in density. This method is widely used in general. The greatest drawback of this method, however, is that the carbon coating is formed by thermal reaction wherein a substrate is heated in the presence of the reactive gas stream comprising methane, propane, etc. at such elevated temperature as high as 1,200° to 2000° C. Because of such high heating temperatures employed in this method, when a substrate is a thin metallic sheet or a material low in heat resisting property, the carbon-coated substrate suffers from its deformation or change in quality of the substrate itself, with the results that the coated substrate obtained thereby cannot be used. Even a substrate is a material which is sufficiently resistant to the aforesaid temperature, the substrate is liable to damages such as thermal deformation because it is heated at high temperature. Particularly, in the case of a shadow mask for color picture tube of television, which is very thin (usually about 0.2 mm or thinner) and in which even a slight deformation of a body of the mask is not permissible, the heating temperature employed therefor should be suppressed at least to 700°C or below.

There have heretofore been proposed various methods as processes to improve a high temperature decomposition method, wherein hydrocarbon-containing compounds are subjected to thermal decomposition at a relatively low temperature such as 850°C or thereabout to deposit carbon onto a substrate to form a carbon coating which is high in density and has an excellent adhesion. Some of the proposed method have been put into practice. However, in case a substrate to be coated with carbon is, for example, such a thin iron sheet as a shadow mask for color picture tube of television, the substrate which is to be treated under such temperature as 850°C or higher brings about such various disadvantages as carburizing, formation of carbide of iron, thermal deformation, decrease in stiffness or spring-back. In order to avoid such disadvantages, one must think of the possibility of effecting carbon-coating at lower temperatures than 850°C, for example, about 650°C or lower. There are few known techniques as to carbon-coating effected at low temperatures, but they are all found unsatisfactory. To cite one example of the said known techniques, for example, there is a method wherein a nickel disc of 30 mm in diameter, and 2 mm in thickness and of a porosity of about 51 percent, formed from nickel powder, is heated at about 650°C for 20 minutes in a gas stream prepared by mixing propane gas with nitrogen in a volume proportion of 1:1, thereby depositing carbon on the surface of disc to form a carbon coating (refer to U.S. Pat. No. 3,311,505). That is, this method is to coat the very porous nickel disc formed from nickel powder on its surface with carbon, and hence this method cannot be applied at all, for example, to the case where such a sheet as a thin iron sheet having a thickness of 0.5 mm or less is intended to be coated on its surface with carbon high in accuracy.

To mention another example of the aforesaid known techniques, there is a method in which an iron substrate is heated at a temperature of below about 650°C for 0.5–2 minutes in the presence of a mixed gas comprising 10 percent by volume of hydrocarbon and 0.75–2.0 percent by volume of carbon dioxide gas, thereby depositing carbon on the surface of the substrate to form a carbon coating thereon (refer to U.S. Pat. No. 2,344,908). In this method, however, when the concentration of hydrocarbon in the mixed gas is increased in order to form a carbon coating having a sufficient thickness and, on the contrary, if the hydrocarbon concentration is decreased in order to form a dense carbon coating, no carbon coating having a sufficient thickness is obtained. According to this method, therefore, it is not possible to coat a substrate with carbon to form a dense carbon coating having a density of 1.9 g/cm^3 and a coating amount of 1 mg/cm^2.

The present invention has been made in the light of various problems mentioned above which are associated with the prior art techniques. A primary object of the present invention is to provide a novel and effective process in which the surface of substrate such as an iron sheet may be coated with a dense carbon to form thereon without forming any carbide on the surface of the substrate and without bringing about such disadvantages as thermal deformation of the coated substrate or decrease in stiffness of the resulting carbon coating.

Another object of the present invention is to provide a process in which a carbon-containing gas is allowed to react at a relatively low temperature of about 700°C or below, thereby forming on the surface of a substrate a dense carbon coating having a firm adhesion between said carbon coating and the surface of the substrate.

Other object of the present invention is to provide a process, according to which even the surface of a thin iron sheet substrate having a thickness of about 0.5 mm or less with carbon to form thereon a carbon coating having a thickness of 1 mg/cm^2 with uniformity and with accuracy, said carbon coating being extremely high in density, having a carbon density of about 1.9 g/cm^3, and having a high adhesive strength so that said carbon coating does not peel off from the surface of the substrate even when subjected to quick heating and cooling tests at a temperature of 600°C or below.

The present inventors have found that in a process for depositing carbon on the surface of a substrate by the reaction of a hydrocarbon-containing gas the above-mentioned objects can be accomplished by previously forming a suitable catalyst material on the surface of the substrate, thereby depositing carbon utilizing a strong catalytic action of said catalyst material to form a dense carbon coating which adheres strongly to the surface of the substrate.

The present invention is illustrated in more detail below with reference to the accompanying drawings.

In the drawings, FIG. **1** is a graph showing the relationship between a pH value of a nickel-phosphorus alloy plating solution and an amount of phosphorus contained in the nickel-phosphorus alloy layer obtained from said plating solution.

FIG. **2** is a sketch showing an example of the manufacturing apparatus illustrating a process for preparing a carbon coating.

FIG. **3** is a graph showing the relationship between an amount of phosphorus contained in the nickel-phosphorus alloy layer, an amount of carbon deposited, and a porosity of carbon.

FIG. **4** is a graph showing the relationship between an amount of carbon deposited and a treatment time.

FIG. **5** is a graph showing the relationship between a Liquefied Petroleum Gas (hereinafter referred to as "L.P.G.") concentration in the reactive gas and an amount of carbon deposited.

FIG. **6** is a graph showing the relationship between an acetylene concentration in the reactive gas and an amount of carbon deposited.

FIG. **7** is a graph showing the relationship between a preliminary heating time at 600°C of a nickel-phosphorus alloy layer and an amount of deposited carbon resulting from a thermal decomposition reaction of acetylene gas.

FIG. **8** is a graph showing the relationship between partial pressures of the resulting hydrogen associated with thermal decomposition of a sample having a catalytic action and a sample which lost its catalytic action in an atmosphere of acetylene gas, and a heat reaction time.

FIG. **9** is a graph showing the relationship between amounts of carbon deposited when an iron sheet substrate plated on its surface with a nickel-phosphorus alloy as a catalyst is heated in an atmosphere of each of the three reaction gases having different compositions, and heating temperature.

FIG. 10 is a graph showing an amount of carbon deposited and an amount of phosphorus contained in a nickel-phosphorus alloy layer having a thickness of about one micron formed on the surface of an iron sheet substrate.

FIG. 11 is a graph showing the relationship between a concentration of oxygen in a nitrogen stream and an amount of carbon deposited in the case where an iron sheet substrate is plated on the surface with a nickel-phosphorus alloy to form a layer thereof having a thickness of one micron and then this nickel-phosphorus alloy layer is subjected to a preliminary oxidation treatment in a nitrogen oxygen atmosphere at about 600°C for 10 minutes.

As stated hereinabove, the present invention intends to coat the surface of a substrate such as a thin iron sheet or a heat resistant material with a dense carbon film having a firm adhesion force, to the substrate by effecting reaction of a hydrocarbon-containing gas at a low heat treatment temperature such as 700°C or below, which temperature was not conceivable at all in the prior art processes. It is impossible to deposit on the surface of a substrate by merely effecting a reaction of a carbon-containing gas at such low temperature as intended in the present invention. As explained previously, in order to accomplish this object, it is necessary to utilize a strong catalytic action of a material formed on the surface of a substrate intended to be coated with carbon. The present inventors conducted experiments, wherein the surface of a substrate on which a carbon coating layer is intended to be formed was subjected to surface treatment of every sort, and also carbon coatings were formed on the surface of the substrates thus heated to a relatively low temperature of about 450° to about 700°C while bringing various types of carbon-containing gases into contact with said substrates. As the result, they have found that when a nickel-phosphorus alloy layer is provided on the surface of the substrate, a reaction of a carbon-containing gas can be effectively brought about even at a low temperature of about 450° to 700°C owing to a catalytic action of said alloy and a dense carbon coating layer having a firm adhesion force can be obtained by deposition of carbon resulted from the reaction. That is, process of the present invention is based on the above finding, wherein the surface of a substrate is plated with a nickel-phosphorus alloy having an appropriate composition and the thus plated substrate is heated in a gas atmosphere comprising a predetermined amount of a hydrocarbon gas up to a predetermined reaction temperature within the range from 450° to 700°C preferably within a fixed time to carry out the reaction under heating, thereby forming a dense carbon coating on the surface of said substrate. Moreover, according to the process of the present invention, it is possible to obtain dense carbon coatings formed on substrates on a large commercial scale and moreover at low treatment temperatures even by use of such flammable and highly explosive gas such as acetylene gas is used as a starting hydrocarbon gas for forming a carbon coating in combination with an appropriate diluent gas or by mixing it with other gases in suitable proportions, thereby rendering the reactive mixed gas inflammable as well as non-explosive.

