

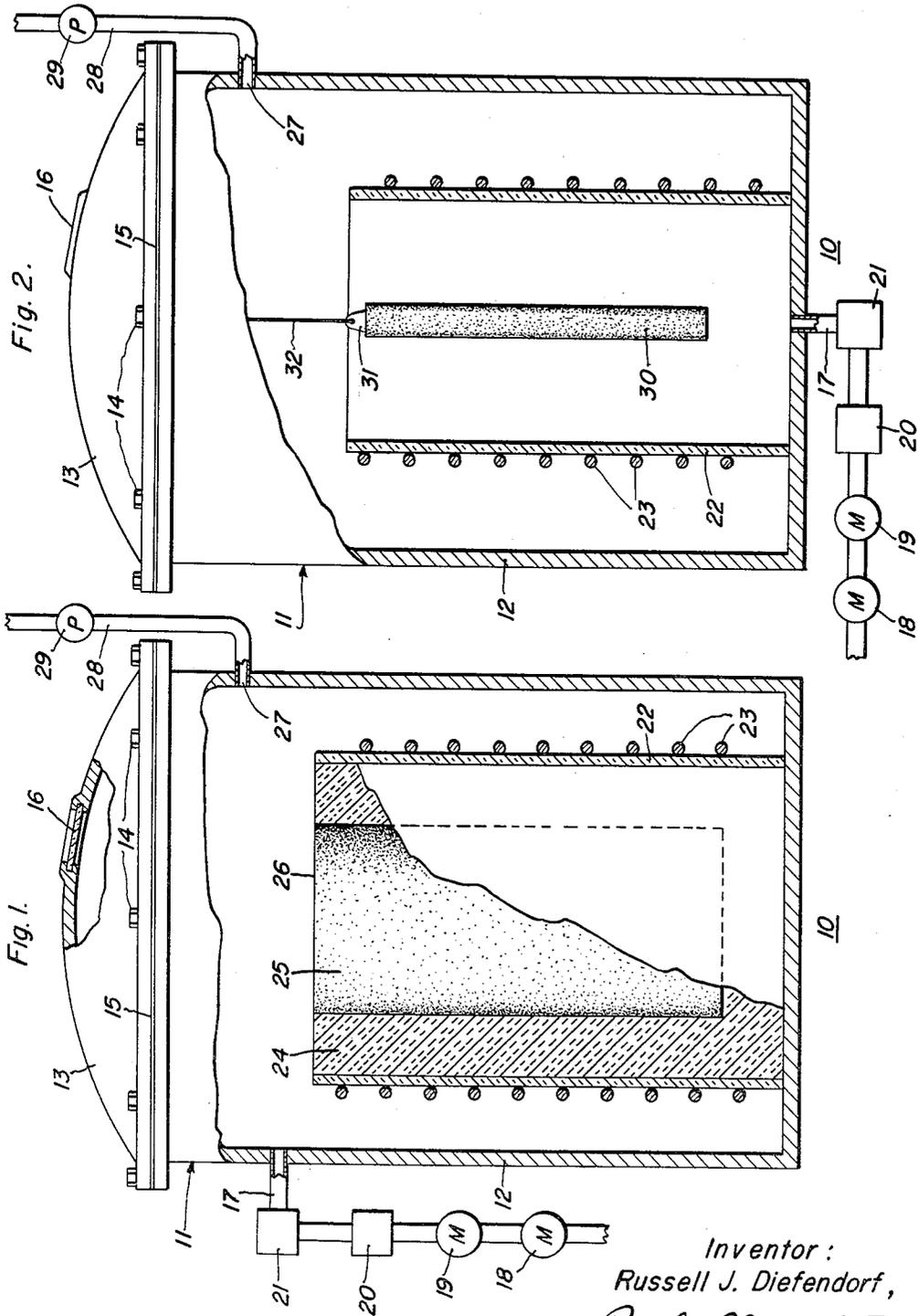
March 9, 1965

R. J. DIEFENDORF

3,172,774

METHOD OF FORMING COMPOSITE GRAPHITE COATED ARTICLE

Filed Feb. 28, 1961



Inventor:
Russell J. Diefendorf,
by Paul R. Webb, II
His Attorney.

1

3,172,774

METHOD OF FORMING COMPOSITE GRAPHITE COATED ARTICLE

Russell J. Diefendorf, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York
Filed Feb. 28, 1961, Ser. No. 92,417
7 Claims. (Cl. 117-46)

This invention relates to methods of forming composite articles and more particularly to methods of forming composite articles having a member and a pyrolytic graphite coating.

