

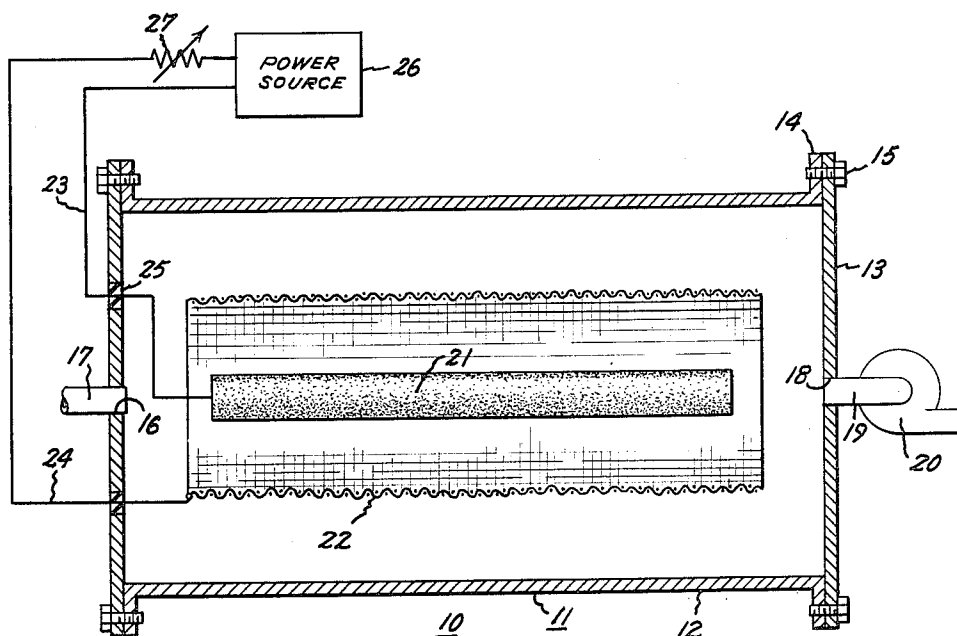
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METHOD OF FORMING CARBON COATING

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METHOD OF FORMING CARBON COATING

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This invention relates to composite articles and to methods of forming composite articles and more particularly to composite articles and methods of forming composite articles having a member with a low density, non-porous carbonaceous coating thereon.

Carbonaceous coatings are desirable to provide wear and abrasion resistant surfaces for members. For example, such coatings would be advantageous for covering bearing members. These coatings would also have application to zirconium process tubes which are employed in the atomic energy industry. Such coated tubes would prevent hydrogen pickup by the zirconium since gas transfer would not be possible through the non-porous coating.

Carbonaceous gases have been thermally decomposed and deposited on a surface to produce pyrolytic graphite. As a result of the decomposition, carbon is removed from the gas and deposits on the surface so that planar graphite crystallites are aligned into a layer structure. It would be desirable to provide composite articles having a member with a smooth, adherent, carbonaceous coating which has a low density, is non-porous, and is continuous. Furthermore, it would be advantageous to provide deposition methods of forming such composite articles.

It is an object of my invention to provide a deposition method of forming adherent, smooth, continuous carbonaceous coatings on members.

It is another object of my invention to provide a deposition method of forming such carbonaceous coatings with a low density.

It is a further object of my invention to provide a deposition method of forming such carbonaceous coatings which are non-porous.

It is a still further object of my invention to provide a composite article having a member with an adherent, smooth, non-porous, continuous carbonaceous coating thereon.

In carrying out my invention in one form, a method of depositing an adherent carbonaceous coating on a member comprises providing a chamber, positioning an electrically conductive member within the chamber, the member having a similar coefficient of expansion to said coating, positioning an anode within the chamber surrounding and spaced from the member, evacuating the chamber, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen, argon and hydrogen, and helium and hydrogen to the chamber, and applying a discharge within the chamber whereby a carbonaceous coating is deposited on the member, the discharge having a current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

The single figure is a sectional view of a deposition apparatus for forming carbonaceous coatings in accordance with my invention.

