METHOD OF FORMING PYROLYTIC GRAPHITE SHEETS

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

Pyrolytic graphite is defined as a material made from carbonaceous gases by thermal decomposition or from a carbonaceous material formed by evaporation and deposition on a surface. In pyrolytic graphite, planar crystallites have a preferred orientation and are arranged so that their layers are generally parallel to the deposition surface. It would be desirable to provide sheets of pyrolytic graphite in varying thicknesses from bodies of such material. These sheets would have application as heating elements, gas-impermeable membranes, and wrapping material.

It is extremely difficult to separate mechanically these bodies into uniform thin sheets. Furthermore, the thickness of any such separated sheets cannot be controlled accurately. Thus, it would be desirable to provide improved methods of forming pyrolytic graphite sheets and to control their thicknesses.

It is an object of my invention to provide an improved method of forming pyrolytic graphite sheets.

It is another object of my invention to provide an improved method of forming annealed pyrolytic graphite sheets.

It is a further object of my invention to provide a method of forming sheets of uniform thickness from an annealed pyrolytic graphite body.

In carrying out my invention in one form, a method of forming a sheet comprises providing a body with a plurality of generally parallel first pyrolytic graphite layers, and with a second pyrolytic graphite layer with different properties between adjacent first pyrolytic graphite layers, contacting the body with an intercalation material thereby inserting the material in the second layers and decreasing the thickness of the second layers, and separating the first layers into sheets. 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 drawings in which:

FIGURE 1 is a sectional view of apparatus for forming a body in accordance with this invention;

FIGURE 2 is an elevational view of a body which was formed initially in the apparatus in FIGURE 1;

FIGURE 3 is a sectional view of the body shown in FIGURE 2 and taken on line 3—3 thereof;

FIGURE 4 is a sectional view of apparatus for contacting the body shown in FIGURE 2 with an intercalation material;

FIGURE 5 is a sectional view of the body partially separated into sheets;

FIGURE 6 shows a plurality of pyrolytic graphite sheets separated from the body shown in FIGURE 5;

FIGURE 7 is a sectional view of a portion of apparatus for annealing a body;

FIGURE 8 is a sectional view of apparatus for contacting the body annealed in the apparatus of FIGURE 7 with an intercalation material;

FIGURE 9 is a sectional view of the body shown in FIGURE 8 which is partially separated into sheets;

FIGURE 10 shows a plurality of pyrolytic graphite sheets separated from the body shown in FIGURE 9; and

FIGURE 11 shows a composite sheet composed of several sheets of FIGURE 10 pressed together.

In FIGURE 1, the drawing 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 12 by means of bolts 14 and employs an O ring 15 therebetween. Viewing window 6 is provided in cover portion 13 to view the operation and to read an optical pyrometer (not shown). An enclosure 17 of graphite or other high temperature material defines a chamber 18 communicating with a bottom opening 19 and a top opening 20. A feed line 21 is connected to a source (not shown) for carbonaceous material and extends therethrough to the bottom wall of body portion 12 and opening 19 in enclosure 17 to communicate with chamber 18 by means of outlet openings 22. Opening 20 of enclosure 17 is provided with a cover 23 having openings 24 therein for removal of fumes.

A pair of high temperature material plates, such as graphite plates 25, are hung within enclosure 17 by means of a flange 26 at one end of each plate 25. Each flange 26 is supported on cover 23 while its associated plate 25 extends through an opening 27 in cover 23 to be suspended within chamber 18 of enclosure 17. Passages 28 are defined by chamber 18 between adjacent plates 25 and between each plate 25 and its associated wall of enclosure 17. Suitable insulation such as carbon black 29 surrounds enclosure 17 and is held in position by a quartz or asbestos paper cylinder 30. Conventional induction heating coils 31 surround cylinder 29 to provide heat for enclosure 17, plates 25 and chamber 18 including passages 28 thereof during the deposition process. Body portion 12 of chamber 11 is also provided with an outlet 32 to which is connected a line 33 associated with a vacuum pump 34 to reduce the pressure in chamber 11.

In the operation of apparatus 10 shown in FIGURE 1, a pair of graphite plates 25 are supported within enclosures 17 by means of their respective flanges 26 on cover 23. In this manner, passages 28 are provided within chamber 18 between adjacent plates 25 and between each plate 25 and its associated wall of enclosure 17. Cover 13 is bolted to lower body portion 12 of chamber 11. The chamber atmosphere is reduced preferably to the lowest obtainable vacuum prior to admitting a gas, although the deposition process can be carried out over a wide range of chamber pressures such as 0.5 mm. to 760 mm. of mercury, at various gas flow rates.

