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[54] PROCESS FOR PRODUCING PYROLYTIC GRAPHITE

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[57] ABSTRACT

A hydrocarbon is pyrolyzed to produce a stream of gas having a presellected average gas temperature. An electric arc heater may be employed having an elongated exhaust nozzle, which may be fluid cooled or not fluid cooled, and carbon in the form of soot and/or crystalline graphite may be deposited on the inside wall of the exhaust nozzle, depending on the temperature difference between the gas and the inside surface of the nozzle. Alternatively, an object to be coated with carbon in the form of soot and/or pyrolytic graphite may be mounted in the stream of gas exhausted from the nozzle. The processes may be carried on at atmospheric pressure. The desired average gas temperature may be obtained by adjusting arc power, adjusting the mass flow rate of the hydrocarbon gas, passing a selected portion of the hydrocarbon gas through the arc path to be pyrolyzed and mixing it with another selected portion not passed through the arc path, or utilizing instant variations in current of an alternating current source as the current varies during each alternation between zero and a peak value. An object placed in the gas stream to be coated may be composed of a refractory metal, a refractory non-metal, or may be fluid cooled. Vacuum pump means is used where desired to maintain a pressure at or near atmospheric pressure in the area where an object to be coated comes in contact with the stream of hot gas.

8 Claims, 7 Drawing Figures
PROCESS FOR PRODUCING PYROLYTIC GRAPHITE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 533,004, filed Mar. 9, 1966 (now abandoned) and assigned to the assignee of the instant invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to improvements in processes for producing and obtaining carbon in the form of soot or pyrolytic graphite or both from a pyrolyzed hydrocarbon.

2. Description of the Prior Art

It has been known for some time that when an organic material is heated in the absence of oxygen at temperatures above its decomposition temperature, the material undergoes a thermal decomposition. One of the principal products formed under these conditions is carbon. If the material is a gas at the decomposition temperature, the carbon usually forms as a finely divided soot. If the gas is at temperatures in excess of 1000°C the carbon undergoes some agglomeration to form platelets of the order of 50 to 100 angstroms in dimension. The precipitated carbon, however, is still a finely divided powder. When the temperature of the gas is in excess of about 2000°C, or more precisely in excess of 1500°C, and the products of decomposition are allowed to come in contact with a suitable surface, which may be graphite, the carbon deposits on the latter in a well defined crystalline order to form pyrolytic graphite. The oriented, pyrolytic graphite has a higher density than ordinary graphite, and is also characterized by a higher mechanical strength in both directions perpendicular and parallel to the plane of orientation.

In the present state of the art, pyrolytic graphite is made largely in graphite resistance furnaces. Prior art is exemplified by U.S. Pat. Nos.: 2,635,994 issued to Tieman; 3,009,783 issued to Sheer et al.; 3,172,774 issued to Diefendorf; 3,107,180 issued to Diefendorf; 3,297,406 issued to Diefendorf; 3,168,592 issued to Cichelli et al.; 3,179,733 issued to Schotte; and 3,318,791 issued to Harris et al. British patents relating to the art are numbers 252,662 and 274,883. Relevant to the prior art is a publication entitled "Research and Development on Advanced Graphite Materials", Vol. XXXVII, Technical Report No. WADD TR 61-72, May, 1964, pp. 1, 2, 23, 24 and 70, prepared for the Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio by National Carbon Company, Division of Union Carbide Corporation, released for publication as a WADD Technical Documentary Report.

SUMMARY OF THE INVENTION

We utilize an arc heater to pyrolyze a process hydrocarbon gas in the absence of oxygen, the arc heater preferably having a fluid cooled nozzle. The first layer of carbon deposited on the nozzle may be amorphous, and may form a thermal barrier, additional layers of carbon deposited on the inside surface of the nozzle being pyrolytic graphite.

Our invention includes the use of apparatus having a continuously cooled member disposed in the exhaust stream or gas from the arc heater, with means for periodically removing layers of pyrolytic graphite from the cooled member to provide a continuous process.