In the single figure of the drawing, a deposition apparatus is shown generally at 10 which comprises a metallic chamber 11 including a cylindrical body portion 12 and end closure plates 13. A flange 14 is located at each end of body portion 12 to which an associated plate 13 is fastened by means of bolts 15 extending through aper-

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tures in both the flange and plate. In one end plate 13, an aperture 16 is located in which an inlet tube 17 is positioned and extended to gas sources (not shown). Suitable gas sources, inlet lines and valves (not shown) are provided for supplying, regulating and mixing the gases. In the other end plate 13, an aperture 18 is located in which a tube 19 is positioned and extended to pump 20 for evacuating chamber 11. An electrically conductive member 21 having a similar coefficient of expansion to the layer to be deposited is positioned within the chamber as a cathode and supported therein by any suitable means (not shown). I have found that molybdenum, zirconium, graphite and tungsten are suitable materials for member 21 which can be of various configurations such as sheet, rod, tube, or wire. An anode 22, for example of copper, nickel or molybdenum, is shown in the form of a wire mesh screen surrounding member 21 within chamber 11. Other metallic anodes can be employed providing that the material does not contaminate the apparatus or melt at operating temperatures. An electrical lead 23 is secured to member 21 while an electrical lead 24 is secured to anode 22 through insulating washers 25 positioned in one of the end closure plates 13. Leads 23 and 24 are connected to a suitable direct current power source 26. A resistance 27 is provided between power source 25 and lead 24 to regulate the current flow.

I discovered unexpectedly that adherent, smooth, continuous carbonaceous coatings with low density and non-porous are produced on a member to form a composite article by positioning an electrically conductive member, such as a molybdenum, zirconium, graphite, or tungsten member within a chamber, the member having a similar coefficient of expansion to the coating to be deposited, positioning an anode within the chamber surrounding and spaced from the member, evacuating the chamber, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen, argon and hydrogen, and helium and hydrogen to the chamber, and applying a discharge within the chamber, the discharge having a current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter.

I found further that it was preferable to clean the member initially by supplying a gas selected from the group consisting of argon and hydrogen, helium and hydrogen, and hydrogen to the evacuated chamber while supplying voltage in the range of 200 to 300 volts to produce a current density of 30-100 milliamperes per square centimeter. During subsequent actual deposition, 200 to 750 volts provides the required current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter. The current supplied by the power source heats the member to a temperature in the range of 600° C. to 1200° C. with a preferred temperature of 600° C. to 800° C. during deposition. At temperatures below 600° C. the rate of deposition drops off drastically while at temperatures above 1200° C. the coating changes to a more crystalline structure.

I found also that the chamber should be evacuated to a pressure of about 2 millimeters of mercury to 50 centimeters of mercury. The hydrocarbon gas is decomposed to carbon and hydrogen. The carbon atoms are positively charged by the discharge to carbon ions which are attracted to member 21, the cathode. The carbon is deposited on member 21 as an adherent, smooth and continuous coating. The argon or helium stabilizes the discharge and prevents arcing whereby higher current densities can be employed. The hydrogen prevents too rapid decomposition of the hydrocarbon gas which would result in sooting.

In the operation of the disposition apparatus in the

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single figure of the drawing, chamber 11 is evacuated to a pressure of 2 millimeters of mercury to 50 centimeters of mercury. A gas selected from the group consisting of argon and hydrogen, helium and hydrogen, and hydrogen is supplied through inlet line 17 to chamber 11 to remove impurities from member 21. Power is supplied to leads 23 and 24 from power source 26 to provide a voltage in the range of 200 volts to 300 volts which produces a current density of 30 milliamperes per square centimeter to 100 milliamperes per square centimeter. A hydrocarbon gas, such as methane or acetylene, is mixed with a gas selected from the group consisting of argon, helium, argon and hydrogen, and helium and hydrogen and supplied through inlet tube 17 to chamber 11. Power is supplied to leads 23 and 24 from power source 26 to provide a voltage in the range of 200 volts to 750 volts which produces a current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter. The current supplied by the power source heats member 21 to a temperature in the range of 600° C. to 1200° C. with a preferred range of 600° C. to 800° C. during deposition. The carbon atoms which are decomposed from the hydrocarbon gas are positively charged by the discharge and attracted to member 21 to deposit a carbonaceous layer thereon. The layer is adherent, smooth and continuous. It has a low density of about 1.3 gm./cm.³ and is non-porous. Pump 20 maintains the desired low pressure in chamber 11 while it removes the products of the reaction therefrom and an adherent, smooth, non-porous, continuous carbonaceous coating is formed on the member.