Acetylene gas is, as is well known, one of the most unstable gases among hydrocarbon gases, and is large in change of free energy associated with the decomposition thereof within a relatively low temperature range such as about 1,000°C or below. That is, generally at a low temperature of about 1000°C or below (hereinafter referred to as "low temperature"), acetylene gas belongs to those which are most liable to thermal decomposition among hydrocarbon gases. The reaction of acetylene is an exothermic reaction and, it is represented, for example, at room temperature by the following equations.

$$C_2H_2 \rightarrow 2C + H_2 \quad -\Delta H_{298^\circ K} = 54.19 \text{ kcal/mol}$$

The generation of heat associated with such reaction will further accelerate the thermal decomposition reaction of acetylene gas, and hence said thermal decomposition reaction proceeds explosively. The carbon results from such abrupt reaction, however, will not form crystal because of its excessively fast rate of deposition and tends to become amorphous. In case such reaction is intended to be carried out on an industrial scale, it is a crux to control skillfully such exothermic reaction to avert a danger of thermal decomposition explosion. That is, an important point for making possible a process in which acetylene gas is used on an industrial scale and thermal decomposition of said gas is carried out is to decrease the amount of acetylene gas used, or to slow down the reaction by increasing partial pressure of hydrogen, or to prevent a chain-like thermal decomposition associated with the reaction of acetylene gas by use of methane gas together with acetylene gas with an eye to the fact that the decomposition reaction of methane gas is an endothermic reaction. As explained above, in order to make it possible to effect selectively a thermal decomposition of acetylene gas in a controlled atmosphere comprising acetylene gas at a relatively low temperature in the presence of an optional substrate, thereby depositing carbon on the surface of the substrate to form thereon a stable crystalline carbon film, it is most effective to coat the surface of said substrate under the conditions as explained previously with a catalyst material which will act in response to the progress of the selective thermal decomposition reaction of acetylene gas. Such catalyst material is preferably a material which can be coated on the surface of an optional substrate in a simple as well as an economical manner.

The present invention has been made with an eye to various problems: such technical difficulties associated with prior art processes as illustrated in detail previously, characteristics of the thermal decomposition reaction of acetylene gas, utilization of the catalyst material as a countermeasure relative to the acetylene gas reaction and so on. Accordingly, the present invention, as explained previously, is to provide a novel process for coating the surface of a substrate with a crystalline carbon layer which is dense and having a high adhesion strength in a safe and stabilized operational condition by utilizing a catalytic action of the nickel-phosphorus alloy layer formed previously on the surface of the substrate in response to the thermal decomposition reaction of acetylene gas.

The nickel-phosphorus alloy layer formed on the surface of a substrate in accordance with the present invention can be chemically plated in a simple manner on an optional substrate, irrespective of conductive and non-conductive materials, according to plating technique known as the electroless plating method without necessitating a direct current power source as may be seen in the case of common plating procedure. Thus, the nickel-phosphorus alloy layer of the present invention satisfies the requirements as catalyst and is sufficiently of commercial value. In the case of electroless nickel, nickel in which a solid solution of phosphorus is supersaturated coexists with a compound of nickel with phosphorus and, they have such properties that they eventually form, when heated, crystalline nickel and a nickel-phosphorus compound of Ni_3P. As to catalytic action of the nickel-phosphorous alloy, amorphous nickel and a nickel-phosphorus compound of Ni_xP in which x is about **2**, play individually the most effective role as catalyst. From a practical point of view, any nickel-phosphorous alloys can display their efficiency as catalyst in practicing the process of the present invention so long as the amount of the total phosphorus component is 4% by weight or more. However, it has been found that this alloy is converted on heating into crystalline nickel and the compound of Ni_3P, whereby catalytic action of said alloy for formation of graphite due to thermal decomposition of acetylene gas is markedly reduced and finally its catalytic action completely disappears. Therefore, in case a hydrocarbon gas is subjected to thermal decomposition, it is necessary to employ such heating temperature or rate of temperature elevation as may not lose a catalytic action of the nickel-phosphorus alloy layer.

According to an embodiment of the present invention, there is provided a process for forming a carbon coating on the surface of a substrate, characterized by comprising the steps of plating the surface of said substrate with a nickel-phosphorus alloy containing 4–12 percent by weight of phosphorus to form thereon a nickel-phosphorous alloy layer, and of heating the nickel-phosphorus alloy layer-coated substrate in a non-combustible reaction gas composed mainly of at least one of such inert gases as nitrogen, helium and argon and admixed with 0.1–1.5 percent by volume of acetylene gas at a temperature of 450°–700°C and at a rate of temperature elevation so that a catalyst ability of said nickel-phosphorus alloy layer in formation of carbon from said acetylene gas.

According to another embodiment of the present invention, there is provided a process according to the embodiment mentioned above, which process is characterized by using the reaction gas composed mainly of at least one of such inert gases as nitrogen, helium, and argon and containing 0.1–1.5 percent by volume of acetylene gas and, in addition thereto, at least one member selected from 0.1 percent by volume or more of L.P.G. and 0.1 percent by volume or more of methane gas in an amount within such a range that the resulting whole mixed gas may become non-combustible.

By virtue of adopting the above-mentioned processes, it is possible to coat with a dense carbon having a high adhesion force the surface of a substrate which is thin and should indispensably be free from post-deformation, particularly the surface of a thin metal sheet, and more particularly, for example, in the case of a shadow mask for color picture tube of television, which mask is thin and, in which no post-deformation is permissible and no heating at a temperature above about 700°C is permissible.

The following procedure may be applicable to the preparation of a plating solution from which is provided a nickel-phosphorus alloy plated layer to be utilized as a catalyst material in the reaction of a carbon-containing gas in accordance with the process of the present invention. As a principal material, "SUMER" (a trade name of a product of Nihon Kanizen K.K.) is used, to which a suitable amount of hydrochloric acid or aqueous ammonia is added so that a pH value of the mixture may be maintained within the range from 4–10. Subsequently, a substrate (having a thickness of 0.1 mm) to be subjected to carbon coating treatment, for example, an iron sheet, is subjected to degreasing and rinsing according to usual procedure and the substrate is then immersed on the said plating solution to effect plating while maintaining the temperature of said plating solution at 80°C according to the electroless plating method, whereby a nickel-phosphorus alloy plated layer is obtained, the phosphorus content in said layer being different according to the pH value of said plating solution.

FIG. **1** is a graph showing the relationship between a pH value of a plating solution and an amount of phosphorus contained in the resulting alloy plated layer.

