

[54] METHOD FOR FORMING CARBON COATING AND COMPOSITE ARTICLE WITH A CARBONACEOUS COATING THEREON

[75] Inventors: Tadashi Saito; Tetsuo Gejyo, both of Tokyo, Japan

[73] Assignee: Hitachi, Ltd., Tokyo, Japan

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[58] Field of Search..... 117/46 CB, 46 CG, 117/216, 217, 131, 226; 29/195; 204/38 R, 204/49; 423/448, 450, 458

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Primary Examiner—William D. Martin

Assistant Examiner—M. Sofocleous

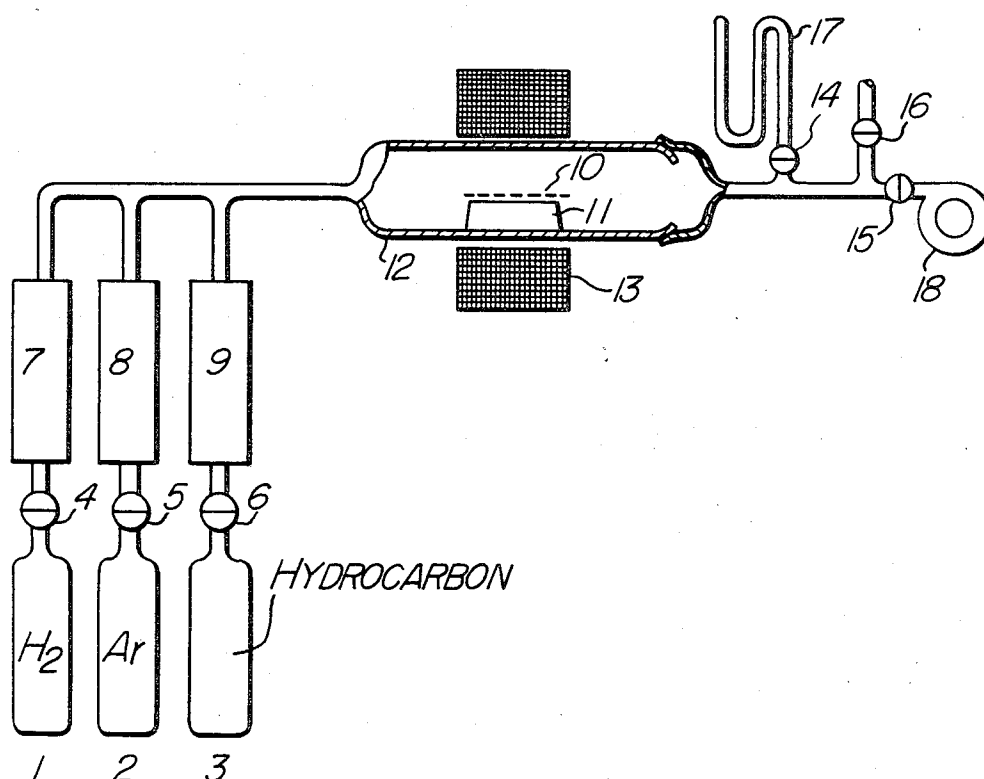
Attorney—Craig, Antonelli and Hill

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ABSTRACT

A carbon coated layer having good property for controlling the secondary electron emission and electron reflecting effect is deposited on a metal article surface having an amorphous nickel layer plated thereon by heating at a temperature of from 500 to 680°C in an atmosphere containing at least one hydrocarbon gas selected from the group consisting of acetylene, ethylene, ethane and propane having a partial pressure of 5 to 50 Torr.