Furthermore, we have invented a new and improved process for obtaining soot which comprises pyrolyzing a hydrocarbon gas, adding an auxiliary gas to quench the decomposed gas mixture to a predetermined temperature, and thereafter utilizing a fluid spray such as water to cool the final product within a period of a few milliseconds to a temperature of the order of 300°C, the exhaust from the arc heater containing a large proportion of soot, the soot being precipitated in precipitating means having exhaust from the arc heater fed thereto.

In addition, we have invented a new and improved process for coating an object with pyrolytic graphite, the object to be coated having a melting temperature greater than the temperature of the gas, the object to be coated being placed at the exhaust nozzle in the gas stream where a gas heated above the 1500°C temperature exits from the arc heater, the last-named decomposed hydrocarbon gas causing a layer of pyrolytic graphite to be deposited on the object. In addition, we provide for heating the object to a temperature higher than 1500°C whereby the pyrolytic graphite is deposited on the object in a manner which causes it to adhere very strongly to the object.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 are views of a suitable arc heater for practicing our invention, the arc heater of FIGS. 1 and 2 constituting no part of the instant invention;

FIG. 3 is a view of apparatus suitable for practicing certain methods of our invention;

FIG. 4A is a view of an arrangement for coating an object with pyrolytic graphite according to our invention;

FIG. 4B is a view of apparatus for depositing material in a controlled atmosphere or at a reduced pressure;

FIG. 5 is an additional view of apparatus for practicing our method of obtaining a continuous production of carbon; and

FIG. 6 is a view of apparatus for obtaining continuous production of pyrolytic graphite.

Particular reference is made now to FIGS. 1 and 2, where an arc heater is shown which comprises means for pyrolyzing a process gas, means for quenching by an auxiliary gas, means for adding a quenching fluid, and a well defined gas exhaust area where the object to be coated may be placed.

The arc heater of FIG. 1 is the invention of Messrs. Bruning, Kienast, Kemeny and Hirayama, and is described and claimed in a copending patent application entitled "Cross-Flow Arc Heater Apparatus And Process For The Synthesis Of Carbon, Acetylene And Other Gases", Ser. No. 507,345, filed Nov. 12, 1965, now U.S. Pat. No. 3,554,715 and assigned to the assignee of the instant invention.

In FIGS. 1 and 2 an arc heater generally designated 10 forms an arc chamber 11, the chamber forming means 10 being generally cylindrical if desired and having cylindrical wall portion 9 and having disposed therein and electrically insulated from each other, two
annular electrodes generally designated 15 and 16, a quenching tube generally designated 17, and nozzle means generally designated 18.

Electrode 15 is seen in FIG. 1 to be generally in the form of an annular cup with inner wall portion 21, outer wall portion 22, these being substantially cylindrically in shape, and a rounded end wall portion 23. All of the wall portions are composed of a highly electrically conductive and heat conductive material such as copper. The aforementioned electrode 16 has inner and outer cylindrical wall portions 25 and 26 with an annular end portion of curved cross section 27, electrode 16 being composed of highly heat conductive and electrically conductive material. By means hereinafter to be described electrodes 15 and 16 have a source of potential connected thereacross for producing the arc 20 shown taking place in the arc chamber generally designated 11.

The annular ends or edges 31 and 32 of the aforementioned inner and outer wall portions 21 and 22 respectively abut against an end plate generally designated 34 composed of insulating material such for example as micarta, the outer end 32 having a groove therein forming an annular shoulder 37. Disposed in this annular groove 36 between the wall 22 and the adjacent inner surface of the cylindrical wall portion 9 of the arc heater 10 is an annular ring 38 composed of electrically insulating material which is also preferably highly refractory, the ring 38 having a plurality of bores 39 at spaced intervals around the periphery thereof. These bores 39 communicate between the chamber 11 and an adjacent annular gas header 40 cut or machined in the aforementioned end plate 34 and having a gas inlet 41 communicating therewith. Means, symbolized by valve 42, is provided for adjusting and controlling the flow rate of gas admitted at 41. Additional bores 39 are shown in the cross-sectional view in FIG. 2 the plane of which passes through the aforementioned annular gas header 40.

