

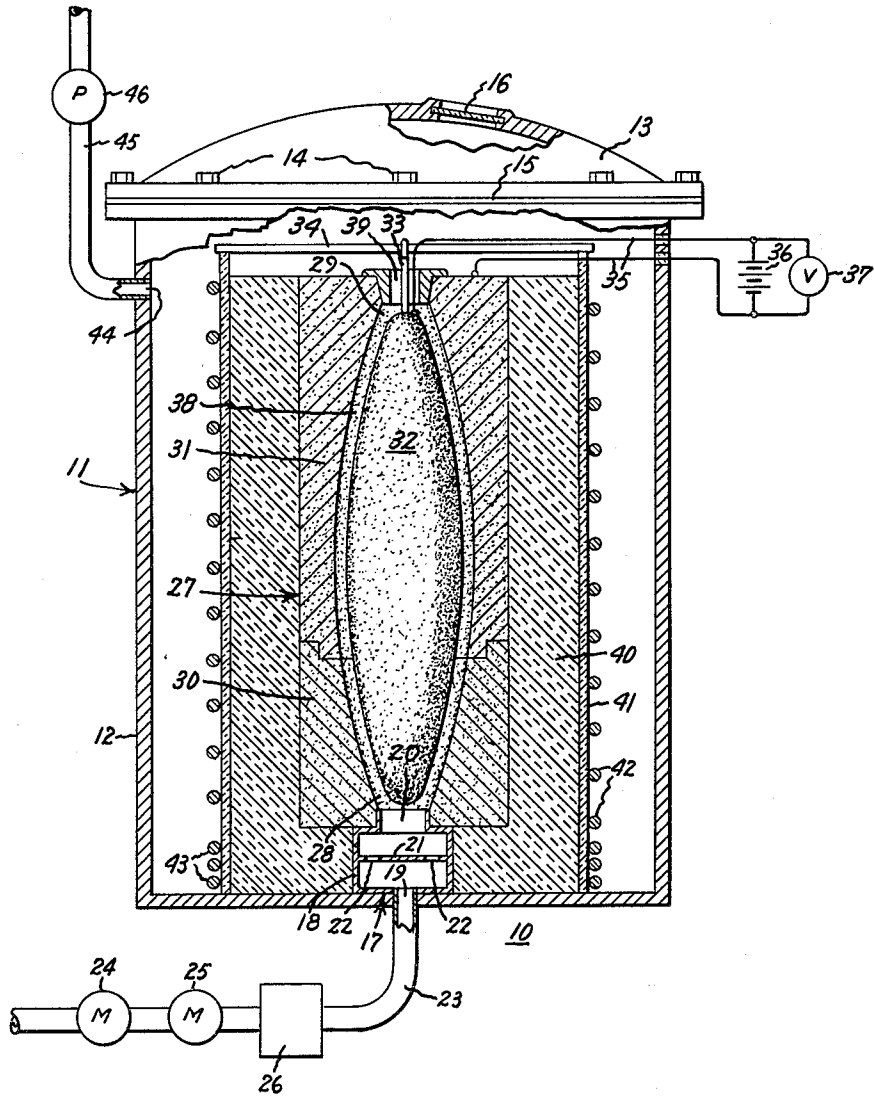
June 23, 1964

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3,138,434

DEPOSITION METHOD OF FORMING A PYROLYTIC GRAPHITE ARTICLE

Filed April 26, 1961



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DEPOSITION METHOD OF FORMING A PYROLYTIC GRAPHITE ARTICLE

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Filed Apr. 26, 1961, Ser. No. 105,791
10 Claims. (Cl. 23-299.1)

This invention relates to methods of forming articles and more particularly to methods of forming pyrolytic graphite articles.

Pyrolytic graphite is defined as a material made from carbonaceous gases by thermal decomposition or from a carbonaceous material by evaporation and deposition on a surface. In pyrolytic graphite material, planar graphite crystallites are arranged so that their layer structures are parallel to the deposition surface. This material 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 pyrolytic graphite components in these systems.