FIG. **2** is a sketch showing an example of the manufacturing apparatus illustrating a process for preparing a carbon coating. In this figure, substrates **1** plated with a nickel-phosphorus alloy in the manner mentioned above are inserted into reaction tube **3** into which is introduced reaction gas **2** comprising a mixture containing, for example, 1.0 percent by volume of acetylene gas, 10% by volume of methane gas, 0.5 percent by volume of a gas obtained by vaporizing L.P.G. and nitrogen gas as the remainder (88.5 percent by volume). In this case, the temperature inside reaction furnace **4** is previously fixed at an optional temperature within the range from 450° to 700°C, and the amount of said reaction gas **2** is previously and sufficiently controlled so that a predetermined amount thereof may accurately flow therethrough. The nickel-phosphorus alloy plated substrate is heated in a very short time such as 0.5 to 1 minute up to a suitable heating temperature within the said range from 450° to 700°C, and the heating of said substrate is effected in an atmosphere of said reaction gas **2** for a predetermined time. After completion of the heating, the said substrates **1** are withdrawin from the said reaction tube **3** through one end **5** of the tube. By virtue of carrying out a series of treatments as illustrated above, it becomes possible to deposit varying amount of carbon on the surface of the nickel-phosphorus layer according to the composition of the nickel-phosphorus alloy plated layer on the substrate, the reaction time and the reaction temperature.

FIG. **3** shows an amount of carbon deposited (curve A), according to the treatment methods explained above, on the surface of a substrate and a porosity (curve B) of said carbon deposited. It is shown from this figure that both the amount of carbon deposited and the porosity thereof change according to the amount of phosphorus contained in the nickel-phosphorus alloy layer formed on the substrate. Generally, it is seen that the more is increased the amount of phosphorus contained in the alloy layer, the more are increased both the amount of carbon deposited and the porosity thereof. The relationship between the rate of deposition of carbon and the composition of the nickel-phosphorus alloy plated layer does not change so much correlatively even when the absolute value of the rate of reaction changes according to change in composition or reaction temperature of the reaction gas. Thus, it is apparent that the catalytic action of the nickel-phosphorus alloy layer exerts a great influence on the carbon-depositing reaction at a low temperature of 450°–700°C. The catalytic action of the nickel-phosphorus alloy layer is closely related to the existence of a nickel-phosphorus compound, Ni_2P, which is separated at the very early stage of reaction from the nickel-phosphorus alloy plated layer. The higher is the content of phosphorus, the more is the amount of Ni_2P separated and the larger is the catalytic ability of the alloy layer. From this, it follows that the amount of carbon deposited is increased. However, if the content of phosphorus exceeds 11 percent by weight, the porosity of the deposited carbon coating tends to excessively increase, as is clear from the porosity of carbon deposited (curve B shown in FIG. 3). When the phosphorus content exceeds 12 percent, the porosity of the carbon deposited becomes 35 percent or more, with the result that the strength of the carbon film obtained thereby is markedly reduced. Accordingly, in order to obtain a dense carbon coating, the upper limit of the phosphorus content in the nickel-phosphorus alloy plated layer is preferably 12 percent by weight. On the other hand, if the phosphorus content becomes less than 4 percent, the amount of carbon deposited thereby is extremely small and, moreover, the thickness of the carbon coating obtained is uneven. Thus, this carbon coating is considered unsuitable for practical application. As will be appreciated from the foregoing, the phosphorus content in the nickel-phosphorus alloy plated layer is preferably within the range from 4 to 12 percent by weight for the purpose of obtaining a dense and stiff carbon film.

In accordance with the process of the present invention, the thickness of nickel-phosphorus alloy plated layer provided on the surface of a substrate does not affect so much the amount of carbon deposited and others. This is because the reaction is carried out at a relatively low temperature such as 450°–700°C, and hence the alloy layer is heated from room temperature up to the reaction temperature in a relatively short time, whereby the alloy reacts with the carbon-containing gas prior to the alloy layer diffuses into the substrate, and then acts to deposit a very slight amount of carbon particles which become henceforth nuclei for carbon to be deposited. That is, the nickel-phosphorus alloy plated layer acts as catalyst for the deposition of carbon even when the thickness of the layer is extremely thin. In practice, however, the thickness of the nickel-phosphorus alloy plated layer on the substrate is preferably about 0.1 micron or thicker, whereby the presence of the alloy layer on the substrate can be confirmed at least by the visual inspection and the subsequent operational steps can be stably assured. Even if the plated layer is thick, no substantial adverse effect on the carbon deposition operation is seen. Since the nickel-phosphorus alloy plating solution is relatively expensive, the use of an unnecessarily thick layer increases the cost of production and is not economically advantageous. Taking all these considerations into account together with other factors, the thickness of the nickel-phosphorus alloy plated layer is advantageously about 6 microns or thinner. The alloy layer having an unnecessarily large thickness is undesirable, because such thick layer sometimes peels off from the substrate during the carbon-deposition step.

As fully stated above, the nickel-phosphorus alloy plated layer plays a very important role in the deposition of carbon at a low temperature and it is also a fact that the properties of said layer exert great influence upon the deposition of carbon. In order to check the above fact, the following experiment was conducted. Specimens were obtained by plating iron sheet substrates with nickel-phosphorus containing 8 percent by weight of phosphorus to form thereon a nickel-phosphorus alloy layer having a thickness of 1 micron. The specimens were subjected to heat treatment in pure nitrogen gas stream for a predetermined time at the heating temperatures of 400°C, 500°C and 600°C, respectively. Using each of the thus treated specimens, an experiment of carbon coating was effected under heating in a mixed reaction gas comprising 1.5 percent by volume of acetylene, 14 percent by volume of methane gas, 1 percent by volume of L.P.G. and nitrogen gas as the remainder (83.5 percent by volume) at a temperature of 560°C for 20 minutes. In each case, the temperature elevation from room temperature up to 560°C was effected in a very short time such as within 30 seconds. The experimental results, i.e. relationship between the heat treatment time (minute) and the amount of carbon deposited (mg/cm^2), were as shown in FIG. 4. In this Figure, curves C, D and E show the cases where the heating temperatures of the nickel-phosphorus alloy plated substrates in the nitrogen gas stream were 400°C, 500°C and 600°C, respectively. As is clear from FIG. 4, the longer is the heat treatment time in the nitrogen gas stream, the smaller is the amount of carbon deposited. Particularly, this figure shows that when the heat treatment temperature of the alloy layer is higher, the amount of carbon deposited by decomposition is sharply decreased by heating for an extremely short time. It has been understood that when heat is applied in the manner as described above to the nickel-phosphorus alloy plated layer prior to the deposition of carbon, the catalytic ability of said layer is reduced. Such phenomenon is considered ascribable to the fact that the catalytic ability of the said layer is reduced due to conversion attended by heating of the compound Ni_2P in the said layer into Ni_3P and other compounds, and to extinction attended by heating of various defects in the lattice which have been introduced into said layer (the nickel-phosphorus alloy plated layer obtained by the method as explained previously is well known to be in a non-crystalline state). Accordingly, in the case of the present invention where a nickel-phosphorus alloy plated layer is utilized as a catalyst, heat treatment of said layer prior to deposition of carbon to form a carbon coating should be avoided as much as possible. From this, it follows that the rate of temperature elevation up to the reaction temperature, i.e. 450°–700°C, be effected as quickly as possible.

Subsequently, on the basis of the abovementioned results an experiment was conducted to confirm the rate of temperature elevation. In this experiment, specimens obtained by plating an iron sheet substrates with a nickel-phosphorus alloy containing 8 percent by weight of phosphorus to form thereon the alloy layer having a thickness of 1 micron were individually heated in a mixed reactive gas comprising 1.5 percent by volume of acetylene, 14 percent by volume of methane gas, 1 percent by volume of L.P.G. and nitrogen gas as the remainder (83.5 percent by volume) from room temperature up to 560°C at varying rates of temperature elevation and the temperature of 560°C was maintained for about 20 minutes, thereby carrying out coating said specimens with carbon. The results obtained showed that when the temperature elevation time was within one minute the best performance of coating was achieved, when the time exceeds 1 minute, the performance became poor very sharply, when the time is more than 30 minutes, formation of the carbon coating became very small, and if the time exceeds 120 minutes the effect of the alloy plated layer was scarcely observed. That is, it has been understood that the rates of temperature elevation confirmed in this experiments tend to give the results substantially identical with those shown in FIG. 4.