This application is a continuation-in-part of my co-pending application filed January 3, 1961, as Serial No. 80,080, now abandoned.

Pyrolytic graphite is defined as a polycrystalline material made from carbonaceous gases by thermal decomposition or from a carbonaceous material by evaporation and deposition on a surface in which the planar graphite crystallites are aligned into a layer structure. It is useful as a high temperature material for lamp filaments, furnace linings and neutron reactor moderators. Development of missile and space propulsion systems has created an additional requirement for composite pyrolytic graphite components in these systems.

The thermal expansion coefficients of a piece of pyrolytic graphite are measured along the "C" direction and the "A" direction, a direction generally perpendicular to the "C" direction. The "C" direction is defined as the component of the maximum measured number of crystallites in the "C" direction or orientation. The "A" direction is defined as the component of the maximum measured number of crystallites in directions perpendicular to the "C" direction. The expansion coefficient of a pyrolytic graphite coating measured along its "C" direction is in the range of about 10.0×10^{-6} to 28.5×10^{-6} per centigrade degree. The average expansion coefficient along its "A" direction, an axis generally perpendicular to its "C" direction, is in the range of about 0.8×10^{-6} to 3.0×10^{-6} per centigrade degree from room temperature to 1000°C .

Carbonaceous gases have been thermally decomposed and deposited on surfaces 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 is desirable to provide composite pyrolytic graphite articles at high deposition rates in which each article includes a pyrolytic graphite coating bonded tightly to a member. Furthermore, it is advantageous to have a coating which has a similar coefficient of expansion to its member at room temperature. It would appear that only the temperature need be increased in the deposition chamber to produce a corresponding increase in deposition rate. However, in a deposition at a temperature above 1000°C ., the pyrolytic graphite coating is applied rapidly but the expansion coefficient of the coating in the plane of deposition or "A" direction is substantially less than the expansion coefficient of the member in the same direction with resulting peeling or popping off of the coating upon cooling the article to room temperature. Thus, a temperature increase does not solve the deposition problem but provides a non-adhering layer which does not produce a composite article. Therefore, it would be desirable to provide methods of forming composite pyrolytic graphite articles at high deposition rates.

2

It is an object of my invention to provide a deposition method of forming composite pyrolytic graphite articles.

It is another object of my invention to provide a deposition method of forming composite pyrolytic graphite articles in which the coating has soot particles deposited uniformly therein.

It is a further object of my invention to provide a deposition method of forming pyrolytic graphite articles of uniform thickness at high rates of deposition.

In carrying out my invention in one form, a member is positioned within a chamber, a carbon vapor is flowed at a temperature in the range of 1450°C . to 2000°C . through the chamber, and the pressure is maintained within the chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury to form a composite article.

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:

FIGURE 1 is a sectional view of a deposition apparatus for forming composite articles in accordance with my invention; and

FIGURE 2 is a sectional view of a modified deposition apparatus.

In FIGURE 1, a deposition apparatus is shown generally at 10 which comprises a chamber 11 having a lower body portion 12 and a cover 13 which is hinged to the lower body portion by means of bolts 14 and employs an O-ring 15 therebetween. Viewing window 16 is provided in cover 13 to view the operation and to read an optical pyrometer (not shown). A feed line 17 extends through the side wall of chamber 11 and is connected to a carbonaceous material source (not shown). For example, a carbonaceous gas is fed from the source through a meter 18 showing the total consumption of gas, a gas rate meter 19, an acetone and Dry Ice trap indicated at 20, a preheater 21, and line 17 to chamber 11. While a pure carbonaceous gas, such as methane, ethane, propane, acetylene, benzene, carbon tetrachloride, or cyanogen, is employed, the carbonaceous material can also be in liquid or solid form which is fed from the source to preheater 21. It is desirable to heat the carbonaceous material in preheater 21 to a temperature in the range of room temperature to 2000°C . to convert the material to its gaseous state or to decompose the material to a carbon vapor.

An insulated cylinder 22 of quartz or alumina is surrounded by conventional heating coils 23. Suitable insulation in the form of carbon black 24 surrounds a member 25 of graphite or other high temperature material with an exposed surface 26. Coils 23 provide heat for member 25 and chamber 11 during the deposition process. Chamber 11 is also provided with an outlet 27 to which is connected a line 28 associated with a vacuum pump 29 to maintain a low pressure in the chamber.

