Oct. 15, 1963 R. J. DIEFENDORF 3,107,180

PROCESS FOR DEPOSITION OF PYROLYTIC GRAPHITE

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Fig. 1.

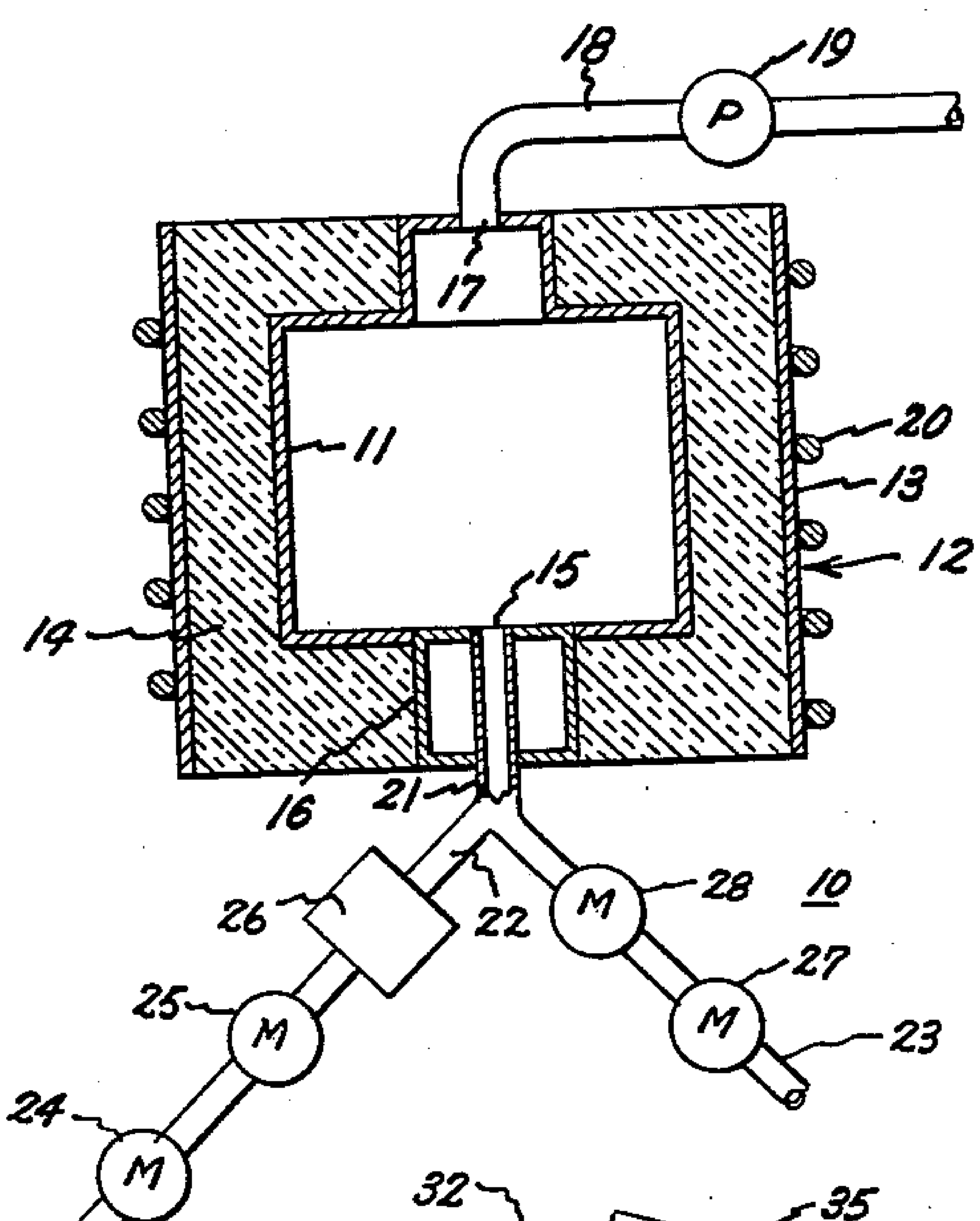
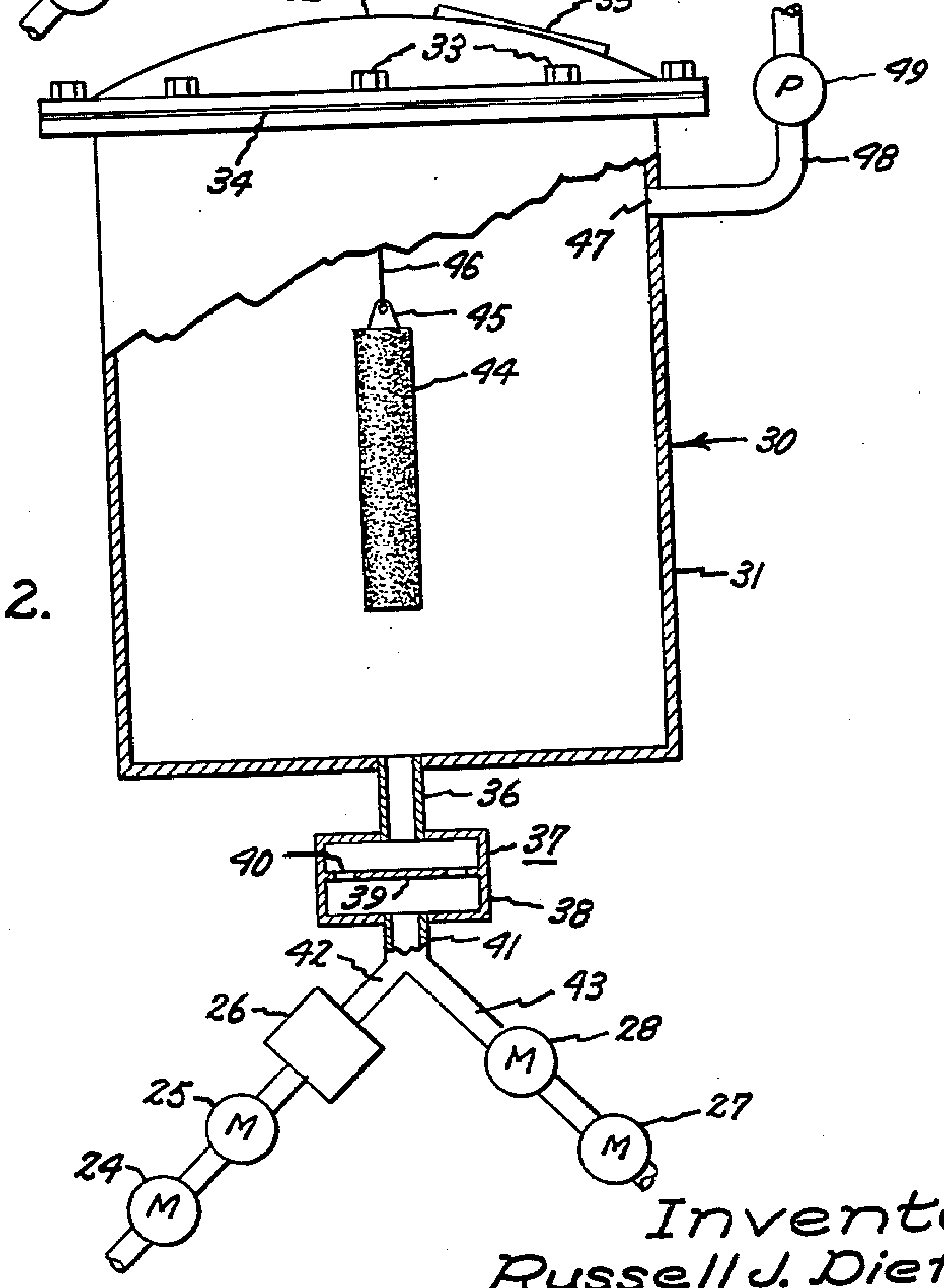