In one method of forming bodies in accordance with the present invention on graphite plates 25, power is supplied to induction coil 31 to bring the temperature of enclosure 17, plates 25 and chamber 18 up to a temperature in the range of 1600° C. to 2500° C. prior to admitting a gas. A carbonaceous gas, such as methane, is fed through suitable metering devices (not shown) and feed line 21 with its associated outlet openings 22 into chamber 18 including passages 28. The carbonaceous gas is decomposed to a carbon vapor which deposits as a pyrolytic graphite layer on both sides of plates 25 and on enclosure 17. This layer is composed of a plurality of individual generally parallel pyrolytic graphite layers. This temperature range and the above pressure range are desirable to produce individual fine-grained pyrolytic graphite layers which are as free as possible from unusually large-particle-nucleated particles which create a microstructure known as coarse-grained "continuously nucleated" or "highly regenerative."

While induction coil 31 is used to heat the carbonaceous gas, enclosure 17, plates 25 and passages 28, the carbonaceous gas can be preheated from a separate heat source to the desired temperature to provide a carbon vapor which flows through feed line 21 into chamber 18. During the operation of apparatus 10, temperatures
are recorded by an optical pyrometer (not shown) which is viewed through window 16 in cover 13 of apparatus 10.

After a first layer of predetermined thickness of a plurality of individual layers thereof is deposited on both sides of plates 25, a perturbation is introduced into the deposition method whereby a second layer of pyrolytic graphite with different properties from the first pyrolytic graphite layer is deposited on the first pyrolytic graphite layer. This second pyrolytic graphite layer and its thickness are not critical since it is desired to form a plurality of first pyrolytic graphite layers of uniform or non-uniform thicknesses which will be separated subsequently into sheets. Such perturbations are introduced in various manners, such as changing the deposition conditions of pressure, temperature, or atmosphere for an interval sufficient to form a second pyrolytic graphite layer with different proportions. The deposition conditions are then returned to the initial conditions and another first pyrolytic graphite layer is deposited on the second layer. Alternate depositions are continued to produce a body with a plurality of generally parallel first pyrolytic graphite layers, and with a second pyrolytic graphite layer with different properties between adjacent first pyrolytic graphite layers. Such a body is of a desired thickness, such as in the order of 10 to 100 mils to 100 mils.

The method of supply and heating are discontinued, and apparatus 10 is allowed to cool to room temperature. The pressure is increased to atmospheric pressure and cover 13 is removed to provide access to enclosure 17. Plates 25 are removed from the enclosure by withdrawing the plates through the openings 27 in cover 23. The deposited body 35 is then removed from each side of each of the plates 25.

In FIGURE 2 of the drawing, there is shown a deposited body 35 which was formed initially in the apparatus of FIGURE 1. In FIGURE 3 of the drawing, there is shown a sectional view of body 35 along line 3-3 in FIGURE 2. Each generally parallel first pyrolytic graphite layer 36 is composed of a plurality of individual pyrolytic graphite layers. The alternate pyrolytic graphite layers 37 with different properties are shown between adjacent layers 36. These layers 37 are introduced as described above by the perturbation in the deposition method.

In FIGURE 4 of the drawing, apparatus 38 is shown for contacting body 35 with an intercalation material. Apparatus 38 includes a container 39, such as glass, with a solution 40 of an intercalation material, such as sulfonic acid. Body 35 is immersed in solution 40. I found unexpectedly that an intercalation material is inserted or added to the second pyrolytic graphite layers 37 when body 35 is contacted by, exposed to or immersed in such a material. I found further that such a material accepts or donates electrons from layers 37 thereby decreasing the strength of layers 37 and thus, the continuity between adjacent layers 36 resulting in partial or complete separation of layers 36.

An intercalation material is an element or compound in liquid or gaseous form which is an electron acceptor with high electron affinity or an electron donor with a low ionization potential. Such a material is inserted or added in a preferred manner to layers of one composition in a laminated body having layers of two different compositions. Such insertion or addition of this material is caused by the exposure, contact, or immersion of a body with the material. The addition of the material in the particular layers of the body decreases the strength thereof, thereby the continuity between adjacent other layers and causes partial or complete separation of the layers which do not include the material.