The aforementioned inner cylindrical wall 21 also has a groove 43 cut therein near the end 31, forming an annular shoulder 44. Mounted adjacent the surface of the groove 43 and maintained in position by the shoulder 44 is an annular ring 46 composed of insulating material having spaced bores 47 passing therethrough, the annular ring 46 being disposed between electrode 15 and electrode 16 for reasons to become hereinafter more clearly apparent. Bore 47 communicates between the chamber 11 and an annular gas header 49 having gas inlet 50. Additional bores 47 are seen in FIG. 2. Means, symbolized by valve 59, is provided for adjusting or controlling the flow rate of gas admitted at gas inlet 50.

The inside of the aforementioned electrode 15 is seen to include a generally annular ring member 52, generally U-shaped in cross-section, having cylindrical wall portions 53 and 54 and an end portion 55 generally semicircular in cross-section. The left-hand end of the ring member 52 is seen to include an annular flange portion 56 having an annular groove 57 therein which is disposed as a 0-ring 58. Wall portion 53 also has a flange portion 60 with an annular groove 61 therein for 0-ring 62. The ends of the flange portions 56 and 60 are seen to abut against two annular retaining rings 65 and 66, respectively, which have portions passing into slots 67 and 68 to be retained in position therein.

Passing through an aperture 70 in the aforementioned end plate 34 is a fluid conduit 71 which is composed of electrically conductive material. Conduit 71 has a source of potential connected thereto symbolized by lead means 72 for bringing a current to the electrode 15 to produce and sustain the aforementioned arc 20 between electrodes 15 and 16. Means for adjusting the value of the arc current is symbolized by rheostat 79.

Disposed within the aforementioned annular U-shaped ring member 52 is a field coil 74 in a housing 75 composed of insulating material, the space between the left-hand end of the housing 75 and the aforementioned annular rings 65 and 66 being filled with a generally annular ring member 77 having an annular fluid header 78 therein communicating with U-shaped passageway 81 and also communicating with a bore 80 which constitutes an extension of the opening in the aforementioned conduit 71. It is seen that the U-shaped passageway 81 extends around the entire annular U-shaped ring member 52 forming a passageway for the flow of fluid from the fluid inlet header 78 in a path adjacent the inside wall of the electrode arcing surface. After fluid has flowed around the U-shaped passageway in the direction indicated by the arrows, it reaches a fluid outlet header on the opposite side of the electrode. Because of the cross-section in which the view is taken, the fluid outlet header of electrode 15 is not shown, but the fluid outlet header of electrode 15 is substantially similar to fluid outlet header 84 of electrode 16 hereinafter to be described in detail. Even though only one inlet header and outlet header are shown it is understood that a multiplicity of such inlet and outlet headers may be utilized. This cooling fluid conducts heat flux away from the surface of the electrode, which is preferably composed of a highly heat conductive material such as copper. This heat flux develops as the result of the intensely hot arc spot of arc 20 as well as a result of radiation and conduction of heat from the arc and conductive or incandescent gases in the arc chamber.

The aforementioned electrode 16 is generally similar to electrode 15 and the parts thereof need not be described in as much exact detail. Generally speaking, disposed within the electrode 16 there is a U-shaped annular ring member 87 having a coil 88 and coil housing 89 wherein, the U-shaped annular ring member 87 forming an annular passageway generally cup-shaped or U-shaped around the entire ring member, this passageway being shown at 90. The output end of the passageway 90 communicates with the aforementioned fluid outlet header 84, which communicates with a bore 91, and thence to the inside of conduit 92 composed of electrically conductive material and having lead 93 connected thereto. The fluid inlet header for the passageway 90 is not shown in the particular plane of the cross-section selected for illustration, but corresponds to the fluid inlet header 78 of electrode 15. Lead 93 is connected to the other terminal of the source to which 72 is connected, for producing a potential difference between electrodes 15 and 16 to produce the aforementioned arc 20.

With further reference to electrode 15, the annular ring member 77 has threaded bores 95 therein at
spaced intervals around the periphery of the electrode for receiving the ends of bolts 96 passing through bores 97 in the end plate generally designated 34, to hold the electrode in position in the arc chamber. It will be understood that electrode 16 also has spaced bolts to hold the electrode in position, these being shown at 99 in FIG. 2.