In FIGURE 2 of the drawing, a chamber 11 is shown which has a lower body portion 12 and a cover 13 hinged to portion 12 by means of bolts 14. An O-ring 15 is employed between portion 12 and cover 13. Viewing window 16 is provided in cover 13 to view the operation and to record the temperature by means of an optical pyrometer (not shown). A feed line 17 extends through the bottom wall of chamber 11 and is connected to a carbonaceous material source (not shown). For example, a carbonaceous gas is fed from the source through

total consumption meter 18, gas rate meter 19, acetone and Dry Ice trap 20, preheater 21, and line 17 to chamber 12. An insulated cylinder 22 of quartz or alumina is surrounded by heating coils 23. For example, a member 30 in the form of a sheet of graphite is suspended by any suitable means, such as a hook 31 and rod 32 within cylinder 22 of chamber 11. If it is desired, cylinder 22 and heating coils 23 can be removed and heat provided only in preheater 21 to produce the carbon vapor for deposition.

I discovered unexpectedly that composite pyrolytic graphite articles were formed with uniform soot deposits in the coatings providing adherence to the member by positioning a member within a chamber, flowing a carbon vapor at a temperature in the range of 1450° C. to 2000° C. through the chamber, and maintaining within the chamber a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury. I found further that the coatings of these composite articles were hard and more isotropic whereby the coating adhered tightly to the member. Additionally, the coefficients of expansion of both the coating and member were more similar at room temperature.

It appears that the soot particle is probably formed by the growth of a large carbon molecule which upon reaching a critical size is coated around its periphery with smaller aromatic molecules. These smaller molecules are oriented with their basal planes parallel to the surface of the larger molecule. If a large diameter chamber is employed at low pressure, the large carbon molecule does not have time to diffuse to the chamber wall before it forms soot. An increase in the pressure or temperature increases the soot formation. If a small diameter chamber is used at low pressure, the large carbon molecule does have time to diffuse to the chamber wall without soot formation. However, an increase in pressure or temperature in the small diameter chamber to increase deposition produces alternate layers of soot and pyrolytic graphite rather than a coating with uniform soot deposits.

In the operation of deposition apparatus 10 shown in FIGURE 1, cylinder 22 surrounded by coils 23 is positioned within chamber 11. Carbon black 24 is placed in the bottom of cylinder 22 after which member 25 is positioned thereon. Additional carbon black 24 is placed in the void between the member and cylinder leaving surface 26 of member 25 exposed to the chamber atmosphere. Cover 13 is bolted to lower body portion 12 of chamber 11 and the chamber atmosphere is reduced to a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury. I prefer to operate between 30 and 40 centimeters of mercury pressure. Power is supplied to induction coils 23 which heats the atmosphere of chamber 11 and member 25 to a temperature in the range of 1450° C. to 2000° C. to decompose the carbonaceous material to a carbon vapor or to maintain the temperature of the carbon vapor during deposition in the chamber.

A carbonaceous gas, such as methane, is fed through a total consumption meter 18, a gas rate meter 19, and an acetone and Dry Ice trap 20 prior to entering preheater 21 through gas line 17. The carbonaceous gas is preheated in preheater 21 to a temperature in the range of room temperature to 2000° C. If a liquid or solid carbonaceous material is used, the material is fed to preheater 21 in which it is converted to its gaseous form. Some hydrocarbon gases will liquify in trap 20 which liquids are then converted to gases in preheater 21. The carbonaceous material can also be fed to chamber 11 where heat from coils 23 decomposes the material to a carbon vapor. I have also found that carbonaceous material can be preheated in preheater 21 to a temperature in the range of 1450° C. to 2000° C., to convert the material to its gaseous state and then to decompose the gas to carbon vapor which is flowed into chamber 11. It is also desirable to heat the chamber in a temperature range

of 1450° C. to 2000° C. to maintain the temperature of the vapor during deposition in the chamber.

Although some of the carbon vapor will deposit on the walls of the preheater and the chamber, most of the vapor will be deposited on exposed surface 26 of member 25. Line 28 and pump 29 remove gases and maintain the desired pressure within chamber 11. While the above process with a carbonaceous gas can be carried out over a range of .2 centimeter of mercury to 70 centimeters of mercury, at various gas flow rates, I prefer to reduce the atmosphere to a pressure of 30 to 40 centimeters of mercury and operate generally at 35 centimeters of mercury for best results.