The amount of the material in liquid form in a liquid vehicle, its volume in gaseous form, or its concentration are not critical. The insertion or addition of the intercalation material in particular layers of a laminated body is observed visually by a separation of the other layers or a change of color in the body, thus, the time of exposure or temperature of immersion of the body with the material is not critical.

Various materials in liquid or gaseous form are suitable for employment as the intercalation material in the practice of the present invention. Examples of intercalation material which are suitable for this purpose are the following: HSO₄, K, Rb, Cs, Br₃, AlBr₃, AlCl₃, AuCl₃, BCl₃, CoCl₃, CrCl₃, CrO₃Cl₂, Cr₂O₃F₂, CuCl₃, CuBr₂, DyCl₃, EuCl₃, FeCl₃, GaCl₃, HCl₄, ICl, I₂Cl, InCl₃, MoCl₅, PCl₃, PbCl₄, ReCl₃, RhCl₃, RuCl₃, ScCl₃, SmCl₃, TaCl₅, TlCl₃, UCl₄, UO₂Cl₂, YCl₃, YbCl₃, and ZrCl₄.

In FIGURE 5, body 35 is shown removed from apparatus 38. It includes a plurality of pyrolytic graphite layers 36 with portions of layers 37 between adjacent layers 36. Areas 41 are separations between adjacent layers 36. Body 35 is washed with distilled water or heated at a temperature in the range of 300°C to 1500°C to break down or remove the remaining portions of layers 37. If desired, layers 63 can be separated into sheets after which they are washed with distilled water.

In FIGURE 6, there is shown a plurality of pyrolytic graphite sheets 42. These sheets 42 are formed from layers 36. These sheets are shown of uniform thickness although non-uniform sheets can also be formed as described above.

In FIGURE 7 of the drawing, there is shown a portion of apparatus for annealing a body produced in the apparatus of FIGURE 1. This apparatus includes an enclosure 43 consisting of commercial graphite 44 with a layer of pyrolytic graphite 45 on both surfaces thereof. Enclosure 43 defines a chamber 46 having an upper opening 47 closed by a cover 48 with a coating of pyrolytic graphite 49 thereon. Cover 48 has a central aperture therein into which a graphite tube 50 is positioned and extends outwardly from cover 48. The bottom of cover 48 carries a pair of clamps 51. Each of these clamps 51 positions a body 35 in chamber 46. Body 35, which is shown in more detail in FIGURE 3, is composed of a plurality of first pyrolytic graphite layers 36 with alternate second pyrolytic graphite layers 37 therebetween.

Enclosure 43 is positioned for example as shown in FIGURE 10 to replace enclosure 17 and feed line 21. If desired, body 35 in sheet or other configuration form can be placed on a support member within enclosure. If a body other than in sheet form is employed, it is desirable to position a weight against the body on the support member to retain the body in its form during subsequent annealing. A pile of spectroscopic carbon powder 52 is positioned on the bottom wall of enclosure 43 to provide material for sealing tube 50. A feed line 53 is connected to an argon or an inert gas source (not shown) and extends therefrom through the bottom wall of body portion 12 to communicate with chamber 11.

In the operation of the apparatus shown in FIGURE 1 as modified by the structure of FIGURE 7, power is supplied to induction coil 51 to heat chamber 46 and bodies 35 to a temperature of at least 2800°C and preferably in the range of 2800°C to 3800°C. Argon gas or an inert gas is supplied to chamber 11 through feed line 53. The gas is circulated through chamber 11 into chamber 46 by means of graphite tube 50. Initially, both chamber 11 and chamber 46 are at subatmospheric pressure.

When the elevated temperature range is reached and maintained, powder 52 evaporates and condenses on the interior surface of tube 50 thereby sealing chamber 46. Pyrolytic graphite coating 45 on the surfaces of enclosure 43 and coating 49 on cover 48 prevent the enclosure and cover from evaporating at this elevated temperature. After tube 50 has been sealed, the pressure within chamber 46 will be approximately at atmospheric pressure.
This elevated temperature transforms each body to an annealed body with a more perfectly oriented structure. After transformation of both bodies, the heat is discontinued and the apparatus is allowed to cool to room temperature. The argon atmosphere is flushed out of the chamber and the apparatus is disassembled. Annealed bodies are removed from enclosure. Each body is composed of a plurality of first pyrolytic graphite layers with alternate second pyrolytic graphite layers therebetween. These layers and correspond to layers and of body. The annealing of body at a temperature of at least 280° C. and preferably varies from 280° C. to 380° C. results in a body with superior crystalline perfection, preferred orientation and least structural defects. This annealing results in complete straightening of the individual layers. The orientation of the resulting body formed in accordance with this method is similar to a single crystal of the material. Additionally, the body has high strength and ductility in bending.