At another position around the periphery of the electrode 15 there are leads to the aforementioned coil 74, these not being seen in the cross-section chosen for illustration in FIG. 1, but the leads to the field coil of the electrode 15 may be similar to those of the field coil 88 of electrode 16. These leads 101 and 102 are seen extending through a bore 103 in the annular ring supporting member 109 and thence pass through the space 104 between annular rings 105 and 106 and thence pass through a bore 107 in the aforementioned end plate 34 composed of insulating material. Means are provided, symbolized by rheostat 100, for varying the strength of the magnetic field to thereby vary and control the rate of rotation of the arc 20. The leads to field coil 74 of electrode 15 are shown at 111 and 112, FIG. 2.

The fluid inlet conduit for electrode 16 is shown at 115, FIGS. 1 and 2, and the fluid outlet conduit for electrode 15 is shown at 116, FIGS. 1 and 2, these passing through the end plate 34 but not in the plane selected for illustration in FIG. 1. It will be understood that these inlet and outlet conduits communicate with fluid headers in the respective electrodes.

The end plate 34 is seen to have a bore of large diameter 120 passing therethrough, through which extends substantially along the axis of the arc chamber 11 a tubular member 121 for bringing a quenching fluid into the chamber, the member 121 being slidable in the bore 120 and having numerous spaced apertures 122 in the end thereof for admitting either a gas or a liquid into the arc chamber 11 for quenching purposes.

Seated in an annular groove 127 in the inside surface of electrode 16, that is, in the wall 25 thereof, is a ring member 128 composed of electrically insulating material and having a plurality of bores 129 therethrough at spaced intervals around the periphery thereof communicating between the interior of the chamber 11 and an annular gas inlet header 130, having gas inlet 131 connected thereto. Means symbolized by valve 134 are provided for adjusting or controlling the flow rate of gas admitted at inlet 131.

There is provided then, lead means 93 and 72 for bringing a potential to electrodes 16 and 15 respectively to produce the arc 20, the electrodes 15 and 16 being insulated from each other, being insulated from the quenching member 121 and being insulated from the cylindrical wall 9 of the arc heater. Conduit 71 which may be connected by way of a hydraulic insulator, not shown for simplicity of illustration, to a source of cooling fluid under pressure, brings a cooling fluid to fluid header 78; from thence the fluid flows through passageway 52 to a fluid outlet header and out of the aforementioned conduit 116. With respect to electrode 16, fluid enters at the inlet conduit 115, flows around the U-shaped passageway 90, out of the annular fluid header 84 into the bore 91 and out the conduit 92, completing a passage for the flow of cooling fluid throughout the cooling passageways of electrode 16. Lead means 101 and 102 bring an energizing potential to the field coil 88 of electrode 16, this potential preferably being direct current, and lead means 111 and 112, FIG. 2, bring an energizing potential to the field coil 74 of electrode 15. Coils 74 and 88 are energized with their fields in opposition to produce a field between the coils which substantially follows the contour of the electrodes and is substantially transverse to the arc path and also transverse to the direction of current, so that a component of force is exerted on the arc which causes the arc to rotate substantially continuously in a closed circular path about the two electrodes.

While only the process gas brought into the chamber through bores 47 passes through the arc path, the process gas in some applications may be brought into the arc chamber 11 through any or all of the three gas inlets provided, that is, bores 39, bores 47, or bores 129, communicating with gas headers 40, 49 and 130 respectively, having gas inlets 41, 50 and 131 respectively. As stated hereinafter, in order to obtain optimum deposition of pyrolytic graphite, it is desirable to have the average temperature of gas passing through or issuing from the exhaust nozzle have a value within a predetermined range of values. One way of accomplishing this is to pass a first selected portion of the hydrocarbon gas through the arc path, and to pass a second portion of the arc heater through a path which does not take the gas through the arc path, but to a region in the arc chamber where turbulent mixing with the pyrolyzed gas produces a desired average gas temperature. A quenching gas or additional or another process gas may be brought in at 39, and a quenching gas or additional or other process gas may be brought in at 129 if desired.