After the desired thickness of pyrolytic graphite coating on the substrate is attained, the gas flow is stopped, the pressure is decreased further, and the composite article within chamber 11 is allowed to cool to room temperature. The pressure is increased subsequently to atmospheric pressure, and cover 13 is removed to provide access to coated member 25 which is removed from chamber 11. During the operation of forming such composite articles, the temperature is recorded by an optical pyrometer (not shown) which is viewed through window 16 in cover 13.

In FIGURE 2 of the drawing, there is shown a modified deposition apparatus wherein cylinder 22 surrounded by coils 23 is positioned within chamber 11. For example, a member 30 in the form of a sheet of graphite is suspended by a hook and rod 32 within cylinder 22. Cover 13 is bolted to lower body portion 12 of chamber 11 and the chamber atmosphere is reduced to a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury. Power is supplied to induction coils 23 which heats the atmosphere of chamber 11 and member 25 to a temperature in the range of 1450° C. to 2000° C. A carbonaceous gas, such as methane, is fed through a total consumption meter 18, a gas rate meter 19, and an acetone and Dry Ice trap 20 prior to entering preheater 21 through gas line 17. The carbonaceous gas is preheated in preheater 21 to a temperature in the range of room temperature to 2000° C. If a liquid or solid carbonaceous material is used, the material is fed to preheater 21 in which it is converted to its gaseous form.

The carbonaceous material can also be fed to chamber 11 where heat from coils 23 decomposes the material to a carbon vapor. I have also found that carbonaceous material can be preheated in preheater 21 to a temperature in the range of 1450° C. to 2000° C., to convert the material to its gaseous state and then to decompose the gas to carbon vapor which is flowed into chamber 11. It is also desirable to heat the chamber in a temperature range of 1450° C. to 2000° C. to maintain the temperature of the vapor during deposition in the chamber. Although some of the carbon vapor will deposit on the walls of the preheater and the chamber, most of the vapor will be deposited on member 30. Line 28 and pump 29 remove gases and maintain the desired pressure within chamber 11. The above process can be carried out over a range of .2 centimeter of mercury to 70 centimeters of mercury, at various gas flow rates.

After the desired thickness of pyrolytic graphite coating on the member is attained, the gas flow is stopped, the pressure is decreased further, and the composite article within chamber 11 is allowed to cool to room temperature. The pressure is increased subsequently to atmospheric pressure, and cover 13 is removed to provide access to coated member 30 which is removed from chamber 11. During the operation of forming such composite articles, the temperature is recorded by an optical pyrometer (not shown) which is viewed through window 16 in cover 13. If desired, a plurality of substrates can be coated simultaneously within chamber 11.

Several examples of methods of forming composite pyrolytic graphite articles in accordance with the present invention are as follows:

Example I

A deposition apparatus was set up generally in accordance with FIGURE 1 of the drawing wherein the member was composed of commercial graphite. After the cover was bolted to the lower body portion, the chamber atmosphere was reduced to a pressure of .0001 centimeter of mercury by the pump. Power was supplied to the induction coil to heat the chamber, and member to an uncorrected optical pyrometer temperature reading of about 1650° C. A carbonaceous gas in the form of methane was supplied to the chamber at an ultimate rate of 20 cubic feet per hour at an ultimate pressure of 350 mm. of mercury subsequent to flowing through metering devices, and an acetone and Dry Ice bath. The pressure of the gas was increased slowly so that large quantities of soot were not visible during the pressure buildup. The carbon vapor which was formed was deposited on the member as it flowed through the chamber. After six hours, the power and gas flow were discontinued and the chamber was restored to atmospheric pressure. After cooling to room temperature, the composite pyrolytic graphite article was removed from the chamber. The coating on the article had a thickness of 30 mils.