10 Claims, 3 Drawing Figures



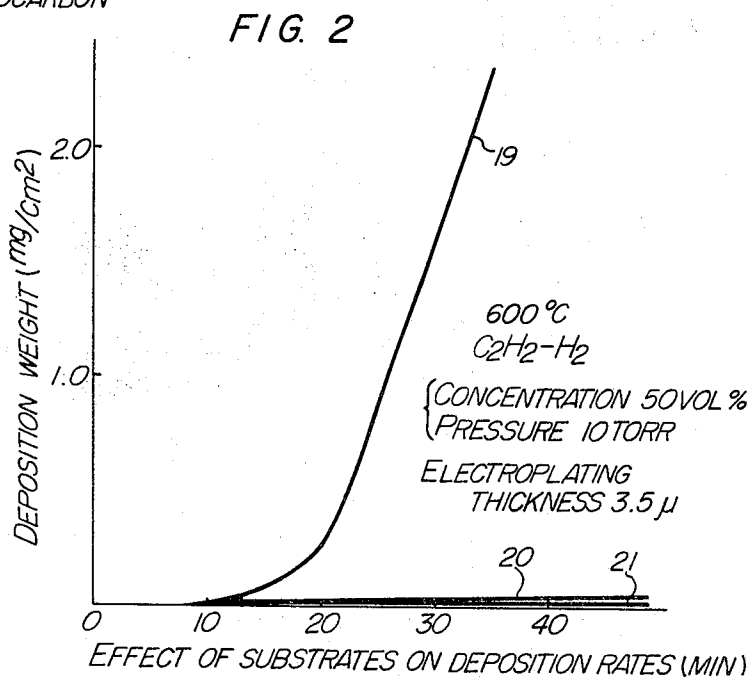
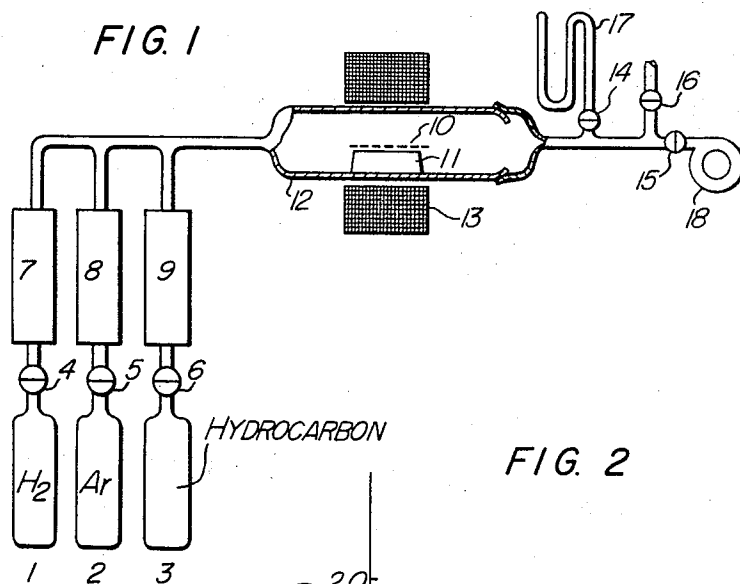
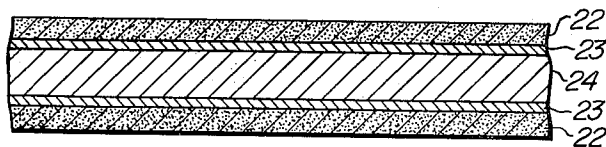


FIG. 3



INVENTORS

TADASHI SAITO and TETSUO GEIYO

BY

Craig, Antonelli, Stewart & Hill

ATTORNEYS

METHOD FOR FORMING CARBON COATING AND COMPOSITE ARTICLE WITH A CARBONACEOUS COATING THEREON

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for forming carbon coating and a composite article with a carbonaceous coating thereon, and more particularly to a method for forming carbon coating on a metal plate and a composite metal member with a carbonaceous coating thereon. Such composite metal member is usable for a shadow mask of a color picture tube and an anode member of an electric discharge tube, or in various fields. For example, in the color picture tube, a color effect has been considerably impaired by the primary electron reflection and the secondary electron discharge from the shadow mask. Accordingly, it has been necessary to reduce such primary electron reflection and secondary electron discharge from the shadow mask, and it has been presumed effective to coat a shadow mask with a substance of low atomic weight, particularly carbon. Thus, the art of coating the shadow mask with such substance has been important to establish.