Particular attention is directed now to the nozzle member generally designated 136 having an annular flange 137 which overhangs an annular passageway 138 and provides optical baffling for an annular ring member 139 composed of electrically insulating material and preferably heat resistant material. The ring member 139 has a plurality of spaced bores therethrough, two of these being shown at 141 and 142. Behind the ring member 139 is a passageway 143 through which an additional quenching gas or liquid may come and pass through the bores including bores 141 and 142, around the edges of the nozzle member and be mixed with the gas in the chamber 11. The nozzle member is seen to have an annular fluid flow passageway 145 therein near the wall 146 thereof, in which wall are numerous bores communicating with the passageway, these bores being shown at 148. If desired, the bores may be at spaced intervals around a circular pattern, with a plurality of axially spaced circles along the length of the nozzle, as shown.

Where soot formation is the primary object, a quenching fluid may be introduced through the bores 148 to quench the gas to a desired temperature. Additionally, a gas or a liquid may be introduced through bores 122 of the quench member 17, the position of which as aforementioned is adjustable, so that the fluid admitted to the chamber 11 through bores 122 may be admitted substantially at the arc path or at any position downstream of the arc path, as well as positions upstream of the arc path. Accordingly, it will be seen that the gas may be quenched at substantially any selected time interval after the gas is pyrolyzed by the arc 20,
and this interval may be adjusted substantially continuously from a fraction of a microsecond to several milliseconds depending upon the position of member 17.

Means, not shown, may be provided for clamping member 17 in its selected position.

There has been provided, then, in the apparatus embodied as shown in FIGS. 1 and 2, means for introducing a quenching liquid or gas at a number of positions into the arc chamber, means for introducing a reactant or process gas or gases at a number of positions in the chamber, and means for introducing a quenching gas or liquid at substantially any desired position with respect to the path of the arc, representing any desired elapsed time interval between the pyrolyzing of the process gas and the quenching to a predetermined temperature. Furthermore, quenching fluid may be introduced through the aforementioned bores in annular ring member 139, and quenching liquid may be introduced through the bores 148 of the nozzle generally designated 18. A most versatile arc heater arrangement is thereby provided in which by selecting the passageways to be employed and the position of member 17 and the materials to be used for quenching purposes, any desired pyrolyzing and synthesizing process may be carried out.

Other methods of obtaining a gas having an average temperature within a desired range of values include adjusting the power of arc, symbolized by rheostat 79, adjusting the mass flow rate of gas in accordance with arc power, symbolized by valves 42, 59 and 134, or utilizing alternating current to produce the arc 20, gas passing through the arc path while the instant arc current is very small during substantial portions of the time interval of each alternation being heated only slightly and mixed in the chamber with gas which is pyrolyzed by coming in contact with the arc at or near peak arc current during each alternation; a desired average gas temperature can be obtained by controlling one of more of the influencing factors.

Particular reference is made now to FIG. 3, which shows in generalized form the portions of an arc heater which are utilized in certain of the processes of our invention. In FIG. 3, the reference numeral 201 generally designates an arc heater which may be similar to the arc heater described heretofore. The arc heater has a nozzle 202 with an annular fluid passageway 203 communicating at one end with a fluid header 204 which has a fluid inlet or outlet, not shown for convenience of illustration. It will be understood that at the other end of the annular fluid passageway 203 there is also a fluid header, not shown, communicating with a fluid inlet or outlet, not shown. It is noted that the annular fluid passageway 203 is close to the inner surface 205 of the nozzle, effectively cooling this inner surface 205. The cooled surface plays an important part in certain of the processes to be described hereinafter.

In utilizing the apparatus of FIGS. 1 and 2 and 3 to produce pyrolytic graphite, a hydrocarbon gas such as methane is fed into the arc heater, which may if desired be flushed of all of the oxygen in the atmosphere by passing nitrogen through the arc heater for a few seconds before supplying the hydrocarbon gas to it. In the arc heater it will be understood that the gas which actually comes into contact with the arc is heated to a very high temperature of perhaps 6000° or 7000° centigrade. Not all of the gas comes into direct contact with the arc, but enough does so that there is an overall rise in gas temperature of perhaps 6000° or 7000° and preferably 2000°. The gas is decomposed into atoms and free radicals and the decomposition products come in contact with the cool surface 205. There is first deposited on the cool surface a layer of amorphous graphite, the graphite thereafter deposited being crystalline pyrolytic graphite of a very high degree of purity.