Example II

A deposition apparatus was set up generally in accordance with FIGURE 2 of the drawing wherein the member was composed of commercial graphite. After the cover was bolted to the lower body portion the chamber atmosphere was reduced to a pressure of .0001 centimeter of mercury. Power was supplied to the induction coil to heat the chamber, and member to an uncorrected optical pyrometer temperature reading of about 1350° C. A carbonaceous gas in the form of methane was supplied to the chamber at an ultimate rate of eight cubic feet per hour and was bubbled through a container filled with dicyclopentadiene at an ultimate pressure of 20 mm. of mercury subsequent to flowing through metering devices, and an acetone and Dry Ice bath. The pressure of the gas was increased slowly so that large quantities of soot were not visible during the pressure buildup. The carbon vapor which was formed was deposited on the member as it flowed through the chamber. After two hours, the power and gas flow were discontinued and the chamber was restored to atmospheric pressure. After cooling to room temperature, the composite pyrolytic graphite article was removed from the chamber. The coating on the article had a thickness of approximately 10 mils.

Example III

A deposition apparatus was set up generally in accordance with FIGURE 2 of the drawing wherein the member was composed of commercial graphite. After the cover was bolted to the lower body portion, the chamber atmosphere was reduced to a pressure of .0001 mm. of mercury by the pump. Power was supplied to the induction coil to heat the chamber, and chamber to an uncorrected optical pyrometer temperature reading of about 1500° C. A carbonaceous gas in the form of methane was supplied at an ultimate rate of 12 cubic feet per hour at an ultimate pressure of 2.3 mm. of mercury to the preheater subsequent to flowing through metering devices, and an acetone and Dry Ice bath. The pressure of the gas was increased slowly so that large quantities of soot were not visible during the pressure buildup. The gas was heated at a temperature of 1500° C. and formed into a carbon vapor in the preheater which vapor was deposited on the member as it flowed through the chamber. After four hours, the power and gas flow were discontinued and the chamber was restored to atmospheric pressure. After cooling to room temperature, the composite pyrolytic graphite article was

removed from the chamber. The coating of the article has a thickness of 10 mils.

While other modifications of this invention and variations of 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 deposition method which comprises providing a chamber, positioning at least one member within said chamber, flowing a carbon vapor at a temperature in the range of 1450° C. to 2000° C. through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury and depositing a pyrolytic graphite coating with uniform soot deposits on said member to form a composite article.

2. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, flowing a carbon vapor into said chamber, heating said chamber, said member, and said vapor to a temperature in the range of 1450° C. to 2000° C., flowing said carbon vapor through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury, and depositing a pyrolytic graphite coating with uniform soot deposits on said member to form a composite article.

3. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, heating said chamber and said member to a temperature in the range of 1450° C. to 2000° C., flowing a carbon vapor at a temperature in the range of 1450° C. to 2000° C. through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury and depositing a pyrolytic graphite coating with uniform soot deposits on said member to form a composite article.

4. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, feeding a carbonaceous material to said chamber, heating said chamber, said member, and said material to a temperature in the range of 1450° C. to 2000° C. whereby said material decomposes to a carbon vapor, flowing said carbon vapor through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury and depositing a pyrolytic graphite coating with uniform soot deposits on said member to form a composite article.

5. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, feeding a carbonaceous material to said chamber, preheating said material at a temperature in the range of 1450° C. to 2000° C. to decompose said material to a carbon vapor, flowing said carbon vapor at a temperature in the range of 1450° C. to 2000° C. through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury, and depositing a pyrolytic graphite coating with uniform soot deposits on said member to form a composite article.

6. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, heating said chamber and said member to a temperature in the range of 1450° C. to 2000° C., feeding a carbonaceous material to said chamber, preheating said material at a temperature in the range of 1450° C. to 2000° C. to decompose said material to a carbon vapor, flowing said carbon vapor at a temperature in the range of 1450° C. to 2000° C. through said chamber, maintaining the pressure within said chamber at a pressure in the range of .2 centimeter of mercury to 70 centimeters of mercury and depositing a pyrolytic graphite coating

7

with uniform soot deposits on said member to form a composite article.

7. A deposition method which comprises providing a chamber, positioning at least one member within said chamber, flowing a carbon vapor at a temperature in the range of 1650° C. to 1850° C. through said chamber, maintaining the pressure within said chamber at a pressure in the range of 30 centimeters of mercury to 40 centimeters of mercury and depositing a pyrolytic graphite

8

coating with uniform soot deposits on said member to form a composite article.

References Cited by the Examiner

UNITED STATES PATENTS

2,405,449	8/46	Robinson et al. -----	117—226	X
2,487,581	11/49	Palumbo -----	117—226	X
2,789,038	4/57	Bennett et al. -----	23—209.4	X

RICHARD D. NEVIUS, *Primary Examiner.*