From the results of the experiment mentioned above, it is certainly necessary that when a nickel-phosphorus alloy-coated iron substrate is heated in a carbon-containing reaction gas, the temperature elevation in a heating furnace up to the reaction temperature should be effected as quickly as possible so that the catalytic ability for carbon deposition of said alloy layer may not be lost. Particularly, at a temperature below about 450°C, no deposition of carbon on the nickel-phosphorus alloy layer is observed and the layer manifest itself, on the contrary, to act only to lose its catalytic ability. It is an effective measure as well as an important requirement that the temperature within a heating furnace be elevated in a short time as shortly as possible up to the reaction temperature necessary for the deposition of carbon.

The results of studies on the composition of reaction gas used in the process of the present invention are illustrated below. Generally speaking, carbon-containing gases are combustible and apt to explode when mixed with air or oxygen. Accordingly, in order to put the present invention into practice on an industrial scale, the practice of the process thereof should be sufficiently safe from all possible dangers. From this viewpoint, in the present invention, the carbon-containing gas, such as acetylene gas and carbon monoxide gas as starting materials for deposition of carbon which tend to decompose at relatively low temperature is mixed into such inert and incombustible gases as helium, argon and nitrogen, and the mixing ratios of these gases are limited to such a range that the resulting mixed reaction gas may be rendered non-explosive even when a large amount of air flows into the apparatus due to destruction of the heating reaction tube. Using such carbon-containing gases having varying compositions as mentioned above, which are completely free from the possibility of danger of explosion, experiments were conducted to carry out the decomposition reaction of said gases under various conditions. As the result, it has been confirmed that in each case of said gases, carbon can be deposited by the reaction on a nickel-phosphorus alloy plated layer so long as said layer has a high catalytic ability and only when the suitable reaction conditions are selected. For example, it is possible to obtain a dense and stiff carbon coating in a stabilized state without any danger of explosion of the reaction gas by use of a gas prepared by mixing at least one of such inert gases as helium, argon and nitrogen.

As a result of a further detailed experimental studies on the above subject, it has been found that when a small amount of L.P.G. is added to the aforesaid three-component gas, the rate of deposition of carbon is more rapidly accelerated and thereby a dense carbon layer can be obtained in a very short time and hence the addition of L.P.G. is extremely advantageous from an economical point of view.

It has also been found that when a part of such inert gases as argon, helium and nitrogen is replaced with methane gas in an amount within such a range that the resulting mixed reaction gas may remain incombustible, the influence of flow of the reaction gas on the deposition of carbon by heat reaction becomes negligibly small, and hence the addition of methane gas is extremely preferrable, in particular, in obtaining a uniform carbon coating on the surface of parts having complicated shapes.

The upper limits of L.P.G. and methane gas illustrated above have been established with consideration for such safety in the operation that the reaction mixed gas containing L.P.G and/or methane gas will never explode even when mixed with air in any proportions. If the object is only to obtain a dense and uniform carbon coating, the whole portion of argon, helium or nitrogen in the reaction mixed gas may be replaced with methane gas, L.P.G., or a mixture thereof. The effect of addition of methane gas and L.P.G. does not change in a wide range of their mixing proportion from several percent to several tens of percent. Further, it should give proper consideration to the problem of toxicity of the starting gas, and from this viewpoint, acetylene gas is safer than carbon monoxide gas and is advantageous when used in the operation carried out on an industrial scale.

The effect on the amount of carbon deposited of the mixed gases of varying compositions explained above is illustrated below. From an economical reason, nitrogen gas was used as an inert gas, i.e. a carrier gas. Even in case of various hydrocarbon gases, for example, L.P.G., methane gas, acetylene gas, etc., actually only acetylene gas decomposes to deposit carbon, and the other gases added act to promote the decomposition of acetylene gas. The above fact has been confirmed by experiment. First of all, the results shown in FIG. 5 are to indicate the effect of the concentration (percent by volume) of L.P.G. on the amount of carbon deposited (mg/cm^2) in the case where a mixed gas containing 0.15 percent by volume of acetylene gas is introduced at a rate of 1 *l* per minute into a reaction tube having an inside diameter of 35 mm to deposit carbon by reaction of acetylene gas under heating to coat an iron sheet substrate of 23 mm in length, 23 mm in width and 0.1 mm in thickness plated with a nickel-phosphorus alloy containing 8 percent by weight of phosphorus. In this case, the reaction temperature, temperature elevation time, and reaction time are 540°C, less than 30 seconds, and 20 minutes, respectively. As is clear from the said figure, the addition of a small amount of L.P.G. has a great effect on the amount of carbon deposited, and it is understood that a sufficiently satisfactory carbon coating can be obtained by the addition of L.P.G. in an amount of at least 0.1 percent by volume. Furthermore, FIG. 5 shows the results of an experiment where commercially available L.P.G. is used. This L.P.G. contains about 60 to about 80 percent by volume of propane gas, and the remainder thereof contains butane gases and impure gases such as propylene, butadiene, butene and others. These contaminant gases, however, do not act disfavorably on the deposition of carbon by the reaction of the reaction gas of nitrogen + acetylene + L.P.G. system, but serve to bring about good results as a whole. The upper limit of the amount of L.P.G. to be added should be limited to such a range that the starting mixed gas may remain incombustible even when brought into contact with any amount of air. Such range is 7–15 percent by volume, though it varies depending on the concentration of acetylene in the starting mixed gas.

On the other hand, when a part (about 10 percent by volume or less) of nitrogen gas in the mixed gas of nitrogen + acetylene + L.P.G. is replaced with methane gas, the resulting mixed gas of nitrogen + acetylene + L.P.G. + methane system brings no unevenness of coating due to flow of the gas without substantially changing of the rate of deposition of carbon, and hence the use of the mixed gas of this system is extremely effective in the case of the treatment of parts having very complicated shapes, where the gas is difficult to uniformly pass through every portion of said parts. If an inexpensive natural gas is used as a supply source of methane gas, the cost of the starting mixed gas can further be reduced, and hence a marked economical effect can be expected.

The amount of acetylene gas used as a starting gas for deposition of carbon is explained below. FIG. 6 shows change in the amount of carbon deposited when the proportion of acetylene gas in the nitrogen + L.P.G. (0.5 percent by volume) mixed gas. In this case, the reaction (heating) temperature is 560°C, the temperature elevation time and the reaction (heating) time are less than 30 seconds and 20 minutes, respectively, the flow rate of the gas is 6 liters per minute, and other conditions are the same as shown in the embodiment illustrated by FIG. 5. As is clear from the results shown in FIG. 6, the larger is the amount of acetylene, the higher is the rate of deposition of carbon deposited. However, if the amount of acetylene is more than 1.5 percent by volume, there is observed a tendency that the resulting carbon coating becomes somewhat porous. When the amount of acetylene gas is more than 2 percent by volume, dust-like carbon particles come to attack to the surface of the carbon film deposited. Accordingly, in order to obtain a dense and stiff carbon film, the upper limit of the amount of acetylene gas to be mixed with a carrier gas is preferably 1.5 percent by volume. On the other hand, in order to obtain a practically useful rate of reaction, at least 0.1 percent by volume of acetylene gas should be mixed with the carrier gas.

When such hydrocarbon gases as ethylene and methane are added to a mixed gas of nitrogen-acetylene-L.P.G. or nitrogen-acetylene-L.P.G.-ethane in an amount within such a range that the resulting mixed gas remains incombustible even when mixed with air, the addition will have no particular adverse effect on the deposition of carbon.

The embodiments of the present invention illustrated hereinbefore refer to the cases where the plating of the nickel-phosphorus alloy onto the surface of substrates is effected according to the electroless plating method using SUMER solution, but it goes without saying that the invention is not limited thereto.

As is apparent from the foregoing, the present invention has such advantages, as compared with the conventional reduced pressure method in which the deposition of carbon is effected in an atmosphere under reduced pressure, that because of the practice of the deposition of carbon under atmospheric pressure the apparatus used therefor is very simple, the size of the object to be treated is not restricted, and the desired carbon coating can be obtained on a large scale with low cost. While the present invention has been described with reference to the cases where the objects (substrates) to be coated with carbon are limited to iron sheet, any materials can be used so long as the materials as substrates can be plated with the present nickel-phosphorus alloy because the deposition of carbon can be achieved due mainly to the properties of said alloy used, and as long as said materials as substrates can resist to heating at a temperature of about 450° to about 700°C. This is also one of the characteristic features of the present invention.