Fig. 2.



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PROCESS FOR DEPOSITION OF PYROLYTIC GRAPHITE

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This invention relates to deposition methods of forming articles and coatings and more particularly to deposition methods of forming uniform, dense pyrolytic graphite articles and coatings.

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 pyrolytic graphite components in these systems.

Carbonaceous gases have been thermally decomposed into carbon vapor 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 uniform, dense pyrolytic graphite articles at high deposition rates. Since such high rates are desirable, it would appear that gas pressure or temperature could 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 variables. Thus, a mere increase in pressure or temperature does not solve the deposition problem but imposes a subsequent limitation by creating soot in the carbon vapor. Therefore, it would be desirable to provide deposition methods of forming pyrolytic graphite without soot particles at an increased rate of deposition.

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

It is another object of my invention to provide a deposition method of forming pyrolytic graphite articles and coatings in which non-sooting carbon vapor is employed.

It is a further object of my invention to provide a deposition method of forming pyrolytic graphite articles and coatings in which a soot inhibiting gas is employed.

It is a still further object of my invention to provide a deposition method of forming pyrolytic graphite articles and coatings with similar properties and at high rates of deposition.

In carrying out my invention in one form, at least one member is positioned within an enclosure, a carbonaceous material is fed to the enclosure, 0.1 volume percent to 5.0 volume percent nitric oxide is mixed with the material, the mixture is heated to decompose into a non-sooting carbon vapor, and the carbon vapor is flowed through the enclosure to form pyrolytic graphite on 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:

FIGURE 1 is a sectional view of a deposition apparatus for forming 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 in which a member 11 in the form of a hollow graphite cylinder is positoned within an enclosure 12 including an insulated cylinder 13 of quartz or alumina, and carbon black insulation 14. Member 11 is provided with an opening 15 in its bottom wall which communicates with the outlet of a preheater 16 and with an opening 17 in its top wall which communicates with an outlet line 18 and associated vacuum pump 19. Insulation 14 surrounds substantially member 11. Heating coils 20 surround cylinder 13 to provide heat for member 11 and preheater 16. The inlet of preheater 16 is connected to an inlet line 21 which branches into lines 22 and 23. A carbonaceous gas is fed from a carbonaceous material source (not shown) through line 22 including a total consumption gas meter 24, a gas rate meter 25, and an acetone and Dry Ice trap indicated at 26, inlet line 21, and preheater inlet to preheater 16. While a carbonaceous gas, such as methane or ethane, is employed, the carbonaceous material can also be in liquid or solid form which is fed from the source to preheater 16 for conversion to a carbon vapor. Second line 23 feeds nitric oxide, a soot inhibiting gas, through a total consumption meter 27 and a gas rate meter 28 from a gas source (not shown) to inlet line 21. The carbonaceous material and nitric oxide are mixed together in line 21 and flow into preheater 16 where additional mixing occurs. If it is desired, lines 22 and 23 can be connected directly to preheater 16 to cause mixing therein.

In FIGURE 2 of the drawing, a modified deposition apparatus is shown which comprises an enclosure 30 having a lower body portion 31 and a cover 32 which is hinged to the lower body portion by means of bolts 33 and employs an O ring 34 therebetween. Viewing window 35 is provided in cover 32 to view the operation and to read an optical pyrometer (not shown). A line 36 extends through the bottom wall of enclosure 30 and is connected to a preheater 37 which consists of a container 38 having an inlet and an outlet. A baffle 39 is positioned within container 38 and a plurality of openings 40 are located near the perimeter thereof. The inlet of preheater 37 is connected to an inlet line 41 which branches into lines 42 and 43. A carbonaceous gas is fed from a carbonaceous source (not shown) through line 42 including total consumption meter 24, gas rate meter 25, and an acetone and Dry Ice trap 26, inlet line 41, and preheater inlet to preheater 37. Second inlet line 43 feeds nitric oxide through total consumption meter 27 and gas rate meter 28 from a gas source to inlet line 41 (not shown). The carbonaceous material and nitric oxide are mixed together in line 41 and flow into preheater 37 where additional mixing occurs. A member 44 in the form of a sheet of graphite is suspended by any suitable means, such as a hook 45 and a rod 46 within enclosure 30. An outlet 47 is provided in enclosure 30 to which is connected a line 48 associated with a vacuum pump 49 to reduce the chamber pressure to a desired level. Heat is supplied to preheater 37 from any suitable source, such as heating coils (not shown).

I discovered unexpectedly that pyrolytic graphite articles and coatings were formed uniformly and without soot particles at high volume carbonaceous gas flow rates by positioning at least one member within an enclosure, feeding a carbonaceous material to the enclosure, mixing 0.1 volume percent to 5.0 volume percent of nitric oxide, a soot inhibiting gas, with the material, heating the mixture to decompose the mixture to a non-sooting carbon vapor, and flowing the carbon vapor through the enclosure. I found further that the preferred range of nitric oxide was 0.1 volume percent to 5.0 volume percent. Within this range, the most desirable addition appeared to be 1.5 volume percent. Additionally, I found that this deposition method was applicable over a wide temperature range, such as 1000° C. to 2300° C.