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 is desirable to provide pyrolytic graphite articles at high deposition rates which articles have similar properties. Since high deposition rates are desirable, it would appear that only the gas pressure need be increased in the deposition chamber to produce a corresponding increase in deposition rate. However, a uniform deposition at an increased rate depends upon a number of variable operating conditions, such as chamber diameter, surface distance from gas flow, gas pressure, pressure drop, temperature, geometry of proposed article and carbon content of the gas flow. Thus, a mere increase in pressure does not solve the deposition problem but imposes a subsequent limitation by creating generally soot which produces a material with poorer physical properties. A deposition apparatus and methods of forming pyrolytic graphite without soot particles at an increased rate of deposition are disclosed and claimed in my copending patent application entitled, "Deposition Apparatus and Method," Serial Number 75,244, filed December 12, 1960, now abandoned, and disclosed and claimed in my co-pending continuation-in-part application, Serial Number 119,538, filed June 26, 1961, and assigned to the same assignee as the present application.

One of the most perplexing problems in forming pyrolytic graphite articles is the variation in properties perpendicular to the basal planes through the deposit. While changes in operating conditions during deposition lead to inhomogeneities layer to layer, these conditions can be held constant as disclosed in my above-identified copending patent application. However, variations in deposition occur which are caused by heating and by time difference in deposition of the layers. Improved methods of forming pyrolytic graphite without soot particles which overcome these variations in deposition are disclosed and claimed in the present application.

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

It is another object of my invention to provide a deposition method of forming pyrolytic graphite articles without adverse deposition variations.

It is a further object of my invention to provide a deposition method of forming pyrolytic graphite articles in which an electrical potential is employed.

In carrying out my invention in one form, a deposition

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method comprises providing an enclosure, positioning a member within the enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating the passage, applying a potential between the enclosure and the member to provide a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor at a temperature between 2000° C. and 2500° C. through the passage whereby a pyrolytic graphite article is formed on the member, and removing the article from the member.

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 embodying my invention.

In the single figure, 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 portion 13 to view the operation and to read an optical pyrometer (not shown). A preheater 17 is positioned on the inner surface of the bottom wall of chamber 11 and consists of a container 18 having an inlet 19 and outlet 20. A baffle 21 is positioned within the preheater and is provided with a plurality of openings 22 around the perimeter thereof.

A feed line 23 is connected at the inlet opening 19 of preheater 17 and extends through the bottom wall of chamber 12 to a carbonaceous material source (not shown). A carbonaceous gas is fed from the source through a meter 24 showing the total consumption of gas, a gas rate meter 25, an acetone and dry ice trap indicated at 26, and line 23 to preheater 17. 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 for conversion to a carbon vapor. Such a carbonaceous gas can be mixed with a noncarbonaceous gas which reacts with the carbonaceous gas during its decomposition to carbon. For example, hydrogen, as the reacting gas, can be employed with the alkanes or alkynes while nitrogen, as the reacting gas, can be used with cyanogen.

As enclosure 27 of graphite or other high temperature material having an inlet 28 and an outlet 29 is positioned on preheater 17 by aligning inlet 28 of the enclosure with outlet 20 of preheater 17. Enclosure 27 can be constructed of several pieces, such as a lower portion 30 and an upper portion 31 joined together. In this manner, a member 32 is placed within the enclosure and supported therein in a relatively simple fashion. There is shown a member 32 of graphite or other high temperature material supported concentrically within enclosure 27 by means of a rod 33 attached to a support member 34 resting on cylinder 41. I found also that the use of reentrant angles on the member allows the pyrolytic graphite article formed thereon to be easily separated from the member.

A pair of electrical connections 35 contact enclosure 27 and member 32, respectively. A direct current power source 36, such as a battery, is connected to connections 35. A voltmeter 37 is connected across battery 36 to measure the voltage. Enclosure 27 and member 32 form a narrow passage 38 between the exterior surface of member 32 and the interior surface of enclosure 27. I prefer to employ a uniform diameter passage or a passage narrowing toward its outlet to produce a more uniform deposition. A chimney 39 surrounds outlet 29 of enclosure 27 to provide for removal of fumes which

pass through passage 35 between member 32 and the interior wall of enclosure 27. Suitable insulation in the form of carbon black 40 surrounds enclosure 27 and is held in position by a quartz or asbestos paper cylinder 41. Conventional induction heating coils 42 surround cylinder 44 to provide heat for enclosure 27, member 32, and passage 38 during the deposition process. An induction heating coil 43 surrounds cylinder 41 adjacent preheater 17 to provide heat for the preheater. Chamber 12 is also provided with an outlet 44 to which is connected a line 45 associated with a vacuum pump 46 to reduce the pressure in chamber 12.