2. Description of the Prior Art

Heretofore, a method for depositing graphite onto a metal by thermally decomposing acetylene at a temperature of $1,000^{\circ} \pm 25^{\circ}\text{C}$ [A.E.B. Presland and P.L. Walker: 7 Jr. Carbon 1 (1969)] or a method for coating a nickel plate with carbon by thermally decomposing methane, ethane, ethylene, etc. on the nickel plate at $870^{\circ}\text{--}1030^{\circ}\text{C}$ [Y. Tamai et al.: 6 Jr. Carbon 593 (1968)] has been known as the conventional method for coating a metal plate with carbon, but any of these two methods is directed to formation of carbon coating by thermal decomposition of hydrocarbon at a temperature higher than 800°C .

However, a mild steel plate having a thickness of 0.15–0.3 mm is usually used for a shadow mask for television receiver, and accordingly, if it is heated to a temperature higher than 800°C , the shadow mask is considerably deformed and no more used practically. Thus, heating to a temperature higher than 800°C must be absolutely avoided.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for forming a carbon coating on a metal substrate by thermally decomposing a hydrocarbon at a temperature lower than 800°C and obtain a composite article with a carbonaceous coating.

The object of the present invention can be attained by forming an amorphous nickel plating on a substrate metal by electrolysis or non-electrolysis, heating the nickel-plated substrate metal in an atmosphere of at least one of such saturated and unsaturated hydrocarbons as acetylene, ethylene, ethane and propane or a gaseous mixture consisting of said hydrocarbon and at least one of hydrogen and inert gases (5–50 Torr) at $500^{\circ}\text{--}680^{\circ}\text{C}$ and thereby thermally decomposing said hydrocarbon.

The amorphous nickel plating layer deposited by electrolysis or non-electrolysis acts as a catalyst for thermal decomposition of hydrocarbon, and thus the thermal decomposition reaction proceeds at about 600°C , which is by more than 200°C lower than the

conventional, lowest temperature possible for the thermal decomposition.

Not only the catalytic action of the amorphous nickel plating layer deposited by electrolysis or non-electrolysis is more effective than a nickel plate, but also the uniformity and adhesiveness of carbon coating deposited on said amorphous nickel plating layer are better than those of the carbon coating deposited on the nickel plate, mild steel plate, copper plate, molybdenum plate, stainless steel plate or other metal plate.

Furthermore, said amorphous nickel plating layer considerably accelerates a carbon build-up speed.

The present invention now will be explained in detail, referring to the drawings.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a block diagram of a thermal decomposition apparatus used for conducting the present method.

FIG. 2 shows influences of the presence of amorphous nickel plating deposited on the surface of thin metal plate, upon the carbon build-up speed.

FIG. 3 is a cross-sectional view of a composite metal plate with a carbonaceous coating.

Explanation is made of the apparatus for effecting carbon coating shown in FIG. 1. A hydrogen cylinder 1, an argon cylinder 2, and a hydrocarbon cylinder 3 are provided with cocks 4, 5 and 6 for controlling gas flow rates and flowmeters 7, 8 and 9 respectively, and a constant flow rate of said hydrocarbon gas or a gaseous mixture of said hydrocarbon and argon and/or hydrogen is always fed to a reaction tube 12 as a reactant gas during the thermal decomposition reaction.

Procedures of operation for effecting carbon coating are given below.

a. A specimen 10 is placed on a specimen base 11.
b. Cocks 4, 5, 6 and 16 are closed and cocks 14 and 15 are opened. Then, exhaustion of gas is effected by a vacuum pump 18.

c. When the inside of the reaction tube becomes vacuum (10^{-2} Torr or less), the cock 15 is closed, and then the cock 4 is opened to introduce hydrogen into the reaction tube. When the inside of the reaction tube reaches the atmospheric pressure, the cock 16 is opened to attain a constant flow rate of the hydrogen stream.

d. The specimen 10 is elevated to a predetermined temperature by means of an electric furnace 13.

e. The cocks 4 and 16 are closed, and the cock 15 is opened. Exhaustion of gas is carried out by the vacuum pump 18.

f. When the inside of the reaction tube becomes vacuum (10^{-2} Torr or less), the cock 15 is closed, and a gas of a definite composition is introduced into the reaction tube by adjusting the cocks 4 and 6, while watching the flowmeters 7 and 9. When the inside of reaction tubes reaches the atmospheric pressure, the cock 16 is opened to attain a definite flow rate of the gas stream.

g. After a predetermined period of time, the cocks 4, 6 and 16 are closed, and the cock 15 is opened. Exhaustion of gas is carried out by the pump 18.