According to another embodiment of the present invention, there is provided a process for forming carbon coatings, which process is characterized by comprising a step of heating a nickel-phosphorus alloy-plated substrate in an atmosphere of a reaction gas comprising acetylene gas, said atmosphere being reduced in pressure to 100 Torr or less, at a temperature of about 500° to about 700°C and at such a rate of the temperature elevation that the nickel-phosphorus plated layer may not lose its catalytic ability for deposition of carbon.

According to a still further embodiment of the present invention, there is provided a process for forming carbon coatings, which process is characterized by using in the above-mentioned process a reaction gas containing acetylene gas and at least one of hydrogen and methane gas.

FIG. 7 shows the results of the formation of carbon coatings on substrates, wherein specimens of iron sheets of 0.18 mm in thickness were coated with a nickel-phosphorus alloy containing 8 percent by weight of phosphorus by use of SUMER plating solution adjusted pH to 6.0 to form thereon an alloy layer of 1 micron in thickness, the specimens were then individually heated at a temperature of about 600°C in vacuo of 10^{-6} Torr for 5 minutes, 10 minutes, and 20 minutes, respectively, and thereafter acetylene gas of a pressure of about 10 Torr was introduced to bring about thermal decomposition reaction. As is clear from FIG. 7, the longer is the preliminary heating time prior to the practice of the thermal decomposition reaction of acetylene gas, the smaller is the amount of carbon deposited, and when the preliminary heating time is prolonged up to 20 minutes, no substantial deposition of carbon is brought about. That is, this means that in such a state as mentioned above, the effect of utilization of a catalytic material, the utilization of which is an original object of the present invention, is totally lost.

FIG. 8 shows the results of the investigation on the efficiency as catalyst of the nickel-phosphorus alloy plated having a thickness of about 0.6 microns layers formed on substrates, wherein each substrate was introduced into an atmosphere of acetylene gas having a pressure of 10 Torr heated at 600°C to effect reaction and thereby to check the relationship between the partial pressure of hydrogen formed by thermal decomposition of acetylene gas and the reaction time. In the said figure, curve A indicates the partial pressure of hydrogen of one of the specimens as measured by previously subjecting said specimen to preliminary heating in vacuo at about 600°C for 30 minutes, thereby rendering the specimen inactive as a catalyst. While curve B shows the partial pressure of hydrogen of the other specimen as measured in its state as plated without subjecting to the said preliminary heating. In this measurement, the temperature of the specimens during the reaction time is represented by curve C. As is apparent from the change in the partial pressure of hydrogen shown in FIG. **8**, in the case of the specimen having its catalytic action, the reaction begins to take place when the heating temperature has reached about 500°C, the thermal decomposition proceeds rapidly for the first 10 minutes of the reaction time and, thereafter a mild reaction continues for 30 minutes or more, i.e. even after extinction of said catalytic action. In contrast thereto, in the case of the specimen, from which its catalytic action has been completely deprived of, evolution of hydrogen is not observed at all. As a natural consequence, no deposition of carbon is observed at all. The above facts shows not only the catalyst plays at the initial stage of deposition of carbon a very important role but also mean that when the deposition of carbon has once started, the carbon successively deposits even after the catalytic action has disappeared. In the cases illustrated above, the thickness of the nickel-phosphorus alloy plated layer is sufficiently 0.1 micron or thicker. In order to obtain a dense carbon coating, the initial deposition of carbon by the catalytic action as mentioned above is very important. If the time required to elevate the temperature of 400°C up to the temperature at which the thermal decomposition of acetylene gas begins to start excessively long, a dense carbon coating can be obtained no longer. This critical time is called a critical heating time. The critical heating time at varying heating temperatures starting from 400°C were investigated to obtain the results as shown in the following table.

Heating temperature	Critical heating time
400°C	200 minutes
500°C	120 minutes
600°C	20 minutes

Within the critical heating time as shown in the above table, a dense carbon coating of apparent gravity of about 2.0 is formed in each case and the carbon deposited is observed as having crystal form according to X-ray diffraction.

FIG. **9** shows the relationship between the heating time and the amount of carbon deposited (mg/cm^2) which is obtained by subjecting each of specimens prepared by plating according to the electroless plating method iron sheet of 20 mm in length, 20 mm in width and 0.2 mm in thickness with a nickel-phosphorus alloy to reaction in a furnace heated at the temperature range from 550° to 640°C in three kinds of acetylene gas for about 30 minutes. In the figure, there are shown the results obtained in the reactions individually effected under heating in an atmosphere of acetylene gas (C_2H_2) having a pressure of **10** Torr in the case of curve D, of a mixed gas comprising acetylene gas having a pressure of 5 Torr and methane gas having a pressure of 5 Torr, and of a mixed gas comprising acetylene gas having a pressure of 5 Torr and hydrogen (H_2) having a pressure of 5 Torr. As is clear from the figure, in the case where acetylene gas is used alone an effective thermal decomposition reaction due to the action of the catalyst material takes place at the ambient heating temperatures of about 600°C, as shown in curve D, and an increase in the amount of carbon deposited is observed. In the case where carbon in amount of 2 mg/cm^2 or more is deposited within a very short time in this thermal decomposition reaction, however, the carbon coated thus obtained is quite apt to become porous and the carbon comes to take a dust-like form which easily peels off from the substrate in many cases. In the light of the above fact, it is also an important significance in the present invention in effectively practicing the present process to include a means to suppress the thermal decomposition reaction with the view of adjusting and controlling the properties of carbon coating formed thereby. As the means of suppressing the thermal decomposition reaction, it has been clarified that altering the components of the reaction gas is rather effective as the suppressing means than control of the furnace temperature and change of the state of activation of the catalyst, and that the introduction of hydrogen or methane gas into acetylene gas is effective as the concrete means for suppressing the reaction, particularly preferred means is the introduction of H_2 into acetylene. That is, in FIG. **9**, the curves E and F are to verify the above fact. Particularly, as is apparent from the results as indicated by the curve E, said results being obtained by thermal decomposition of a mixed gas comprising acetylene gas and hydrogen, it is possible to control the deposition of carbon deposited to a given amount at each heating temperature. Furthermore, the addition of methane gas has the effect to that of the case of hydrogen, the decomposition reaction of methane gas is an endothermic reaction. As shown by the curve E in FIG. **9**, when the heating temperature is below about 600°C, a rapid deposition of carbon from acetylene gas due to the action of the catalyst has been suppressed. As the means for suppressing the rapid deposition of carbon resulted from the thermal decomposition of acetylene gas under the action of the catalyst, it is preferable, including a method in which the amount of acetylene is reduced and the reaction is effected under reduced pressure, in addition to the above-mentioned means, that the temperature of below about 700°C is selected as the heating temperature. At a temperature above about 700°C, the reaction is undesirably effected because there are brought about not only an undesirable effect of the heating temperature on the substrate but also decomposition of methane gas in the case the mixed reaction contains methane gas, whereby other factors arise, which factors should also be taken into consideration.

According to another embodiment of the present invention, there is provided a process for forming a carbon coating on the surface of a substrate, characterized by comprising a step of plating the surface of the substrate with a nickel-phosphorus alloy to form thereon a nickel-phosphorus alloy layer containing at least 5 percent of phosphorus, a step of oxidizing said nickel-phosphorus alloy layer, and a step of heating the substrate having thereon the oxidized nickel-phosphorus alloy layer at a temperature of 500° to 650°C in a non-oxidative reaction gas containing 0.015 to 5 percent by volume of acetylene gas.