While it is disclosed that the enclosure is a two-piece structure, a one-piece structure or a plurality of pieces can be employed. If a plurality of pieces are used, the interior surface of the enclosure can be machined to conform to the exterior contour of the mandrel. Additionally, the chimney can be supported from the interior wall of lower body portion 12 or cover 13. If desired, the member support can be extended through the enclosure inlet.

Variations in deposition are caused by heat supplied to the carbonaceous gas or carbon vapor and by time difference in deposition of the layers. Heat is supplied from heating coils through the enclosure and the deposit forming thereon to the carbonaceous gas or carbon vapor. This heat and heat from the carbon vapor is supplied to the member through its associated deposit forming thereon. This variation in temperature through the deposits leads to a variation in physical properties, since the amount of crystal growth will vary through the deposits. The difference in time that the first layer of pyrolytic graphite is held at temperature by heat from the heating coils versus the last layer produces differences in thermal expansion resulting in subsequent warpage. One approach to eliminate the adverse results of these variations is annealing the article at a high temperature. Unfortunately, the resulting material has less desirable properties for most applications.

I discovered unexpectedly that pyrolytic graphite articles were deposited uniformly at high volume carbonaceous gas flow rates without the above adverse variations in deposition by positioning concentrically a member within an enclosure, spacing the member from the enclosure to provide a narrow passage therebetween, evacuating the passage, applying a potential between the enclosure and the member, and flowing a carbon vapor at a temperature in the range of 2000° C. to 2500° C. through the passage. A fixed diameter passage should have a diameter of at least twice the deposition thickness since both the member and enclosure wall are coated in the process. The passage diameter is also determined by the member diameter and passage length to provide a negligible pressure drop. The concentration gradient of carbon to be deposited should also be small.

I found that a potential from a power source applied between the enclosure and the member produced a constant temperature at the deposition surfaces thereby eliminating the above deposition variations of heat and difference in time. Thus, a large increase in temperature occurs through the deposit because the thermal conductivity perpendicular to the deposit surface is low. I found that a direct current potential from a power supply in the range of 50 volts to 100 volts in a range of 100 amperes to 500 amperes produced an economical method of heating. It is desirable to heat the member and enclosure initially about 2000° C. since the thermionic emission of carbon is high in this temperature range. The heating is accomplished by induction, by heating the carbonaceous material and decomposing it to carbon vapor prior to feeding it to the enclosure, or by a combination of both steps. Although electrons carry most of the current, the current carried by ions at high current densities increases the deposition rate. The pyrolytic graphite deposited in the present methods is of higher quality and

is produced at high rates by applying a potential between the enclosure and the member.

In the operation of deposition apparatus 10 shown in the single figure, a member 32 is positioned concentrically within upper body portion 31 by means of rod 33 and support member 34. Portion 31 is affixed to lower body portion 30 to form enclosure 27. Member 32 and enclosure 27 are spaced apart to provide a narrow, substantially uniform diameter passage therebetween. Since the narrow passage diameter will be fixed, it is determined by the member diameter and passage length to provide a negligible pressure drop and by a requirement for a diameter at least twice the thickness of the proposed member deposition. Enclosure 27 is then positioned on preheater 17 with outlet 20 of preheater 17 and inlet 28 of enclosure 27 in alignment. A pair of electrical connections 35 contact enclosure 27 and member 32, respectively and are connected to a direct current power source 36. A voltmeter 37 is connected across power source 36. Chimney 39 is placed over outlet 29 of enclosure 27. Cylinder 41 surrounds enclosure 27 and provides a space which is filled with carbon black insulation 40. An induction coil 42 surrounds cylinder 41 for heating enclosure 27, member 32, and passage 38 while an induction coil 43 provides heat for preheater 17. Cover 13 is bolted to lower body portion 12 of chamber 11.