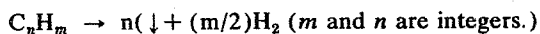
By carrying out the procedures (a) to (g), coating of the specimen with carbon can be completed.

When said carbon coating is carried out in a reactant gas under a pressure less than the atmosphere, the reactant gas of a definite pressure is introduced into the re-

action tube in said operation (f), and then the reduced pressure can be attained by closing cocks 4 and 6.

Further, when argon is used as a carrier gas, the cock 5 for feeding argon gas is adjusted while watching the flowmeter 8 in said operation (f) in place of the cock 4 for supplying the hydrogen and the flowmeter 7.

In the present invention, hydrocarbon undergoes the thermal decomposition reaction represented by the following general formula:



Said hydrocarbon includes acetylene, ethylene, ethane and propane alone or their gaseous mixtures.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

To clarify the effect of the present invention, thin plates ($2.0 \times 1.5 \times 0.02$ cm) of such metals as mild steel, copper, molybdenum and stainless steel were plated with amorphous nickel by electrolysis or non-electrolysis and used as specimens.

The conditions for amorphous nickel plating by non-electrolysis are given below:

Mild steel plates were subjected to surface treatments of trichloroethylene defatting, quirlinse pickling, water washing and drying. When said surface-treated mild steel plate was dipped into a non-electrolytic plating solution (bath composition: 30 g/l of $NiCl_2 \cdot 6H_2O$, 10 g/l of $NaH_2PO_4 \cdot H_2O$ and 10 g/l of $NaC_2H_3O_2$) for 10 minutes, an amorphous nickel plating having a thickness of about 2μ was obtained. The pH of the plating bath was 4-8, and the bath temperature was $80^\circ C$.

The conditions for amorphous nickel plating by electrolysis were given below:

Surface defatting and washing were carried out in the same manner as in the nickel plating by non-electrolysis.

Plating bath composition:

240 g/l of Nickel sulfate

45 g/l of Nickel chloride

30 g/l of Boric acid

pH = 4-4.5, $40^\circ C$

Anode: Nickel plate containing 10 percent of phosphorus

Electrolysis condition: 1 A/dm², 1.2 V

The thus prepared specimens were subjected to different thermal decomposition conditions and the thus obtained results are shown in Table 1, Examples 1 to 18. Examples 1 to 5 of Table 1 are to investigate the optimum thermal decomposition temperature of acetylene reactant gas.

In order to efficiently prevent the secondary electron discharge and electron reflection as in the color picture tube, it is an essential requirement that a uniform and thick carbon coating having a high apparent density be deposited on a substrate with a good adhesiveness.

Accordingly, if any of average thickness, apparent density, adhesiveness and uniformity be extremely worse, an improvement in color effect by the carbon coating is considerably reduced. The values of the adhesiveness and the uniformity in Table 1 are based on the values of Example 3. In Example 1, a gaseous mixture of acetylene and hydrogen (containing 50 percent by volume of hydrogen) was subjected to reaction at a thermal decomposition temperature of $480^\circ C$ under a pressure of 10 Torr for 35 minutes. Under such conditions, the average thickness was 0.7μ , the apparent

density 0.4, the adhesiveness 0.5 and the uniformity 0.3, and these properties were considerably worse. This is because the thermal decomposition temperature is too low and as a result the thermal decomposition is not carried out sufficiently.

At the thermal decomposition temperatures of Examples 2 to 4, the average thickness was $5-11 \mu$, the apparent density 0.5-1.8, the adhesiveness 0.8-1.0, and the uniformity 0.53-1, and thus a carbon coating having a good influence upon the improvement in color effect was obtained in Examples 2 to 4.