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 pressure 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, a large increase in pressure in the small diameter chamber to increase deposition produces soot rather than a uniform, dense pyrolytic graphite article or coating.

In the operation of deposition apparatus **10** shown in FIGURE 1, cylinder **13** is placed on a surface and surrounded by coils **20**. Member **11** with preheater **16** is positioned within cylinder **13** and placed on the surface. The void around and beneath member **11** is filled with carbon black **14**. Outlet line **18** is connected to opening **17** in member **11** and with its associated pump **19**. Additional insulation is placed on top of member **11** to complete enclosure **12**. Inlet line **20** with its associated branch lines **21** and **22** is connected to the preheater inlet. A carbonaceous gas, such as methane, is fed through line **22** including total consumption meter **24**, gas rate meter **25** and acetone and Dry Ice trap **26**, inlet line **21**, and preheater inlet to preheater **16**. Nitric oxide is fed through line **23** including total consumption meter **27** and gas rate meter **28** to inlet line **21**. The carbonaceous material and nitric oxide are mixed together in line **21** and flow into preheater **16** where additional mixing occurs. The mixture is heated in preheater **16** to decompose the mixture to form a non-sooting carbon vapor. I have found that a wide temperature range can be employed to decompose the carbonaceous material and nitric oxide mixture. Since the rate of deposition of such a carbon vapor on a surface to form a pyrolytic graphite article is increased by increasing the temperature, it is preferred to heat the mixture in a temperature range between 1000° C. and 2300 C. Generally, maximum deposition occurs in a temperature range of greater than 2000° C.

When soot forms during the heating of a carbonaceous material, it forms heavily in the preheater and continues its formation in the deposition chamber. 0.1 volume percent to 5.0 volume percent of nitric oxide is mixed with the carbonaceous material and the mixture is heated to decompose into a non-sooting carbon vapor in the preheater. Approximately 1.5 volume percent of nitric oxide mixed with a carbonaceous material appeared to be the optimum amount of soot inhibiting gas to produce a non-sooting carbon vapor. Increased amounts of nitric oxide produced only small additional effects. A wide pressure range can be employed since a non-sooting carbon vapor is used. While a pressure range, such as 0.5 mm. to 760 mm. of mercury at various gas flow rates is desirable, I prefer to reduce the chamber atmosphere to a pressure of 0.5 to 80 mm. of mercury at gas flow rates of 8 to 150 cubic feet per hour.

As shown in FIGURE 1 of the drawing, non-sooting carbon vapor which has been formed in preheater **16** is fed through opening **15** into hollow member **11** where it forms pyrolytic graphite on the inner wall of the member. Line **18**, with its associated pump **19**, maintains enclosure **12** at the desired pressure. Since an increase in pressure produces generally an increase in deposition rate, the required time period to produce the desired article thickness can be reduced.

In the operation of the deposition apparatus shown in FIGURE 2, a member **44** in the form of a sheet of graphite is suspended by hook **45** and rod **46** within enclosure **30**. Cover **32** is bolted to lower body portion **31** of enclosure **30** and the enclosure atmosphere is reduced to a pressure in the range of 0.5 mm. of mercury

to 760 mm. of mercury. Heat is supplied to preheater **37** from any suitable source, such as heating coils (not shown).

A carbonaceous gas, such as methane, or a mixture of a carbonaceous gas and a reacting gas, such as hydrogen, is fed from a source (not shown) through line **42** including meter **24**, meter **25**, and trap **26**, inlet line **41**, and preheater inlet to preheater **37**. Nitric oxide is fed through line **43** including meters **27** and **28** from a gas source (not shown) to inlet line **41**. The carbonaceous material and nitric oxide are mixed together in line **41** and flow into preheater **37** where additional mixing occurs. The mixture is heated in preheater **37** to decompose the mixture to a non-sooting carbon vapor. As in the apparatus in FIGURE 1, a wide temperature range can be employed in the apparatus of FIGURE 2 to decompose the carbonaceous material and nitric oxide mixture. It is preferred to heat the mixture in a temperature range between 1000° C. and 2300° C. 0.1 volume percent to 5.0 volume percent of nitric oxide is mixed with the carbonaceous material and the mixture heated to the desired temperature without soot formation in the preheater. A wide pressure range, as set forth above for apparatus **10** in FIGURE 1, can also be employed.