The chamber atmosphere is evacuated preferably to the lowest obtainable vacuum. Power can be supplied to induction coils 42 and 43 which heats enclosure 27, member 32, and preheater 17 and passage 38 to a temperature of at least 2350° C. to remove impurities from member 32 and the interior wall of enclosure 27. This heating step removes iron and other impurities, which boil to the surfaces of the member and enclosure, and adsorbed gases which are present. I have found that the employment of this heating step provides member 32 with a surface on which fine-grained pyrolytic graphite is formed. The power is then shut off and the assembly within chamber 11 is allowed to cool. While it is not necessary, I generally prefer to bring the chamber to atmospheric pressure and open the chamber to inspect the member and enclosure prior to forming pyrolytic graphite articles. Any carbon black present on the surfaces is removed manually. After such an inspection, cover 13 is bolted again to lower body portion 12, and chamber 11 atmosphere is reduced below atmospheric pressure of 2 to 6 mm. of mercury.

A carbonaceous gas, such as methane, is fed through a total consumption meter 24, a gas rate meter 25, and an acetone and Dry Ice trap 26 prior to entering preheater 17 through gas line 23. Power is supplied to induction coils 42 and 43 to bring the temperature of enclosure 27, member 32, passage 38 and preheater 17 up to a temperature of at least 2000° C. and preferably in the range of 2300° C. to 2500° C. I have found that this temperature range is desirable to produce uniform pyrolytic graphite articles which can be removed readily from the member. For example, carbonaceous gas is preheated in preheater 17 at a temperature in the above temperature range whereby a carbon vapor is formed. If a liquid or solid carbonaceous material is used, the material is fed to preheater 17 in which it is converted to its gaseous form and then to a carbon vapor. Additionally, the carbonaceous gas can be fed to passage 38 where heat is supplied to enclosure 27, member 32, and passage 38 by coils 42 to decompose the gas to a carbon vapor.

However, I prefer to preheat the material or gas in preheater 17 and feed the carbon vapor through passage 38 while enclosure 27, mandrel 32, and passage 38 are heated to maintain the temperature of the vapor in the passage. A potential is applied between enclosure 27, as anode, and member 32, as cathode, to maintain a constant temperature at the deposition surfaces. This potential causes the pyrolytic graphite to form at an increased rate. Although some of the carbon vapor deposits on the walls of

the preheater, most of the vapor is deposited on the member and on the enclosure. I have found also that the most beneficial results are secured from employing additionally a narrow, uniform diameter passage or a passage narrowing toward its outlet. The preheating step and uniform or tapering passage tend to maintain a uniform coating thickness.

The above process with a carbonaceous gas can be carried out over a wide range of conditions such as 0.5 mm. to 760 mm. of mercury, at various gas flow rates, such as 20 to 150 cubic feet per hour which is similar to molecular flow. The addition of a reacting gas, such as hydrogen, with the carbonaceous gas creates a flow condition which is also similar to molecular flow in that the reacting gas slows down growth of the carbon particles to provide more time for diffusion to the wall prior to attaining critical size for soot formation. Generally, a ratio of at least one to one of reacting gas to carbonaceous gas is employed.

In the course of my research on uniform deposition at an increased rate which disclosed that such deposition depends upon a number of variables which were mentioned above, I have found, also unexpectedly, that the highest rate of deposition occurs immediately prior to a sooting environment. Accordingly, the carbon vapor flow rate is increased to produce a sooting environment which is observed through window 16 in cover 13 of the apparatus. Thereafter, the vapor flow is reduced below sooting environment and the flow is continued to form pyrolytic graphite on the member and enclosure. After the desired thickness of the pyrolytic graphite article is attained, the gas flow is stopped and the assembly 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 enclosure 27.

Portion 31 is detached from portion 30, and member 32 removed from portion 31. With the particular type of member 32 employed in the single figure, the coated member is cut in two or the article is cut at approximately its midpoint to remove the pyrolytic graphite articles therefrom. Additionally, reentrant angles can be employed to provide for easy separation of the article from member. I found also that the member can be constructed of several pieces and include a partial central bore which causes the member to collapse upon removal of the article. During the operation of forming such articles, the temperature is recorded by an optical pyrometer (not shown) which is viewed through window 16 in cover 13.