According to this process, formation on a substrate of a desired carbon coating can be accomplished by the following four procedures, the first one is to limit the heating temperature of the substrate, such as an iron sheet, employed at the time of coating step to a relatively low temperature of below about 650°C, the second one is to previously provide a nickel-phosphorus alloy layer on the surface of the substrate, such as an iron sheet, by means of plating, the third one is to carry out a preliminary oxidation treatment of said nickel-phosphorus alloy layer prior to a coating treatment with thermally decomposed carbon, and the fourth one is to the optimum composition of a mixed gas from which the carbon is deposited by reaction under heating.

Referring first to FIG. **10**, there is indicated an influence on the amount of carbon deposited of the content of phosphorus in a nickel-phosphorus plated layer having a thickness of about 1 micron formed on the surface of an iron sheet substrate. In the embodiment of the present invention shown in FIG. **10**, the carbon coating treatment was carried out and the conditions mentioned hereinbelow. After plating of a nickel-phosphorus alloy, a preliminary oxidation treatment to oxidize the nickel-phosphorus alloy plated layer was effected by heating in a nitrogen gas containing 0.005 percent by volume of oxygen at a temperature of about 580°C for 10 minutes. Subsequently, the carbon coating treatment was carried out in an incombustible reaction gas containing 0.05 percent by volume of acetylene gas at about 600°C for 20 minutes. It may be said from the results of the above embodiment that at least 4 percent by weight of phosphorus should indispensably be contained in the nickel-phosphorus alloy layer in order to deposit carbon to be coated on the surface of the substrate.

FIG. **11** shows the influence on the amount of carbon deposited of the concentration of oxygen in the nitrogen gas stream as an atmosphere gas when the aforesaid nickel-phosphorus alloy layer has been subjected to the aforesaid preliminary oxidation treatment, provided that the content of phosphorus in the aforesaid nickel-phosphorus alloy layer was 8 percent by weight. In this case, the treatment subsequent to the preliminary oxidation treatment was carried out in the manner similar to that in the case of FIG. **10**, i.e. the subsequent carbon coating treatment was effected in a reaction gas containing about 0.05 percent by volume of acetylene at about 600°C for 20 minutes. According to the results of this embodiment, it is indicated that when the oxygen concentration in the nitrogen gas stream is less than 1×10^{-4} percent by volume, the amount of carbon deposited extremely decreases. Accordingly, it is understood that the oxygen concentration in the nitrogen gas stream should necessarily be more than 1×10^{-4} percent by volume.

The above-mentioned embodiment is considered as merely illustrative, and hence the present preliminary oxidation treatment is not limited to such treatment conditions as illustrated above. For example, a preliminary oxidation of the nickel-phosphorus alloy layer in air of about 0.1 Torr at about 600°C for 10 minutes leads to formation of a favorable carbon coating. Furthermore, it should be understood that the heating temperature in the preliminary oxidation treatment is not limited to 600°C. Any conditions under which the oxidation of the said alloy layer is effected to a slight extent may be preferably employed for obtaining favorable carbon coatings in a manner as illustrated in the aforesaid case. The effect of the preliminary oxidation treatment of the alloy layer is that by virtue of such oxidation treatment, the catalytic ability of said alloy layer is revived.

The present invention is illustrated below with reference to examples. All the nickel-phosphorus alloy layers used in these examples were formed according to the electroless plating method using a commercially available plating solution known as a trade name, "SUMER." In Examples 1–4, all the alloy layers used contain 8 percent by weight of phosphorus. The preliminary oxidation treatment was carried out in each case in a nitrogen atmosphere comprising 0.005 percent by volume of oxygen at a temperature of about 600°C for 10 minutes.

EXAMPLE 1

An iron sheet substrate of 0.15 mm in thickness plated on its one surface with nickel-phosphorus alloy to form thereon a nickel-phosphorus alloy layer of about **1** micron in thickness was subjected to a preliminary oxidation. The substrate was then heated at a temperature of 560°C for 20 minutes in the presence of a reaction gas stream comprising nitrogen gas containing 0.05 percent by volume based on the nitrogen gas of acetylene gas, thereby allowing carbon contained in said reaction gas to deposit on the surface of said nickel-phosphorus alloy layer coated substrate to form a carbon coating thereon. The thus obtained carbon coating was found to be extremely dense and have an amount of carbon deposited of 1 mg/cm^2 and a carbon density of 1.94 g/cm^3.

EXAMPLE 2

An iron sheet substrate of 0.15 mm in thickness plated on its one surface with nickel-phosphorus alloy to form thereon a nickel-phosphorus alloy layer was subjected to a preliminary oxidation treatment. The substrate was then heated at a temperature of 560°C for 20 minutes in the presence of a reaction gas stream comprising methane gas containing 0.5 percent by volume based on the methane gas of acetylene gas, thereby allowing carbon contained in said reaction gas to deposit on the surface of the nickel-phosphorus alloy layer-coated substrate to form a carbon coating thereon. The carbon coating thus obtained was found to be extremely dense and have an amount of carbon deposited of 1.2 mg/cm^2 and a carbon density of 2.20 g/cm^3.

In this example, the concentration of acetylene gas contained in the methane gas may be increased upmost to 5 percent by volume. In that case, however, a density of carbon in the resulting carbon coating tends to decrease to a some extent.

EXAMPLE 3

An iron sheet substrate of 0.15 mm in thickness plated on its one surface with nickel-phosphorus alloy to form thereon a nickel-phosphorus alloy layer was subjected to a preliminary oxidation treatment. The substrate was then heated at a temperature of about 560°C for 20 minutes in the presence of a reaction gas stream comprising a gas obtained by vaporizing L.P.G., said gas containing 0.7 percent by volume based on L.P.G. of acetylene gas, thereby allowing carbon contained in said reaction gas to deposit on the surface of the nickel-phosphorus alloy layer coated-substrate to form a carbon coating thereon. The carbon coating thus obtained was found to be relatively thick in its thickness and dense, and have an amount of carbon deposited of about 2.5 mg/cm^2 and a carbon density of 2.18 g/cm^2.

In this example, the concentration of acetylene contained in L.P.G. may be increased upmost to 5 percent by volume. In that case, however, a density of carbon in the resulting carbon coating tends to decrease to some extent.

EXAMPLE 4

An iron sheet substrate of 0.15 mm in thickness plated on its one surface with nickel-phosphorus alloy to form thereon a nickel-phosphorus alloy layer of about 1 micron in thickness was subjected to a preliminary oxidation treatment. The substrate was then heated at a temperature of about 560°C for 20 minutes in the presence of a reaction gas stream comprising a mixture of 0.2 percent acetylene gas, 1 percent L.P.G., 4 percent methane gas and 94.8 percent nitrogen gas in terms of percent by volume based on the mixture, thereby allowing carbon contained in said reaction gas to deposit on the surface of the nickel-phosphorus alloy layer-coated substrate to form a carbon coating thereon. The carbon coating thus obtained was found to be dense and have an amount of carbon deposited of about 1.8 mg/cm^2 and a carbon density of 1.96 g/cm^2.

Since the reaction gas used in this example was non-combustible, it has been found quite effective to use said reaction gas in promoting a safe operation.

That is, it has been found possible to use a reaction gas having any composition, from which the carbon contained therein is allowed to deposit, so long as said reaction gas contains 0.01–5 percent by volume based on the reaction gas of acetylene gas and is of a non-oxidative composition free from such an oxidative gas as oxygen. In that case, the reaction gas may be mixed suitably with such combustible gas as L.P.G. or methane gas, however, it is preferably from the standpoint of handling to use a reaction gas comprising a mixture of such an inert gas as nitrogen or argon and such a combustible gas as L.P.G. and/or methane gas in an amount within such a range that the resulting whole mixed gas may become non-combustible.

While there have been described the preferred embodiments of the present invention with reference to the cases where the nickel-phosphorus alloy layer was coated on the surface of the substrate by the electroless plating using "SUMER" solution (a trade name of a plating solution). It is needless to say, however, that the invention is not limited thereto.

As fully explained hereinabove, according to the process of the present invention it is possible to coat the surface of a very thin iron sheet substrate having a thickness of 0.15 mm with dense carbon in any given thickness with unerring precision and in a simple and safe manner, while it was almost impossible in the prior art processes to practice such coating as in the present invention. The process of the present invention, moreover, has such characteristic that since the temperature necessary for effecting a carbon-depositing reaction in the present process is low as compared with that used in the prior art processes, various disadvantages which may be associated with a high temperature heating employed in the prior art processes can be effectively avoided.