As shown in FIGURE 2 of the drawing, the non-sooting carbon vapor which has been formed in preheater **37** is fed through line **36** to enclosure **30** where it forms pyrolytic graphite on member **44** suspended within enclosure **30**. Line **48**, with associated pump **49**, maintains enclosure **30** at the desired pressure. Since an increase in pressure produces generally an increase in deposition rate, the required time period to produce the desired article thickness can be reduced.

An example of an attempted method of forming a pyrolytic graphite article without the inclusion of nitric oxide is set forth below in Example I. Examples II and III are deposition methods of forming pyrolytic graphite in accordance with the present invention.

Example I

A deposition apparatus was set up generally in accordance with FIGURE 1 of the drawing wherein a member in the form of a hollow cylinder was composed of commercial graphite. The enclosure atmosphere was reduced to a pressure of .001 mm. of mercury by the pump. Power was supplied to the induction coil to heat the enclosure and member to an approximate temperature of about 2010° C. A carbonaceous gas in the form of methane was supplied at a rate of 60 cubic feet per hour at a pressure of 20 mm. of mercury to the preheater subsequent to flowing through metering devices, and an acetone and Dry Ice bath. No soot inhibiting gas was employed. The gas was heated in the preheater and formed into a sooting carbon vapor which was deposited on the member as it flowed through the enclosure. After 12 minutes, a sooty coating was formed on the member.

Example II

After the sooty coating was formed in Example I, nitric oxide was supplied at a rate of one cubic foot per hour to the preheater subsequent to flowing through metering devices. The gases were mixed in the preheater. The gases were heated in the preheater and formed a non-sooting carbon vapor in the preheater which vapor was deposited on the member as a non-sooty coating as it flowed through the enclosure. After two minutes, the nitric oxide flow was stopped. A sooty coating was then formed on the member.

Example III

After the sooty coating was formed subsequent to stopping the nitric oxide flow in Example II, the temperature in the enclosure was reduced to 1900° C. A soot inhibiting gas in the form of nitric oxide was supplied at a rate of one cubic foot per hour to the preheater subsequent to flowing through metering devices. The gases were mixed in the preheater. The gases were heated in the preheater and formed a non-sooting carbon vapor in the preheater which vapor was deposited on the member as a non-sooty coating as it flowed through the enclosure. After two minutes, the nitric oxide flow was stopped and a sooty coating was again formed on the member. The power and gas flow were discontinued and the chamber was restored to atmospheric pressure.

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 at least one member within said enclosure, heating a carbonaceous material to decompose said carbonaceous material to a carbon vapor, mixing 0.1 volume percent to 5.0 volume percent of nitric oxide with said carbon vapor to produce a non-sooting carbon vapor, and flowing said non-sooting carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

2. A deposition method which comprises providing an enclosure, positioning at least one member within said enclosure, heating a carbonaceous material to a temperature in the range of 1000° C. to 2300° C. to decompose said carbonaceous material to a carbon vapor, mixing 0.1 volume percent to 5.0 volume percent of nitric oxide with said carbon vapor to produce a non-sooting carbon vapor, and flowing said non-sooting carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

3. A deposition method which comprises providing an enclosure, positioning at least one member within said enclosure, feeding a carbonaceous gas to said enclosure,

mixing 0.1 volume percent to 5.0 volume percent of nitric oxide with said first gas, heating said mixture to decompose said mixture to a non-sooting carbon vapor, and flowing said carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

4. A deposition method which comprises providing an enclosure, positioning at least one member within said enclosure, heating a carbonaceous material to decompose said carbonaceous material to a carbon vapor, mixing 1.5 volume percent of nitric oxide with said carbon vapor to produce a non-sooting carbon vapor, and flowing said non-sooting carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

5. A deposition method which comprises providing an enclosure, positioning at least one member within said enclosure, feeding methane gas to said enclosure, mixing 1.5 volume percent of nitric oxide with said methane gas, heating said mixture at a temperature in the range of 1000° C. to 2300° C. to decompose said mixture to a non-sooting carbon vapor, and flowing said carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

6. A deposition method which comprises providing an enclosure, positioning at least one member within said enclosure, mixing a carbonaceous gas and 0.1 volume percent to 5.0 volume percent of nitric oxide, heating said mixture to decompose said mixture to a non-sooting carbon vapor, and flowing said carbon vapor through said enclosure whereby pyrolytic graphite is formed on said member.

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