If it is desired to provide a thicker deposition on a portion of member 32, the member can be eccentrically positioned within enclosure 27. In this manner, a pyrolytic graphite article can be formed with a wall of varying thickness.

Additionally, pyrolytic graphite sheets are formed in a similar manner by employing members in sheet form. A plurality of these sheets are positioned within an enclosure and spaced apart to provide a passage between adjacent pairs of sheets. A passage can also be provided between the enclosure and the members. Pyrolytic graphite is formed on these sheets in the same manner as described above for forming an article on member 32. The pyrolytic graphite article is subsequently removed from each of the sheet members.

In the following examples of methods of forming pyrolytic graphite articles, Examples I, III and IV are in accordance with the present invention. In Example II, no potential is employed. In Example I, the member is the anode, while in Example III, the member is the cathode.

Example I

A deposition apparatus was set up generally in accordance with the single figure of the drawing wherein both the enclosure and the member were composed of commercial graphite to form a 3/8 inch diameter annular passage. The member had a diameter of two inches, and a length of

four inches. After the cover was bolted to the lower body portion, the chamber atmosphere was reduced to a pressure of 0.001 mm. of mercury by the pump. Power was supplied to the induction coils to heat the member, enclosure, and passage to a temperature of about 2400° C. During heating the pressure rose. After removal of iron, other impurities and adsorbed gases, the pressure fell. A carbonaceous gas in the form of methane was supplied at a rate of 60 cubic feet per hour at a pressure of 1140 mm. of mercury to the preheater subsequent to flowing through metering devices, and an acetone and Dry Ice bath. A direct current potential of about 13 volts was applied between the enclosure, as cathode, and the member, as anode, to provide a current density of 0.05 amps/cm.². The gas formed into a carbon vapor in the preheater which was deposited on both the member and interior enclosure wall as it flowed through the narrow passage at a pressure of approximately 10.0 mm. of mercury. After 15 minutes, the pressure was increased until sooting occurred and maintained under sooting conditions for about 10 seconds to produce an identifying soot layer. The potential was discontinued and the pressure reduced to its value of 10.0 mm. of mercury.

Example II

The apparatus in Example I was continued in operation under the same conditions of temperature, pressure and gas flow. However, no potential was applied. After 15 minutes, the pressure was increased until sooting occurred and maintained under sooting conditions for about 10 seconds to produce an identifying layer. The pressure was reduced to its value of 10.0 mm. of mercury.

Example III

The apparatus in Examples I and II was continued in operation under the same conditions of temperature, pressure and gas flow. A direct current potential of about 10 volts was applied between the enclosure, as anode, and the member, as cathode, to produce a current density of 0.05 amps/cm.². After 15 minutes, the gas flow, heat and potential were discontinued and the chamber was restored to atmospheric pressure. After cooling to room temperature, the member was removed from the enclosure. In Table I, the thickness of pyrolytic graphite is shown for the member and enclosure in Examples I, II and III. The soot layers were employed to identify the individual pyrolytic graphite layers.

Example	Member, mm.	Enclosure, mm.
I.....	1.0+	0.5
II.....	0.5	0.7
III.....	0.6-	1.4

Example IV

A deposition apparatus was set up generally in accordance with the single figure of the drawing. Three sheets of commercial graphite having dimensions of 6 inches by 7 inches were spaced apart within an enclosure of commercial graphite. Each passage between adjacent sheets had a space of 1 inch. After the cover was bolted to the lower body portion, the chamber atmosphere was reduced to a pressure of 0.008 mm. of mercury. Power was supplied to the induction coils to heat the member, enclosure, and passage to a temperature of about 2310° C. During heating the pressure rose. After removal of iron, other impurities and adsorbed gases, the pressure fell. The power was discontinued, and the deposition apparatus was allowed to cool to room temperature. The chamber was then opened, inspected, and closed. The chamber atmosphere was again reduced to a pressure of 0.008 mm. of mercury. Power was supplied to the induction coils to heat the enclosure, member, passage, and preheater to a temperature of 2420° C. A carbonaceous gas in the form of methane was supplied at a rate of 60 cubic feet