Furthermore, the process of the present invention is extremely effective as a process, in particular, for coating with carbon a shadow mask for color picture tube of television and leads to excellent results in an improvement in technique for the production of the shadow mask.

EXAMPLE 5

A 0.15 mm thick iron sheet shadow mask for color picture tube of television was washed with hydrochloric acid to remove completely from the surface thereof the oxide formed thereon. The mask thus washed as such was immersed for about 2 minutes in "SUMER" electroless nickel plating bath (temperature of the bath had been controlled to be maintained at 80°C), a pH value of which had been previously adjusted to 6.0. In this case, special consideration was given so that the plating bath was thoroughly stirred so as to extend sufficiently uniformly over the circumferences of a large number of small pores provided on the shadow mask, thereby uniformly plating every portion of the shadow mask with a nickel-phosphorus alloy in thickness of about 0.3–0.5 micron. After completion of the plating treatment, the shadow mask was pulled out from the plating bath and washed thoroughly with pure water and thereafter dried quickly. Subsequently, the inside of a heating furnace was once evacuated until a pressure of 1×10^{-6} to 1×10^{-5} Torr was attained, said heating furnace being constructed by use of such material, for example, as quartz which may not deposit carbon by reaction with acetylene at about 600°C. Therafter, acetylene was introduced into the heating furnace so that the degree of vacuum indicated by Pirani indicator provided in the said furnace may reach 5 Torr. Into the furnace, the inside temperature of which had been heated to about 600°C, was then placed the shadow mask while giving sufficient consideration not to destruct the above-mentioned inside atmosphere of the furnace (in this case, the shadow mask had not been preheated). The reaction was carried out at that temperature for about 30 minutes, thereby forming on the surface of said shadow mask a carbon coating having an amount of carbon deposited of about 1 mg/cm^2 and a thickness of about 4.5 microns. Thereafter the carbon-coated shadow mask was conveyed to a cooling chamber and then taken out of the chamber. Microscopic observation of the thus obtained carbon coating under magnification of about 600 times showed in some cases that small spheres of carbon in the form of a ball of waste thread were present on the surface of the carbon coating. If such carbon spheres are actually present on the surface of the carbon coating formed on a shadow mask, they come readily to float with a color picture tube and cause spark when a high voltage is applied thereto, and hence it is necessary to remove completely such carbon spheres, prior to use of the carbon-coated shadow mask, by washing with water or by rinsing treatment with ultrasonic wave. The carbon-coated shadow mask after being subjected to the above-mentioned treatment was actually fitted in a color picure tube, and a test was effected. As a result, there was obtained such excellent effects that secondary-electron emission from the shadow mask due to heat electron jetted under accelerated voltage of 25–30 KV could be prevented and a good colored picture could be provided without observing substantial halation.

While there has been described what is at present considered to be a preferred embodiment of the present invention with reference to the case where the shadow mask substrate was plated with nickel-phosphorus alloy by the electroless plating method using "SUMER" solution (a trade name of a plating solution). It is needless to say, however, that the invention is not limited thereto.

As explained hereinabove, in accordance with the process of the present invention it is possible to plate a substrate, on the surface of which a carbon coating is to be provided, with a nickel-phosphorus alloy to form thereon a layer thereof, to deposit from acetylene on the surface of the nickel-phosphorus alloy layer-coated substrate by thermal decomposition reaction of the acetylene gas at relatively low temperatures utilizing catalytic action of the said nickel-phosphorus alloy layer, and to suppress or control the thermal decomposition reaction of the acetylene gas by adjusting the composition of the reaction gas containing the acetylene gas, thereby forming a dense and uniformly thick carbon coating on the surface of the substrate in a simple manner with high operational stability. The present invention, therefore, greatly contributes to advancement and improvement in the industrial technology concerned and also brings about large economical advantages.

What is claimed is:

1. A process for forming a carbon coating on an iron surface of an article to be coated, which process comprises the steps of first forming on the iron surface of said article a nickel-phosphorus alloy layer having an amount of 4 - 12 percent by weight of phosphorus, and of then heating the nickel-phosphorus alloy layer-coated article in a non-combustible gas mixture containing a thermally decomposable hydrocarbon gas, thereby effecting a thermal decomposition reaction of said gas at a temperature below 700°C to deposit carbon contained in said gas on the surface of said nickel-phosphorus alloy layer-coated article to form the carbon coating thereon, said nickel-phosphorus alloy layer effecting catalytic action to deposit carbon with a nickel-phosphorus compound of said alloy layer, so that said carbon coating is firmly bonded to said surface at said temperature.

2. A process according to claim **1**, wherein the nickel-phosphorus alloy layer is formed by the electroless plating method.

3. A process according to claim **2**, wherein an amount of phosphorus to be contained in the nickel-phosphorus alloy layer is controlled by adjusting a pH value of a solution of the electroless plating.

4. A process according to claim **1**, wherein the amount of phosphorus contained in the nickel-phosphorus alloy layer is at least 5 percent by weight based on the nickel.

5. A process according to claim **1**, wherein a thickness of the nickel-phosphorus alloy layer is 0.1 to 6 microns.

6. A process according to claim **1**, wherein the hydrocarbon is an acetylene-containing gas.

7. A process according to claim **6**, wherein the non-combustible gas containing 0.1 to **1.5** percent by volume of acetylene gas.

8. A process according to claim **7**, wherein the non-combustible gas contains an inert gas selected from the group consisting of nitrogen, helium, and argon.

9. A process according to claim **7**, wherein the non-combustible gas also contains Liquefied Petroleum Gas or methane gas.

10. A process according to claim **6**, wherein the non-combustible gas is composed mainly of an inert gas selected from the group consisting of nitrogen, helium, and argon, said non-combustible gas containing at least one member selected from the group consisting of 0.1 – 1.5% by volume of acetylene gas, 0.1% or more of Liquefied Petroleum Gas, and 0.1 percent or more of methane gas in an amount within such a range that the resulting whole mixed gas is non-combustible.

11. A process according to claim **10**, wherein the non-combustible gas contains further at least one member selected from the group consisting of ethane and ethylene gases in an amount within such a range that the resulting whole mixed gas is non-combustible.

12. A process according to claim **6**, wherein the non-combustible gas comprises acetylene gas and at least one member selected from the group consisting of hydrogen and methane gases.

13. A process according to claim **1**, wherein the non-combustible gas constitutes a reduced pressure atmosphere surrounding the article to be coated.

14. A process according to claim **13**, wherein the reduced pressure is 100 Torr or less.

15. A process according to claim **1**, wherein the nickel-phosphorus alloy layer coated-article is heated in the presence of the non-combustible gas at such a rate of temperature elevation that a catalytic ability of the nickel-phosphorus alloy layer may not markedly be reduced, thereby effecting at a temperature of 450°–700°C a thermal decomposition of said non-combustible gas to deposit carbon contained in said gas on the surface of said nickel-phosphorus alloy layer-coated article to form a carbon coating thereon.

16. A process according to claim **15**, wherein the article to be coated with carbon is a shadow mask for color picture tube of television.

17. A process according to claim **15**, wherein the nickel-phosphorus alloy layer is applied to the article to be coated by the electroless plating method.

18. A process according to claim **17**, wherein an amount of phosphorus to be contained in the nickel-phosphorus alloy layer is controlled by adjusting a pH value of a solution of the electroless plating.

19. A process according to claim **15**, wherein the non-combustible gas contains 0.1 to **1.5** percent by volume of acetylene gas.

20. A process according to claim **19**, wherein the non-combustible gas contains an inert gas selected from the group consisting of nitrogen, helium, and argon.