In summary, in the above-described process the steps comprise causing a hydrocarbon gas to flow in a predetermined path, producing a substantially continuously moving electric arc at a certain position in said path, the arc heating the gas to at least 1500° C in the absence of oxygen and pyrolyzing the gas, and causing the gas to come into contact with a surface, most of the carbon which is formed as a decomposition product being precipitated in the form of pyrolytic graphite.

It will be understood that the above-described structure offer certain advantages in obtaining the graphite; it will also be understood by those skilled in the art that carbon will start depositing at about 3600° with any surface which comes in contact with a decomposed hydrocarbon gas.

By way of further summary, the first layer of carbon deposited on the cool surface 205 acts as a thermal insulator. This first layer deposited is amorphous carbon because the temperature is too low as a result of the water cooled surface and any carbon deposited on the cool surface is amorphous. After a layer is formed, it is essentially a thermally insulating barrier. This first layer of amorphous carbon is at least a few microns thick. Thereafter, the temperature of the gas is kept above 1500°, pyrolytic graphite will be deposited.

It will be understood that the apparatus of FIG. 3 may be used in a process for producing a cylinder of pyrolytic graphite. Because of the fluid cooled inner surface of exhaust nozzle 202, a substantial difference in temperature may exist between this surface and the exhausted gas, which may have an average temperature in the range 1500° to 2000° C. This substantial temperature difference encourages the deposit of amorphous carbon, until the carbon deposit becomes so thick that it forms a thermal barrier; thereafter pyrolytic graphite may be deposited to form a cylinder of any desired thickness. If the arc heater is turned off and the apparatus allowed to cool, assuming for example that the nozzle is composed of copper, the relative coefficients of thermal expansion of the pyrolytic graphite and copper will be such that, when cooled, the cylinder of pyrolytic graphite may be removed without destroying its cylindrical form.

Our invention contemplates the use of mechanical means for periodically removing the deposited pyrolytic graphite so that a continuous graphite forming process is provided.

Particular reference is made now to FIG. 4A where an arc heater, not shown for convenience of illustration, has a nozzle 210 with a water cooled inner surface 211. Disposed at the nozzle and preferably in the center of the gas stream of the exhaust is an object to be coated with pyrolytic graphite. The object, which may be cylindrical in shape or have other desired
shapes, is designated 214; as an example of an object which could profitably be coated with pyrolytic graphite, 214 may be the nose cone of a space vehicle and may be composed for example of a ceramic or of titanium, both of which can withstand the temperature of 2000°C. If the object 214 is relatively cool to start with, the first layer of carbon deposited may be amorphous forming a thermal barrier so that additional layers are pyrolytic graphite. If desired, the object 214 may be heated by means not shown for convenience of illustration, to a temperature of, for example, 1500°C whereby pyrolytic graphite is deposited in a manner which adheres very strongly to the object 214. Accordingly, it will be seen that we have provided a method of coating an object with a layer of pyrolytic graphite including the steps of pyrolyzing a hydrocarbon gas in the absence of oxygen to a temperature of at least 1500°C in a chamber having a well defined exhaust area for the heated gas, and disposing the object to be coated at the exhaust area whereby the object is in the hot gas stream, the object to be coated having a melting temperature greater than the temperature of the gas, pyrolytic graphite being deposited on the object.

Particular reference is made to FIG. 4B. An enclosing structure generally designated 260 forms an enclosed chamber 270 into which exhaust nozzle 210 delivers the hot gas. The object to be coated is designated 214a, is shown as having passageway 261 therein for the flow of cooling fluid, with fluid inlet and fluid outlet connections 265 and 266 extending to the outside of the enclosure. Means for mounting the object to be coated in the hot gas stream is shown at 263. A vacuum pump, which is adjustable, is shown at 268 communicating with chamber 270 by conduit 272.