When the thermal decomposition temperature reached $700^\circ C$, the average thickness was considerably reduced to 3μ , the apparent density 0.9, the adhesiveness 0.48 and the uniformity 0.4, because the catalytic action of the nickel plating seemed to be lowered at that temperature.

It is seen from the foregoing result that the thermal decomposition temperature is suitably $500^\circ C$ to $680^\circ C$, and most preferably about $600^\circ C$.

The experiment on the pressure of the reactant gas reveals, as clearly shown in Examples 6-9, that the adhesiveness was 0.4 and the uniformity was 0.51 under 200 Torr of Example 9, and that the reactant gas pressure was suitably 5-50 Torr. Further, it was found that the adhesion state at the edge part of a shadow mask was considerably more improved, if the pressure was lower.

An influence of the amorphous nickel plating layer upon the carbon build-up speed is hereunder examined. In FIG. 2, the carbon deposit amount is indicated on the ordinate and the time on the abscissa, whereby the carbon build-up speeds on the different substrate metal plates are shown individually. The curve 19 is for a metal plate for an amorphous nickel plating layer of the present invention, the curve 20 for a nickel plate and the curve 21 for a mild steel plate having no nickel plating layer.

As is clear from FIG. 2, the carbon build-up speed, that is, a speed of forming a carbon coating on a substrate is considerably higher when a substrate having a nickel plating layer thereon is used, than when simply a nickel plate or mild steel substrate is used. A case only of acetylene is shown in Example 15, where the average thickness is 4μ and the apparent density 1.5 g/cm³, and the adhesiveness and the uniformity are somewhat inferior to those of Example 3.

In FIG. 3, a cross-sectional view of a carbon-coated metal plate prepared by carbon coating of the present invention is given, wherein numeral 22 is a carbon coating film, 23 an amorphous nickel plating layer and 24 a substrate metal plate.

Further, comparison of Example 3 with Examples 16 and 17 in Table 1 reveals that the carbon coating deposited on a substrate plated with amorphous nickel by non-electrolysis is superior in the average thickness, apparent density, adhesiveness and uniformity, to the mild steel plate and the nickel plate.

It is seen from the foregoing that in coating a thin metal plate with carbon by thermal decomposition of hydrocarbon, it is an important essential requirement for the present invention to effect amorphous nickel plating on the thin metal plate in advance by electrolysis or non-electrolysis.

Examples 1-9 and 13-18 show the cases where acetylene is a main reactant gas, but it is possible to effect carbon coating by thermal decomposition of other re-

TABLE I

Example	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Substrate	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate with Ni plating	Copper plate with Ni plating	Mo plate with Ni plating	Mild steel plate with Ni plating	Mild steel plate without Ni plating	Nickel plate	Mild steel plate with Ni plating
Reaction conditions:																		
Reactant gas composition (percent by volume)	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	H ₂ :50 C ₂ H ₂ :50	Ar:50 C ₂ H ₂ :50
Thermal decomposition temperature, ° C.	480	500	600	680	700	600	600	600	600	600	600	600	600	600	600	600	600	600
Reaction time (min.)	35	120	35	24	10	35	20	8	200	74	10	50	35	35	35	35	35	35
Pressure (torr)	10	10	10	10	10	5	10	50	3	3	3	3	10	10	10	10	10	10
Results:																		
Average thickness (μ)	0.7	6	5	11	3	3	10	3	1.0	0.5	1.7	1.5	1.7	1.6	1.5	1.1	1.1	4.9
Adherent density (g/cm. ³)	0.4	0.5	1.8	1.1	0.9	1.9	1.72	1.6	0.46	0.57	0.72	0.68	0.85	0.81	0.74	0.27	0.41	1.9
Adhesiveness	0.5	0.85	1	0.6	0.4	0.6	0.55	0.51	0.51	0.57	0.65	0.57	0.81	0.79	0.89	0.17	0.32	0.95
Uniformity	0.3	0.53	1	0.6	0.4	0.7	0.6	0.55	0.51	0.57	0.65	0.57	0.81	0.79	0.89	0.17	0.32	0.92

*LPG: liquid petroleum gas.

actant gases than acetylene, for example, ethane, ethylene and propane, at a thermal decomposition temperature of 600°C, though the properties of deposited carbon coating are somewhat poorer than those obtained from acetylene, as shown in Examples 10 to 12.