Several examples of carbonaceous coatings which were made in accordance with the methods of the present invention are as follows:

Example I

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A molybdenum sheet having a length of 3 inches, a width of 1 inch and a thickness of about 20 mils was suspended within the chamber of as the cathode. A molybdenum mesh screen surrounded and was spaced uniformly from the sheet to provide an anode. A mixture of argon and hydrogen was supplied to the chamber which was evacuated to a pressure of about 15 millimeters of mercury. The power source supplied current through the leads to provide a current density of 45 milliamperes per square centimeter. This cleaning of the cathode was continued for 5 minutes to remove impurities from the molybdenum sheet. Acetylene gas was then supplied to the chamber and the gases adjusted to provide a mixture of 1 part of acetylene, 1 part of argon and 4 parts of hydrogen. The deposition was continued for about 40 minutes at a pressure of about 15 millimeters of mercury and a current density of 15 milliamperes per square centimeter. The molybdenum sheet was heated to 700° C. The sheet had an adherent, smooth, non-porous, continuous carbonaceous coating of 5 mils thickness. The coating had a density of about 1.3 grams per cubic centimeter.

Example II

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A graphite rod having a length of 3 inches and a diameter of 1/4 inch was suspended within the chamber as the cathode. A molybdenum mesh screen surrounded and was spaced uniformly from the sheet to provide an anode. A mixture of argon and hydrogen was supplied to the chamber which was evacuated to a pressure of about 15 millimeters of mercury. The power source supplied current through the leads to provide a current density of 45 milliamperes per square centimeter. This cleaning of the cathode was continued for 5 minutes to remove impurities from the graphite rod. Acetylene gas was then supplied to the chamber and the gases adjusted to provide a mixture of 1

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part of acetylene, 1 part of argon and 4 parts of hydrogen. The deposition was continued for about 40 minutes at a pressure of about 15 millimeters of mercury and a density of 15 milliamperes per square centimeter. The graphite rod was heated to 700° C. The rod had an adherent, smooth, non-porous, continuous carbonaceous coating of 5 mils thickness. The coating had a density of about 1.3 grams per cubic centimeter.

Example III

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A zirconium sheet having a length of 3 inches, a width of 1 inch and a thickness of about 40 mils was suspended within the chamber as the cathode. A molybdenum mesh screen surrounded and was spaced uniformly from the sheet to provide an anode. A mixture of argon and hydrogen was supplied to the chamber which was evacuated to a pressure of about 15 millimeters of mercury. The power source supplied current through the leads to provide a current density of 45 milliamperes per square centimeter. This cleaning of the cathode was continued for 5 minutes to remove impurities from the zirconium sheet. Acetylene gas was then supplied to the chamber and the gases adjusted to provide a mixture of 1 part of acetylene, 1 part of argon and 4 parts of hydrogen. The deposition was continued for about 40 minutes at a pressure of about 15 millimeters of mercury and a current density of 15 milliamperes per square centimeter. The zirconium sheet was heated to 700° C. The sheet had an adherent, smooth, non-porous, continuous carbonaceous coating of 5 mils thickness. The coating had a density of about 1.3 grams per cubic centimeter.

Example IV

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A rolled-up tube of tungsten having a length of 2 inches, and a thickness of 5 mils was suspended within the chamber as the cathode. A molybdenum mesh screen surrounded and was spaced uniformly from the sheet to provide an anode. A mixture of argon and hydrogen was supplied to the chamber which was evacuated to a pressure of about 15 millimeters of mercury. The power source supplied current through the leads to provide a current density of 45 milliamperes per square centimeter. This cleaning of the cathode was continued for 5 minutes to remove impurities from the tungsten tube. Acetylene gas was then supplied to the chamber and the gases adjusted to provide a mixture of 1 part of acetylene, 1 part of argon and 4 parts of hydrogen. The deposition was continued for about 40 minutes at a pressure of about 15 millimeters of mercury and a current density of 15 milliamperes per square centimeter. The tungsten tube was heated to 700° C. The sheet had an adherent, smooth, non-porous, continuous carbonaceous coating of 5 mils thickness. The coating had a density of about 1.3 grams per cubic centimeter.