As previously stated, one of the more important advantages of our processes is that they may all be carried out at atmospheric pressure. Since it may be inherent in the nature of an arc heater that the heat supplied to the gas by the electric arc increases the pressure within the arc chamber, pump 268 may be regulated to produce and maintain atmospheric pressure in chamber 270. In the alternative, pump 268 may be regulated to produce and maintain a reduced pressure in chamber 270, although it is to be understood that all of our processes can be carried out at atmospheric pressure.

We have also invented a process for producing continuously pyrolytic graphite. In FIG. 6, let it be assumed by way of example that the object 216 is continuously cooled as by water flowing through suitable passageways therein, cooled to a temperature below 1500°C, and is maintained in the hot gas stream. Pyrolytic graphite will be continuously deposited on the object 216, and a suitable mechanical device 221 shown as a scraper in FIG. 6 is operatively associated with the cooled member 216 for periodically removing the pyrolytic graphite from the member.

We have further invented a process for producing carbon. Particular reference is made again to FIG. 1 of the patent drawings. In a process for continuously producing carbon in the form of soot a hydrocarbon gas is fed into the arc chamber, for example, at the passageways 47 where the hydrocarbon will pass through the arc flame. An inert gas is added to the chamber at one of the points downstream of the arc, for example passageways 141 and 142, the inert gas rapidly quenching the decomposed hydrocarbon gas to a temperature less than 1500°C. The tubular axially disposed quenching member 17 is utilized to bring a liquid, such as cold water, into the chamber downstream of the point where the auxiliary gas is added. The liquid rapidly quenches the mixture to a temperature in the range of 300° to 500°C in a period not exceeding 3 milliseconds. Carbon in the form of finely divided soot is formed, and forms a considerable portion of the exhaust product from the arc heater. If desired, the exhaust from the arc heater may be fed to a chamber 228 where the carbon in the form of soot is precipitated in any convenient manner, for example by electrostatic precipitation, and is removed as a useful product. Such an arrangement of structure is shown in FIG. 5 of the patent drawings, to which particular reference is made.

Referring again now to the process for continuous production of pyrolytic graphite, particular reference is made to FIG. 6 where the electrically actuated periodic scraper device for periodically removing pyrolytic graphite from the member 216 is shown at 221. Other devices for periodically removing graphite from cooled member 216 could be employed, and our invention is not limited to the one shown.

The periodic scraping device of FIG. 6 may be applied to the apparatus of FIGS. 3, 4A and 4B if desired to provide for the continuous production of pyrolytic graphite, means, not shown for convenience of illustration, being provided in FIG. 4B for periodically removing accumulated pyrolytic graphite from chamber 270.

It is to be noted that in many of the processes heretofore described, the formation and deposition of amorphous carbon as a first layer is in some cases a desirable and perhaps inherent step in the deposition of pyrolytic graphite, and that the two processes cannot be logically separated. To hasten the completion of this step, at the beginning of a run a quenching fluid can be temporarily used to quench the gas to a temperature of the order of 300° in accordance with teachings hereinbefore, and after a thermal barrier of amorphous carbon has been built up on the object to be coated or on the inside surface of the exhaust nozzle, the use of the quenching fluid can be discontinued, and adjustments made in arc current, the power of an alternating current arc, the mass flow rate of gas, the proportion of the hydrocarbon gas passing through the arc path, or any or all of the same, to create conditions which will enhance or optimize the deposition of pyrolytic graphite.

Whereas object 214 in FIG. 4A is hatched for a non-metallic refractory material, it will be understood that certain refractory metallic materials can be employed. Where refractory materials are used for objects 214 or 214a, the first deposit will not necessarily be a soot layer, depending on temperature conditions.

Another advantage of our processes is that there is no “race” in the cooling or quenching process to avoid the formation of undesirable recombination products. Generally speaking, the longer the residence time of the pyrolyzed gas in the arc chamber, the better the production of carbon, either soot or pyrolytic graphite.

General speaking, the lower the temperature difference between the gas stream and the surface to be deposited on, the better the crystalline structure of deposited pyrolytic graphite; the crystal sizes will be larger.
It will be understood that the fluid cooled object 214a of FIG. 4B may be used in FIG. 4A.

