May 6 1969 M. TURKAT ET AL 3,442,617

METHOD FOR DEPOSITING PYROLYTIC GRAPHITE

Filed June 28, 1967 Sheet 1 of 2

Fig. 1.

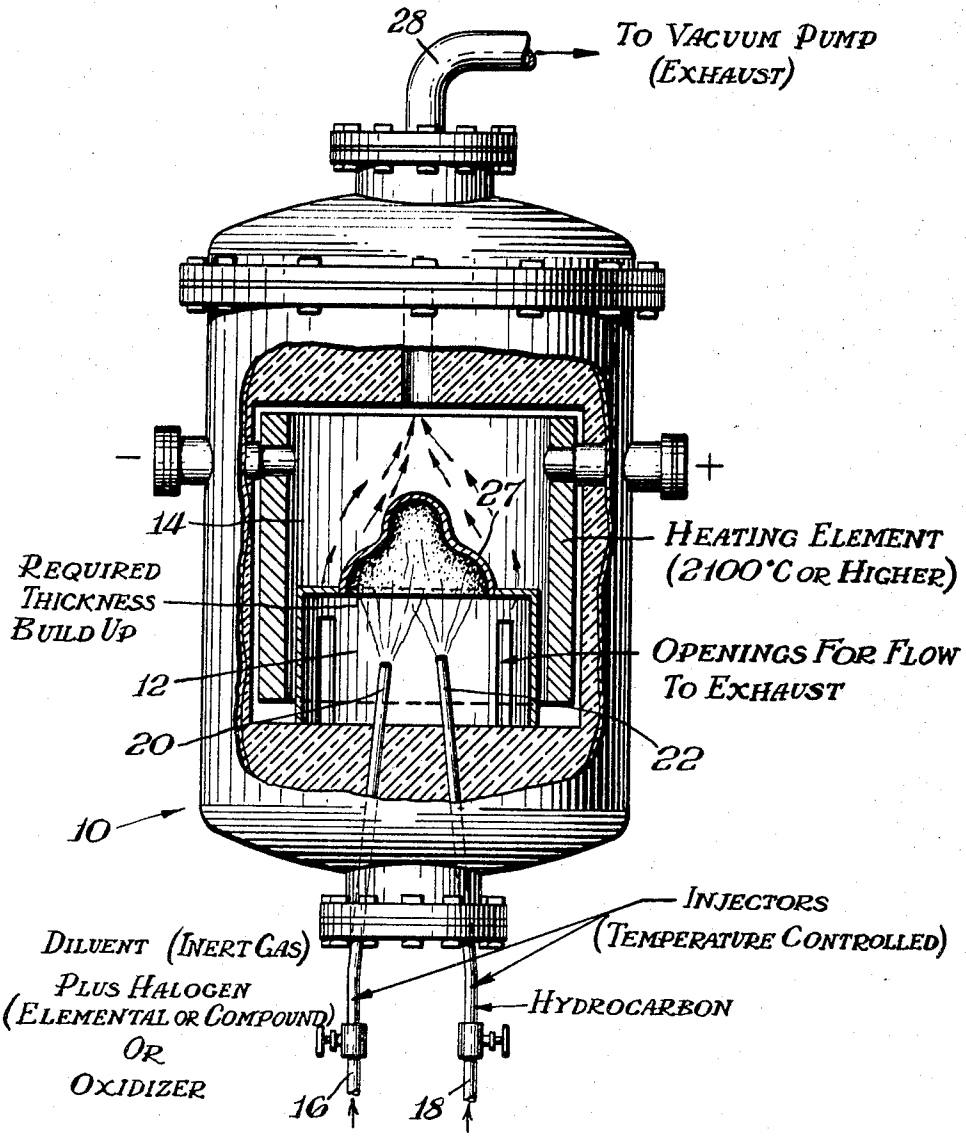
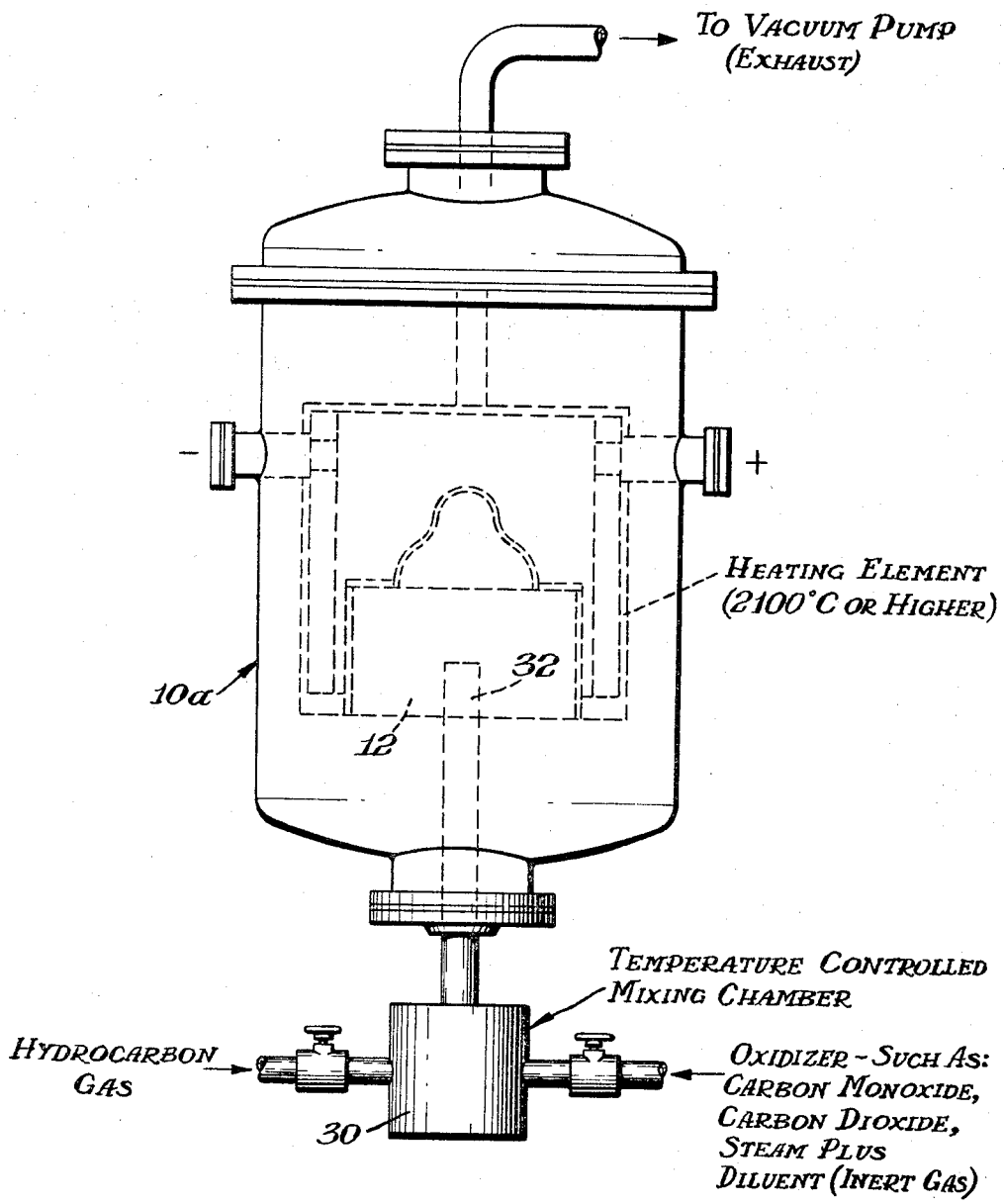