21. A process according to claim **19**, wherein the non-combustible gas is composed mainly of an inert gas selected from the group consisting of nitrogen, helium, and argon, said hydrocarbon-containing gas containing at least one member selected from the group consisting of 0.15–1.5 percent by volume of acetylene gas, at least 0.1% by volume of Liquefied Petroleum Gas, and at least 0.1% by volume of methane gas in an amount within such a range that the resulting whole mixed gas is non-combustible.

22. A process according to claim **21**, wherein the non-combustible gas contains further at least one member selected from the group consisting of ethane and ethylene gases in an amount within such a range that the resulting whole mixed gas is non-combustible.

23. A process according to claim **21**, wherein the nickel-phosphorus alloy layer has a thickness of at least 1 micron.

24. A process according to claim **15**, wherein the non-combustible gas constitutes a reduced pressure atmosphere surrounding the article to be coated with carbon.

25. A process according to claim **24**, wherein the reduced pressure is 100 Torr or less.

26. A process according to claim **1**, wherein the nickel-phosphorus alloy layer-coated article is heated at such a rate of temperature elevation that a catalytic ability of said nickel-phosphorus alloy layer may not be markedly reduced, thereby effecting at a temperature of 500°–700°C a thermal decomposition of said non-combustible gas to deposit carbon contained in said gas on the surface of said nickel-phosphorus alloy layer-coated article to form a carbon coating thereon.

27. A process according to claim **26**, wherein the article to be coated with carbon is a shadow mask for color picture tube of television.

28. A process according to claim **26**, wherein the nickel-phosphorus alloy layer is applied to the article by the electroless plating method.

29. A process according to claim **28**, wherein an amount of phosphorus to be contained in the nickel-phosphorus alloy layer is controlled by adjusting a pH value of a solution of the electroless plating.

30. A process according to claim **26**, wherein the hydrocarbon is an acetylene-containing gas.

31. A process according to claim **30**, wherein the acetylene-containing gas comprises acetylene gas and at least one member selected from the group consisting of hydrogen and methane gases.

32. A process according to claim **26**, wherein the non-combustible gas constitute a reduced pressure atmosphere surrounding the artilce to be coated with carbon.

33. A process according to claim **32**, wherein the reduced pressure is a pressure of 100 Torr or less.

34. A process according to claim **26**, wherein an atmosphere of the non-combustible gas is an acetylene-containing gas having a pressure of 100 Torr or less.

35. A process according to claim **34**, wherein the acetylene-containing gas comprises acetylene gas and at least one member selected from the group consisting of hydrogen and methane gases.

36. A process according to claim **34**, wherein the nickel-phosphorus alloy layer has a thickness of at least **1** micron and the acetylene-containing gas comprises acetylene gas and at least one member selected from the group consisting of hydrogen and methane gases.

37. A process according to claim **1**, wherein the nickel-phosphorus alloy layer coated on the surface of the article is oxidized and then heated in the presence of said non-combustible gas, thereby thermally decomposing said gas to deposit carbon contained in said gas on the surface of the nickel-phosphorus alloy layer-coated article to form a carbon coating thereon.

38. A process according to claim **37**, wherein the article to be coated with carbon is a shadow mask for color picture tube of television.

39. A process according to claim **37**, wherein the nickel-phosphorus alloy layer is applied to the article to be coated with carbon by the electroless plating method.

40. A process according to claim **37**, wherein an amount of the nickel-phosphorus alloy layer is controlled by adjusting a pH value of a solution of the electroless plating.

41. A process according to claim **37**, wherein the nickel-phosphorus alloy layer contains at least 5 percent by weight of phosphorus based on the nickel.

42. A process according to claim **37**, wherein the non-combustible gas contains 0.01–5 percent by volume of acetylene gas.

43. A process according to claim **37**, wherein the non-combustible gas contains an inert gas selected from the group consisting of nitrogen, helium, and argon.

44. A process according to claim **37**, wherein the non-combustible gas is composed mainly of an inert gas selected from the group consisting of nitrogen, helium, and argon, said non-combustible gas containing at least one member selected from the group consisting of 0.01–5 percent by volume of acetylene gas, at least 0.1 percent by volume of Liquefied Petroleum Gas, and at least 0.1 percent by volume of methane gas in an amount within such a range that the resulting whole mixed gas is non-combustible.

45. A process according to claim **37**, wherein the nickel-phosphorus alloy layer contains at least 5 percent by weight of phosphorus based on the nickel, and the non-combustible gas contains 0.01–5 percent by volume of acetylene gas.

46. A process according to claim **45**, wherein the non-combustible gas contains an inert gas selected from the groups consisting of nitrogen, helium, and argon.

47. A process according to claim **45**, wherein the non-combustible gas is composed mainly of an inert gas selected from the group consisting of nitrogen, helium, and argon, and containing at least one member selected from the group consisting of Liquefied Petroleum Gas and methane gas in an amount within such a range that the resulting whole mixed gas is non-combustible.

48. A process according to claim **45**, wherein the nickel-phosphorus alloy layer has a thickness at least 1 micron.

49. A process according to claim **37**, wherein the oxidation is carried out in an oxygen-containing atmosphere while increasing temperature.

50. A process according to claim **1**, wherein said temperature is 650°C or lower, such that thermal deterioration of said article to be coated is prevented.

51. A process according to claim **1**, wherein said temperature is in the range of about 450°C to near 700°C.

52. A process according to claim **1**, wherein said carbon coating has a carbon density of at least 1.9 g/cm^3.

53. A process according to claim **1**, wherein said carbon coating is a stable crystalline film.

54. A process according to claim **1**, wherein said nickel-phosphorus compound is Ni_xP wherein x is about 2.

55. A process according to claim **1**, wherein said nickel-phosphorus alloy acts to deposit an initial small amount of carbon particles thereon such that said carbon particles become nuclei for carbon to be deposited.

56. A process according to claim **1**, wherein said temperature is achieved within one minute or less.

57. A process according to claim **1**, wherein said thermal decomposition reaction is maintained for at least about 40 minutes.

58. A process according to claim **57**, wherein said thermal decomposition reaction is maintained for at least about **20** minutes.

59. A process for forming a carbon coating a surface comprising

coating a carbon layer on a surface comprising a substrate of iron coated with a nickel-phosphorus alloy layer containing 4 – 12 percent by weight of phosphorus by heating a non-combustible hydrocarbon containing gas at a temperature below 700°C to thermally decompose said gas, thereby depositing carbon on said surface, said nickel-phosphorus alloy layer effecting catalytic action to deposit carbon with a nickel-phosphorus compound of said alloy layer, so that carbon is firmly bonded to said surface at said temperature.

60. A process according to claim **59,** wherein the hydrocarbon is an acetylene-containing gas.

61. A process according to claim **60,** wherein the non-combustible gas contains 0.1–1.5 percent by volume of acetylene gas.

62. A process according to claim **61,** wherein the non-combustible gas contains an inert gas selected from the group consisting of nitrogen, helium, and argon.

63. A process according to claim **59,** wherein the non-combustible gas is composed mainly of an inert gas being at least one of nitrogen, helium, and argon, said non-combustible gas containing at least one of 0.1 –1.5 percent by volume of acetylene gas, 0.1% or more of

Liquefied Petroleum Gas, and 0.1percent or more of methane gas in an amount within such a range that the resulting whole mixed gas is non-combustible.

64. A process according to claim **63,** wherein the non-combustible gas contains further at least one of ethane and ethylene gases in an amount within such a range that the resulting whole mixed gas is non-combustible.

65. A process according to claim **59,** wherein the non-combustible gas comprises acetylene gas and at least one of hydrogen and methane gases.

66. A process according to claim **59,** further comprising the step of oxidizing said nickel-phosphorus alloy layer prior to said deposition of carbon on said surface.

67. A process according to claim **59,** wherein said surface is a shadow mask surface for a color picture tube.

68. A process according to claim **59,** wherein said temperature is 650°C or lower, such that thermal deterioration of said article to be coated is prevented.

69. A process according to claim **59,** wherein said temperature is in the range of about 450°C to near 700°C.

70. A process according to claim **59,** wherein said nickel-phosphorus compound is Ni_xP wherein x is about **2.**

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