In FIGURE 8 of the drawing, apparatus is shown for contacting body, which was annealed in the apparatus of FIGURE 7. Apparatus includes a container as a glass, with a solution of an intercalation material, such as sulfuric acid.

Body is shown immersed in solution. The insertion or addition of the intercalation material in layers is observed visually by a separation of layers or a change of color. As described above in connection with body, the amount of the material in liquid form, its concentration and the time of immersion of the body are not critical. Body is immersed in the solution until partial or complete separation of layers occurs.

In FIGURE 9 of the drawing, body is shown removed from apparatus. It includes a plurality of pyrolytic graphite layers with portions of layers between adjacent layers. Areas are separations between adjacent layers. Body is washed with distilled water or heated at a temperature in the range of 300° C. to 1500° C. to break down or remove the remaining portions of layers. If desired, layers can be separated after which they are washed with distilled water.

Another method of forming a sheet comprises producing a pyrolytic graphite body in the apparatus of FIGURE 1 under the same conditions as body with the exception that no intercalation is performed. The resulting body with a plurality of generally parallel pyrolytic graphite layers is then annealed as described above in the apparatus of FIGURE 7. The annealed body with a plurality of generally parallel pyrolytic graphite layers is immersed in solution in container as shown in FIGURE 8. The intercalation compound will be inserted or added in the body between adjacent individual pyrolytic graphite layers. The insertion, which produced a decrease in strength between the layers is observed visually by an expansion in size of the body. The body is then removed from container and heated rapidly at a temperature in the range of 300° C. to 1500° C. in any suitable manner. The body expands about one hundred-fold upon this heating. After cooling, the body is separated into sheets by cutting to desired thicknesses. If desired, the sheets can be pressed into foils or formed into other shapes.

In FIGURE 10 of the drawing, there is shown a plurality of pyrolytic graphite sheets. These sheets are formed from washed layers which are dried. These ductile, annealed sheets are shown of uniform thickness although non-uniform sheets can be also formed as described above.

In FIGURE 11 of the drawing, a composite pyrolytic graphite sheet is shown. This sheet consists of a plurality of sheets which have been pressed together subsequent to their formation to produce a predetermined thickness.

Examples of methods of forming a sheet from a body in accordance with the present invention are as follows:

Example I

Apparatus is set up in accordance with FIGURE 1 of the drawing wherein both the enclosure and the plates are composed of commercial graphite. The cover is affixed to the lower body portion and the chamber atmosphere is reduced at a pressure of 0.001 mm. of mercury by the pump. Power is supplied to the induction coil which heats the enclosure, plates and passages to an uncorrected optical pyrometer temperature reading of about 2300° C. A carbonaceous gas in the form of methane is supplied at the rate of 33 cubic feet per hour through the feed line to the enclosure. The gas is formed into a carbon vapor in the enclosure which vapor is deposited uniformly on both the plates and on the interior enclosure wall as it flows through the enclosure chamber at a pressure of approximately 18 mm. of mercury.

Under the above conditions, a pyrolytic graphite body of 30-mil thickness would be formed on each surface of each plate after about 60 minutes. To provide a plurality of sheets of uniform thickness from this body. Accordingly, the above conditions are maintained for a period of about two minutes to produce a first 1-mil thick pyrolytic graphite layer. The rate of the methane being supplied to the enclosure is then cut off for a period of several seconds. This change in the deposition conditions results in a second pyrolytic graphite layer with different properties deposited on the first pyrolytic graphite layer. The gas rate is then adjusted to its initial layer of 33 cubic feet per hour for an additional two minutes to produce another 1-mil thick pyrolytic graphite layer. This procedure is continued for approximately 20 minutes during which 10 first pyrolytic graphite layers of 1-mil thickness each are produced with a second pyrolytic graphite layer with different properties between adjacent first pyrolytic graphite sheets. The power and gas flow are then discontinued and the chamber is restored to atmospheric pressure.

After cooling to room temperature, the chamber cover is removed. The plates, which are coated with a laminated pyrolytic graphite body on both sides, are removed from the enclosure. The laminated pyrolytic graphite body is removed from each surface of each sheet and has a thickness of about 13 mils.