Fig. 2.


TO VACUUM PUMP
(EXHAUST)
HEATING ELEMENT
(2100°C OR HIGHER)
10a
32
12
TEMPERATURE CONTROLLED
MIXING CHAMBER
HYDROCARBON
GAS
OXIDIZER - SUCH AS:
CARBON MONOXIDE,
CARBON DIOXIDE,
STEAM PLUS
DILUENT (INERT GAS)
30

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METHOD FOR DEPOSITING PYROLYTIC GRAPHITE

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Int. Cl. C01b *31/00*

U.S. Cl. 23—209.1 2 Claims

ABSTRACT OF THE DISCLOSURE

A deposition method for making pyrolytic graphite whereby there are achieved unusually thick deposits in complex shapes, and rates of deposition greatly in excess of those heretofore attainable. The method involves high-temperature oxidation or halogenation of a hydrocarbon with concurrent thermal reduction. Preferred conditions utilize acetylene as the hydrocarbon, temperatures of 1900° C. or higher and furnace pressures of 1 to 6 mm. Hg absolute, and result in deposition rates of 17 to 60 mils per hour.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of our earlier copending application, Ser. No. 345,487 filed on Feb. 17, 1964, now abandoned.

The present invention comprises a novel method for depositing pyrolytic graphite.

Pyrolytic graphite is pure polycrystalline graphite which has conventionally been deposited upon a substrate or mandrel by a carbon bearing vapor at temperatures at about or in excess of 2000° C. The crystalline structure of pyrolytic graphite is evidenced by an unusually high degree of preferred orientation, the crystal lattice forming a lamination of layer planes ordinarily substantially parallel to each other and, where a mandrel is used, substantially parallel to the surface of the mandrel. Its physical properties are such that it may be utilized wherever environmental extremes of high temperature stress and erosion are experienced, as in missile nose cones and rocket thrust nozzles.

Heretofore the method for manufacturing pyrolytic graphite has been to crack a hydrocarbon bearing gas such as methane, propane or benzene at reduced pressures, at temperatures approximating and above 2000° C. Rates of deposition thus realized have ranged between 5 and 40 mils of pyrolytic graphite per hour. The product usually obtained in the upper region of such range of deposition rates—i.e., 20 to 40 mils per hour—is generally of poor quality, having disordered crystalline growth and having nodule formations resulting from the creation of soot particles caused by gas phase nucleation.

Better quality material has been obtained with chemically pure methane at lower regions of such range of deposition rates—i.e., 6 to 10 mils per hour—in the production of flat plates of pyrolytic graphite, but in curved pieces, the long time required to produce thick portions causes growth stresses which cause excessive delamination and cracking on internal surfaces of the curved pieces, whether they be produced on male or female mandrels. For this reason, it has heretofore been impossible to produce massive deposits of pyrolytic graphite without excessive growth stresses and resultant cracks. General limitations on deposit thickness have been about 1¼ inches for plates and less than ¼ inch for coated or curved structures for radii of curvature less than 6

inches. Heretofore it has been extremely difficult, if not impossible, to produce thick complex shapes on specially designed mandrels due to growth and anisotropy stresses which combine to delaminate and crack the product.

Accordingly, the present invention provides methods for the manufacture and formation of pyrolytic graphite having rates of deposition greatly in excess of those heretofore attainable.

The present invention also provides methods for the manufacture and formation of pyrolytic graphite of quality superior to that heretofore attainable, such material having very high purity, well ordered and uniform crystalline growth, having negligible or no nodule formations and having extremely little soot.

The present invention further provides a method for the manufacture and formation of massive bulk deposits of pyrolytic graphite, such deposits having no structural defects such as excessive growth stresses or internal surface cracks. The first bulk deposit of pyrolytic graphite made according to the present invention had a diameter of approximately 7 inches with much larger and more massive deposits being foreseen.

The present invention still further provides methods for the manufacture and formation of pyrolytic graphite which, although possibly containing delaminations at room temperature, maintains its structural integrity at high temperatures and under severe environmental conditions due to the conformity and tightness of its planes.

In the drawing:

FIGURE 1 is a partially cut-away representation of an electric furnace showing a method of introduction of reactants into the deposition chamber.

FIGURE 2 is a phantom representation of the furnace of FIGURE 1, showing a second method of introduction of reactants into the deposition chamber.

Referring to the drawing, an electric furnace **10** has heating elements capable of heating the interior of furnace **10** to 2100° C. or higher. The interior of furnace **10** contains a deposition chamber **12** and an exhaust chamber **14**, the latter disposed generally above the former. Two injectors **16**, **18** extend from outside furnace **10** to deposition chamber **12**, both of said injectors ending in said deposition chamber **12** and having, respectively, nozzles **20**, **22** at such ends. Injectors **16** and **18** are normally made from stainless steel and, because of the high temperatures experienced within furnace **10**, are water cooled to prevent melting. Other materials, such as graphite, are also used. An exhaust tube **28** extends from exhaust chamber **14** to a vacuum pump outside furnace **10**.

The reactions utilized in the present invention involve the oxidation or halogenation of a hydrocarbon alone or in combination with thermal reduction of the hydrocarbon.