Examples 13 and 14 show cases where other copper and molybdenum plates than the mild steel plates are used, and a practical carbon coating can be effected, though the properties of deposited carbon coating are somewhat poorer than those of Example 3.

The foregoing results can be summarized as follows:

1. The thermal decomposition speed of hydrocarbon is higher when an amorphous nickel plating is applied to a shadow mask substrate in advance by electrolysis or non-electrolysis than when the mild steel plate or the nickel plate is used as a substrate directly.

2. The secondary electron discharge- and electron reflection-controlling effect of carbon coating film deposited on the amorphous nickel-plated substrate by electrolysis or non-electrolysis is considerably higher than those of carbon coating film deposited directly on the mild steel plate or the nickel plate.

3. Thermal decomposition reaction is suitably carried out in a temperature range of 500° to 680°C, and the most preferable temperature is about 600°C.

4. The pressure of reactant gas is suitably in a range of 5-50 Torr, and the most preferable pressure is 10 Torr.

5. Saturated and unsaturated hydrocarbons or a gaseous mixture consisting of said hydrocarbon and hydrogen and/or argon are suitable as a reactant gas.

6. Acetylene, ethylene, ethane and propane are suitable as saturated and unsaturated hydrocarbons, and acetylene is most suitable.

We claim:

1. A method for forming a carbon coated metal substrate which comprises the steps of (a) forming an amorphous nickel layer on the surface of a metal substrate to thereby form an amorphous nickel plated metal substrate and (b) heating said amorphous nickel plated metal substrate at a temperature of 500° C. to 680° C. in an atmosphere comprising a hydrocarbon having a partial pressure of 5 to 50 Torr., thereby coating said amorphous nickel plated metal substrate with carbon.

2. A method according to claim 1, wherein said amorphous nickel layer has a thickness of about 2 μ.

3. A method according to claim 1, wherein said amorphous nickel layer is electrolytically formed.

4. A method according to claim 1, wherein said amorphous nickel layer is nonelectrolytically formed.

5. A method according to claim 1, wherein said hydrocarbon is at least one member selected from the group consisting of acetylene, ethylene and ethane.

6. A method according to claim 1, wherein said atmosphere comprising hydrocarbon comprises at least one member selected from the group consisting of acetylene, ethylene, ethane and propane having a partial pressure of 5 to 50 Torr. and a carrier gas selected from the group consisting of an inert gas and hydrogen.

7. A carbon coated metal article, which comprises a metal substrate, an amorphous nickel plated layer on said substrate and a carbon coating on said amorphous nickel plated layer said carbon coating being formed by heating said amorphous nickel plated metal substrate in an atmosphere containing a hydrocarbon at a partial pressure of 5 to 50 Torr. at a temperature of from 500° C. to 680° C.

8. A metal coated article according to claim 7, wherein the substrate of said metal article is a member

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selected from the group consisting of mild steel, nickel, copper, molybdenum and stainless steel.

9. A shadow mask for color television which comprises a metal substrate, an amorphous nickel plating layer thereon, and a carbon coating on said amorphous nickel plating layer, said carbon coating being coated on said amorphous nickel plating layer by heating a metal substrate having an amorphous nickel plating layer in an atmosphere comprising a hydrocarbon having a partial pressure of 5 to 50 Torr. at 500°-680° C.

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10. An electric discharge tube plate material which comprises a metal substrate, an amorphous nickel plating layer thereon, and a carbon coating on said amorphous nickel plating layer, said carbon coating being coated on said amorphous nickel plating layer by heating a metal substrate having an amorphous nickel plating layer in an atmosphere comprising a hydrocarbon having a partial pressure of 5 to 50 Torr. at 500°-680° C.

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