Whereas we have described our invention and processes relating to the deposit of pyrolytic graphite with reference to an average gas temperature of at least 1500°C and which may be of the order of 2000°C, deposit of pyrolytic graphite may occur at any temperature where both the average gas temperature and the surface temperature are maintained at values less than the sublimation temperature of pyrolytic graphite.

Our processes do not require the addition of oxygen or air to combine with the atoms of hydrogen liberated by pyrolysis to thereby increase the amount of free carbon.

The controlled atmosphere or reduced pressure step in our processes, which is exemplified by the apparatus of FIG. 4B, may be employed in any other processes described in connection with other figures of the patent drawings.

We claim as our invention:

1. A process for producing pyrolytic graphite comprising the steps of causing a hydrocarbon gas to flow in a predetermined path without reducing the pressure of said gas in said path below atmospheric pressure, producing a substantially continuously moving electric arc at a predetermined position in said path, the arc heating the gas and pyrolyzing the same and producing an average gas temperature of at least 1500°C, and at a position in said path downstream of the arc position placing an object having a melting temperature higher than the average gas temperature at that portion of the path and a cooled surface at an operating temperature below the sublimation temperature of carbon and less than the temperature of the heated gas to cause the carbon which is formed as a decomposition product to be precipitated in the form of amorphous carbon to form a thermal barrier and thereafter substantially all of the carbon formed being precipitated as pyrolytic graphite.

2. The process according to claim 1 including the additional step of periodically removing pyrolytic graphite from said object to provide a continuous process for the formation of pyrolytic graphite.

3. A method of coating an object with a layer of pyrolytic graphite comprising the steps of utilizing an electric arc to pyrolyze a hydrocarbon gas in the absence of oxygen without reducing the pressure below atmospheric pressure in a chamber having a well defined exhaust area for heated gas, the average temperature of the heated gas being at least 1500°C, and disposing a cooled object to be coated at the exhaust area and in the hot gas stream, the object to be coated having a melting temperature greater than the temperature of the gas and being maintained at an operating temperature less than the sublimation temperature of carbon and less than the temperature of the heated gas, the object to be coated having amorphous carbon first deposited thereon and thereafter having a coating of pyrolytic graphite deposited thereon.

4. A process according to claim 3 in which the gas is heated to an average temperature substantially above 1500°C Centigrade and including the additional step of maintaining the object to be coated at a temperature of at least 1500°C but less than the temperature of the gas whereby the pyrolytic graphite is deposited in a manner to adhere very strongly to the object.

5. A process for continuously obtaining pyrolytic graphite which comprises utilizing an electric arc in a confined space to decompose a hydrocarbon gas filling said confined space and produce an average gas temperature of at least 1500°C, causing the decomposed gas to flow in a stream through a well defined path while at least said average temperature, inserting a continuously cooled member cooled below 1500°C in the hot gas stream to produce a deposit thereon including a first layer of amorphous carbon adjacent the surface of the cooled member and pyrolytic graphite deposited on the layer of amorphous carbon.

6. A process according to claim 3 in which the object is substantially cylindrical and a cylinder of pyrolytic graphite is formed.

7. A process for producing pyrolytic graphite which comprises producing an arc which follows a predetermined path in an arc chamber having a well defined exhaust area, passing a first portion of a hydrocarbon gas into the arc chamber by a path which causes at least a substantial part of the gas of said first portion to pass through the arc path and to be pyrolyzed, passing a second portion of the hydrocarbon gas into said chamber by a different path whereby the second portion of the gas does not pass through the arc path, the first portion and the second portion being mixed by turbulent mixing after the first portion has passed through the arc path and producing an average gas temperature of at least 1500°C in the gas exhausted through the exhaust area, and placing an object to be coated with carbon in the path of gas exhausted from the exhaust area, the object having a temperature below 1500°C and below the sublimation temperature of carbon.

8. A process according to claim 7 in which the object to be coated with carbon is at a substantial temperature below the temperature of the gas, in which carbon in the form of soot is first deposited on the object forming a carbon surface in contact with the gas which carbon surface becomes increasingly close to the temperature of the gas as the thickness of the layer of soot is increased, the temperature difference between the carbon surface and the gas ultimately becoming so small that substantially all of the carbon thereafter deposited thereon is deposited in the form of crystalline pyrolytic graphite.