Example V

A deposition apparatus was set up generally in accordance with the single figure of the drawing. A tungsten wire having a length of 3 inches, and a diameter of 10 mils was suspended within the chamber as the cathode. A molybdenum mesh screen surrounded and was spaced uniformly from the sheet to provide an anode. Hydrogen was supplied to the chamber which was evacuated to a pressure of about 15 millimeters of mercury. The power source supplied current through the leads to provide a current density of 45 milliamperes per square centimeter. This cleaning of the cathode was continued for 3 minutes to remove impurities from the tungsten wire. Acetylene gas was then supplied to the chamber and the gases adjusted to provide a mixture of 1 part of methane and 5 parts of hydrogen. The deposition was continued for 5 minutes at a pressure of about 130 millimeters of mercury

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and a current density of 250 milliamperes per square centimeter. The tungsten wire was heated to 1100° C. The sheet had an adherent, smooth, non-porous, continuous carbonaceous coating of 3 mils thickness.

While other modifications of this invention and variation in the method which may be employed within the scope of the invention have not been described, the invention is intended to include such that may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of depositing an adherent carbonaceous coating on a member which comprises providing a chamber, positioning an electrically conductive member within said chamber, said member having a similar coefficient of expansion to said coating, positioning an anode within said chamber surrounding and spaced from said member, evacuating said chamber, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen, argon and hydrogen, and helium and hydrogen to said chamber, and applying a discharge within said chamber whereby a carbonaceous coating is deposited on said member, said discharge having a current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter.

2. The invention as claimed in claim 1 wherein said electrically conductive member is molybdenum.

3. The invention as claimed in claim 1 wherein said electrically conductive member is graphite.

4. The invention as claimed in claim 1 wherein said electrically conductive member is zirconium.

5. The invention as claimed in claim 1 wherein said electrically conductive member is tungsten.

6. A method of depositing an adherent carbonaceous coating on a member which comprises providing a chamber, positioning an electrically conductive member within said chamber, said member having a similar coefficient of expansion to said coating, positioning an anode within said chamber surrounding and spaced from said member, evacuating said chamber, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen argon and hydrogen, and helium and hydrogen to said chamber, and applying a direct current potential between said anode and said member to heat said member to a temperature in the range of 600° C. to 1200° C. whereby a carbonaceous coating is deposited on said member.

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7. A method of depositing an adherent carbonaceous coating on a member which comprises providing a chamber, positioning an electrically conductive member within said chamber, said member having a similar coefficient of expansion to said coating, positioning an anode within said chamber surrounding and spaced from said member, evacuating said chamber, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen, argon and hydrogen, and helium and hydrogen to said chamber, and applying a direct current potential between said anode and said member to heat said member to a temperature in the range of 600° C. to 800° C. whereby a carbonaceous coating is deposited on said member.

8. A method of depositing an adherent carbonaceous coating on a member which comprises providing a chamber, positioning an electrically conductive member within said chamber, said member having a similar coefficient of expansion to said coating, positioning an anode within said chamber surrounding and spaced from said member, evacuating said chamber, supplying a gas selected from the group consisting of argon and hydrogen, helium and hydrogen, and hydrogen to said chamber, applying a discharge having a current density of 30 milliamperes per square centimeter to 100 milliamperes per square centimeter within chamber to remove impurities from said member, supplying a mixture of hydrocarbon gas and a gas selected from the group consisting of argon, helium, hydrogen, argon and hydrogen, and helium and hydrogen to said chamber, and applying a discharge within said chamber whereby a carbonaceous coating is deposited on said member, said discharge having a current density of 15 milliamperes per square centimeter to 500 milliamperes per square centimeter.

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