per hour at a pressure of 1140 mm. of mercury to the preheater subsequent to flowing through metering devices, and an acetone and Dry Ice bath. A direct current potential of 28 volts was applied between the enclosure, as cathode, and the member, as anode, to provide a current of 350 amps. The gas formed into a carbon vapor in the preheater which was deposited on both the member and interior enclosure wall as it flowed through the passage at a pressure of approximately 28 mm. of mercury. After 50 minutes, the heat, gas flow and potential were discontinued and the chamber was restored to atmospheric pressure. After cooling to room temperature, one of the members was removed from the enclosure. The pyrolytic graphite on this member had an average thickness of 90 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 an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor at a temperature in the range of 2000° C. to 2500° C. through said passage whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

2. A deposition method which comprises providing an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a mixture of a carbon vapor and a reactive gas at a temperature in the range of 2000° C. to 2500° C. through said passage whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

3. A deposition method which comprises providing an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, heating said member and said enclosure to a temperature in the range of 2000° C. to 2500° C., applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor through said passage whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

4. A deposition method which comprises providing an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, feeding a carbonaceous gas to said passage, heating said member and said enclosure to a temperature in the range of 2000° C. to 2500° C. to decompose said gas to a carbon vapor, applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said mem-

ber, flowing said carbon vapor through said passage whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

5. A deposition method which comprises providing an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor through said passage at a temperature in the range of 2000° C. to 2500° C., increasing said flow to a rate in excess of the highest rate of deposition resulting in a sooting environment, reducing said flow to a flow rate immediately below said sooting environment to maintain the highest rate of deposition, continuing said flow whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

6. A deposition method which comprises providing an enclosure, positioning a member within said enclosure, providing a narrow, substantially uniform diameter passage between said member and said enclosure thereby providing a negligible pressure drop during deposition, evacuating said passage, heating said member and said enclosure to a temperature in the range of 2000° C. to 2500° C., applying a potential between said enclosure and said member to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor through said passage, increasing said flow to a rate in excess of the highest rate of deposition resulting in a sooting environment, reducing said flow to a flow rate immediately below said sooting environment to maintain the highest rate of deposition, continuing said flow whereby a pyrolytic graphite article is formed on said member, and removing said article from said member.

7. A deposition method which comprises providing an enclosure, positioning a plurality of members within said enclosure, providing a narrow passage between said members and said enclosure, providing a narrow passage between each pair of adjacent members, evacuating said passages, applying a potential between said enclosure and said members to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor at a temperature in the range of 2000° C. to 2500° C. through said passages whereby pyrolytic graphite articles are formed on said members, and removing said articles from said members.

8. A deposition method which comprises providing an enclosure, positioning a plurality of members within said enclosure, providing a narrow passage between said members and said enclosure, providing a narrow passage between each pair of adjacent members, applying a potential between said enclosure and said members to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor at a temperature in the range of 2000° C. to 2500° C. through said passages, increasing said flow to a rate in excess of the highest rate of deposition resulting in a sooting environment, reducing said flow to a flow rate immediately below sooting environment to maintain the highest rate of deposition, continuing said flow whereby pyrolytic graphite articles are formed on said members, and removing said articles from said members.

9. A deposition method which comprises providing an enclosure, positioning a plurality of members within said enclosure, providing a narrow passage between each pair of adjacent members, applying a potential between said enclosure and said members to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a

carbon vapor at a temperature in the range of 2000° C. to 2500° C. through said passages whereby pyrolytic graphite articles are formed on said members, and removing said articles from said members.

10. A deposition method which comprises providing an enclosure, positioning a plurality of members within said enclosure, providing a narrow passage between each pair of adjacent members, evacuating said passages, applying a potential between said enclosure and said members to produce a constant temperature at the surface of said enclosure and a constant temperature at the surface of said member, flowing a carbon vapor at a temperature in the range of 2000° C. to 2500° C. through said passages, increasing said flow to a rate in excess of the highest rate of deposition resulting in a sooting environment, reducing said flow to a flow rate immediately below sooting environment to maintain the highest rate of deposi-

tion, continuing said flow whereby pyrolytic graphite articles are formed on said members, and removing said articles from said members.

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