A one inch square. The center of one of these laminated pyrolytic graphite bodies which has a thickness of 13 mils is placed in a container with an intercalation material consisting of a sufficient amount of concentrated sulphuric acid to which has been added a small non-critical amount of nitric acid to immerse the body completely therein. The body is immersed in this solution for a sufficient period of time until the intercalation material is inserted in the second pyrolytic graphite layers. Certain layers in the body turn blue indicating visually the insertion of the intercalation material and the first pyrolytic graphite layers separate partially. Therefore, it is not necessary to preserve a specific time period.

The body is then removed from the solution and the layers of pyrolytic graphite which are of 1 mil thickness each, are readily separated one from the other into pyrolytic graphite sheets. After the separation, the individual sheets are washed with distilled water and dried.

Example II

A 10 mil thick pyrolytic graphite body is formed on each side of each plate in the apparatus of FIGURE 1 in approximately 20 minutes. The method of Example I is followed to produce a pyrolytic graphite body. However, the deposition conditions are not interrupted to provide second pyrolytic graphite layers of different proper-
ties between the first adjacent layers of pyrolytic graphite. One of the pyrolytic graphite bodies produced in the apparatus of Figure 1 is supported in the enclosure as shown in Figure 7 and placed in the apparatus described in Figure 1. This body is subjected to a temperature of 3600° C. for one hour in an argon atmosphere. The heat is discontinued and the apparatus is allowed to cool to room temperature. The pyrolytic graphite body, which is removed from the enclosure, provides an annealed pyrolytic graphite body with a more perfect oriented structure.

This body is then immersed completely in an intercalation material consisting of a concentrated sulphuric acid solution to which a small amount of nitric acid had been added. The body is retained in the solution for a period of time sufficient to turn the body to a blue color which indicates the insertion of the material between adjacent individual pyrolytic graphite layers. The body expands ten-fold during immersion. After the body is removed from the solution, it is heated rapidly to a temperature of 1300° C. providing a further expansion to about one hundred-fold. The body is then cut into plurality of pyrolytic graphite sheets.

The annealed pyrolytic graphite body produces a plurality of thin pyrolytic graphite sheets.

A number of the sheets from this pyrolytic graphite body are pressed together gently by hand and provide a thicker composite sheet of pyrolytic graphite. In this manner it is possible to produce a desired thickness very easily from the thin pyrolytic graphite sheets.

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

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

1. A method for forming a sheet which comprises providing a body with a plurality of generally parallel first pyrolytic graphite layers, and with a second pyrolytic graphite layer with different properties located between each pair of adjacent first pyrolytic graphite layers, contacting said body with an intercalation material, said intercalation material being a fluid selected from the group consisting of an electron acceptor material with high electron affinity and an electron donor material with low ionization potential and the continuity between said first layers, and separating said first layers into sheets.

2. A method for forming a sheet which comprises providing a body with a plurality of generally parallel first pyrolytic graphite layers, and with a second pyrolytic graphite layer with different properties located between each pair of adjacent first pyrolytic graphite layers, annealing said body at a temperature in the range of 2800° C. to 3800° C., contacting said body with an intercalation material, said intercalation material being a fluid selected from the group consisting of an electron acceptor material with high electron affinity and an electron donor material with low ionization potential, whereby said intercalation material enters said second layers decreasing the strength thereof and the continuity between adjacent first layers, and separating said first layers into sheets.

3. A method of forming a sheet which comprises depositing a first layer of pyrolytic graphite, depositing a second layer of pyrolytic graphite with different properties on said first pyrolytic graphite layer, depositing subsequent alternate first and second pyrolytic graphite layers to form a body, contacting said body with an intercalation material, said intercalation material being a fluid selected from the group consisting of an electron acceptor material with high electron affinity and an electron donor material with low ionization potential, whereby said intercalation material enters said second layers decreasing the strength between said first layers, and separating said first layers into sheets.

4. A method of forming a sheet which comprises depositing a first layer of pyrolytic graphite, depositing a second layer of pyrolytic graphite with different properties on said first pyrolytic graphite layer, depositing subsequent alternate first and second pyrolytic graphite layers to form a body, annealing said body at a temperature in the range of 2800° C. to 3800° C., contacting said body with an intercalation material, said intercalation material being a fluid selected from the group consisting of an electron acceptor material with high electron affinity and an electron donor material with low ionization potential, whereby said intercalation material enters said second layers decreasing the strength between said first layers, and separating said first layers into sheets.

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