The typical formula for thermal reduction of a hydrocarbon is:

(A) hydrocarbon+heat→carbon+hydrogen

The typical formulae for oxidation of a hydrocarbon are:

(B) hydrocarbon+oxygen→carbon+hydrogen oxide
(C) hydrogen+oxygen compound→carbon+hydrogen oxide

The typical formulae for halogenation of a hydrocarbon are:

(D) hydrocarbon+halogen→carbon+hydrogen halide
(E) hydrocarbon+halogen compound→carbon+hydrogen halide

One aspect of this invention is the thermal reduction of acetylene under specific process conditions. Although the

use of acetylene as a hydrocarbon source gas for the production of pyrolytic graphite has been published many times, the results achieved have never been very satisfactory or at most have been only equivalent to the results achieved by using other hydrocarbons such as methane. For the most part, any attempts to duplicate the production of pyrolytic graphite with acetylene by using process conditions similar to those of methane have resulted in an inferior product. For this reason the standard gas used for the manufacture of pyrolytic graphite has been methane or, if economy is more important than high purity, natural gas has been used.

We have discovered that, by using acetylene at certain pressures and with certain flows, it is possible to obtain a rapid deposition rate which produces pyrolytic graphite of superior quality. Specifically, in the temperature range 1900° C. to 2300° C. with a flow of acetylene such as to maintain a furnace pressure of between 1 mm. and 6 mm. Hg absolute pressure (0 mm. Hg being full vacuum), a deposition rate of between 17 and 60 mils per hour is obtained. The deposition rate is strongly dependent upon pressure, volume, hydrocarbon concentration, temperature and area. High pressures (e.g., 4.5 mm.), flow 7 l.p.m., in small volumes (e.g., 0.25 cubic foot) at high temperature (e.g., 2100° C.) can produce deposition rates of 50 to 60 mils per hour, but these conditions are close to sooting and so it is safer to operate at 3.5 mm., flow 5 l.p.m., in 0.25 cubic foot at 2100° C. wherein the deposition rate will be approximately 25 to 30 mils per hour and higher quality material results.

Numerous test runs are recorded which substantiate these results. An extremely important consequence of this rapid deposition rate is the reduced effect of growth stresses which permit those who use this invention to make thicker and heavier pieces of pyrolytic graphite without internal cracking, though delamination of layers is still present. Growth stresses result when pyrolytic graphite deposited initially is held at its deposition temperature while additional layers are depositing. The initial layers expand while soaking at such temperature, thus stressing the material that is put down later and aggravating the stress problem upon cool down. Thus the shorter the time required for deposition the more uniform will be the material deposited, and there will be less stress upon cool down. Anisotropy stresses will still be present, but these are reduced by applying another technique pertaining to this invention, that is, the use of temperature programming to reduce residual stresses in the material. This programming relieves stresses by counteracting mandrel stress when using internal or so-called female-type mandrels. This is done by increasing the temperature during the run. This increase also relieves growth stresses. A typical case using acetylene would start depositing at 1950° C. and raise the temperature 25° C. every 3 hours until, in 24 hours, the temperature is 2150°. At a deposition rate of 25 mils per hour average, 0.6 inch of pyrolytic graphite have been produced. Normally with methane it would take from 60 to 120 hours to produce the same thickness. It has also been found in this invention that slow cool down is important, since it helps distribute remaining residual stresses more uniformly.

The inclusion of diluents, hydrocarbon or non-carbon containing, in the acetylene stream is useful in achieving optimal deposition rates, greater evenness of deposition and in producing a higher quality of pyrolytic graphite. When inert, non-carbon containing diluents are used to improve the evenness of deposition, the average deposition rate, with the diluent, remains substantially equivalent to the average deposition rate, without diluents, at any given acetylene partial pressure. The total pressure, of course, will be increased where diluents are used together with acetylene at a constant partial pressure of acetylene. Suitable inert diluents include nitrogen, argon or helium. Hydrogen, which may affect the reaction, may also be used. Where diluents of any type are used the acetylene partial pressure should be held at 1 to 6 mm. Hg.

It has further been found that where hydrocarbon diluents such as methane are used, the deposition rate with methane as a diluent is higher than the deposition rate with non-hydrocarbons as diluents, at the same partial pressure of acetylene. Consequently, the use of methane or another hydrocarbon as a diluent enables the production of more even deposits of pyrolytic graphite at deposition rates somewhat higher than that which are achievable with the use of inert diluents at the same partial pressure of acetylene. A convenient and economical source of methane for this purpose is natural gas.

Other hydrocarbons may also be used as carbon containing diluents. These include, but are not limited to, propane, butane and benzene. Generally, hydrocarbons containing from one to six carbon atoms may be used.

Another aspect of this invention is the use of an activator in conjunction with a hydrocarbon. The hydrocarbons normally used include acetylene, benzene, propane and butane.

The addition of a second gas (oxygen, oxygen compound, halogen or halogen compound) to the hydrocarbon increases or accelerates the rate of deposition and, when appropriate compounds are used, supplies additional carbon for deposition. The activator or reaction agent used must not cause gas phase reduction of the hydrocarbon to carbon, but rather must accelerate the removal of hydrogen from the deposition surface **27** by combining with the hydrogen where the reaction is taking place.

Certain of the reactions employed may occur at room temperature. It is therefore undesirable to allow the reaction to take place outside deposition chamber **12** as soot will form, detracting from both the quality and quantity of the pyrolytic graphite. It is mainly for this reason that injectors **16** and **18** extend into deposition chamber **12** and prevent contact between the reactants until the last moment. An example of such a reaction is Example 3 below.

Additional reasons for using multiple injectors include more uniform distribution of the gases in the working region, the reduction of gas phase nucleation and a directable stream impinging upon the deposition surface.

For reactions which occur too slowly, even at the high temperatures prevalent in deposition chamber **12**, a mixing chamber **30** is used before the reactants reach deposition chamber **12**. Such reactions typically are hydrocarbon oxidations. With mixing chamber **30** only one injector **32** is required. Other physical and mechanical aspects of a furnace **10***a* using such a mixing chamber **30** are similar to those of furnace **10**.

Examples of reactions are:

(1) $C_2H_2+Q\rightarrow 2C+2H\uparrow$
(2) $C_2H_2+Cl_2\rightarrow 2C+2HCl\uparrow$
(3) $2C_2H_2+CCl_4\rightarrow 5C+4HCl\uparrow$
(4) $C_2H_2+CO\rightarrow 3C+H_2O\uparrow$
(5) $CH_4+2I_2\rightarrow C+4HI\uparrow$

Example 1 is the thermal reduction, or cracking, of the hydrocarbon. In Example 2 a halogen has been added as an activator. In Example 3 a carbon halogen compound has been added to act as an activator, and to supply additional carbon for deposition. Examples 4 and 5 are additional typical reactions.

Examples of the results obtained are as follows.

Example I

One injector introduced C_2H_2 at 4.0 liters per minute, and the other injector introduced the inert gas argon at 0.1 liter per minute. Temperature was 2100° C., furnace pressure was 3.5 mm. Hg absolute, and area of deposition surface approximately 10 square inches. The deposition rate was found to be 20 mils per hour.

Example II

Conditions of Example I above were duplicated. C_2H_2 was again introduced at 4.0 liters per minute. Chlorine

replaced the argon and was similarly introduced at 0.1 liter per minute. The deposition rate was 40 mils per hour.

Example III

Conditions of Example I above were duplicated. Chlorine was introduced at a constant 0.1 liter per minute. C_2H_2 was introduced initially at 7.5 liters per minute and reduced by 0.5 liter per minute every two hours after the start. The average deposition rate was 65 mils per hour.

Example IV

One injector introduced acetylene into the furnace at 4.0 liters per minute and the other injector introduced methane at 2.0 liters per minute. The furnace temperature was 2100° C., and the total furnace pressure was 4.5 mm. Hg absolute. The deposition rate was found to be 25 mils per hour with an overall deposited carbon yield of 90% based on carbon initially contained in the acetylene.

The pyrolytic graphite obtained as described in the above runs was of good quality, having a density of 2.2 gm./cm.^{3} and low nodule content.

There is normally injected with the reactants a diluent gas such as hydrogen or a hydrogen, inert gas combination.

What is claimed is:

1. A deposition method of making high quality pyrolytic graphite, comprising the steps of: cracking acetylene under a pressure of about 2.5–5 mm. Hg absolute, at a temperature above 2000° C., in the presence of an activating amount of a halogenating agent selected from the group consisting of halogen and those compounds of halogen which combine with hydrogen to remove it at the deposition surface but do not cause gas phase reduction of the acetylene; removing the gaseous product of the cracking; and collecting the solid pyrolytic graphite product thereof on a deposition surface; all three steps occurring concurrently and at the point of contact with the deposition surface.

2. The method of claim 1 wherein the activating agent is chlorine.

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