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[54] **PROCESS FOR EXPANDING PYROLYTIC GRAPHITE**

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[58] **Field of Search** ..... 264/29, 43, 42; 23/209.1 P, 209.2

[56] **References Cited**

UNITED STATES PATENTS

3,297,406	1/1967	Diefendorf	23/209.2

FOREIGN PATENTS OR APPLICATIONS

991,581	5/1965	United Kingdom	23/209.1

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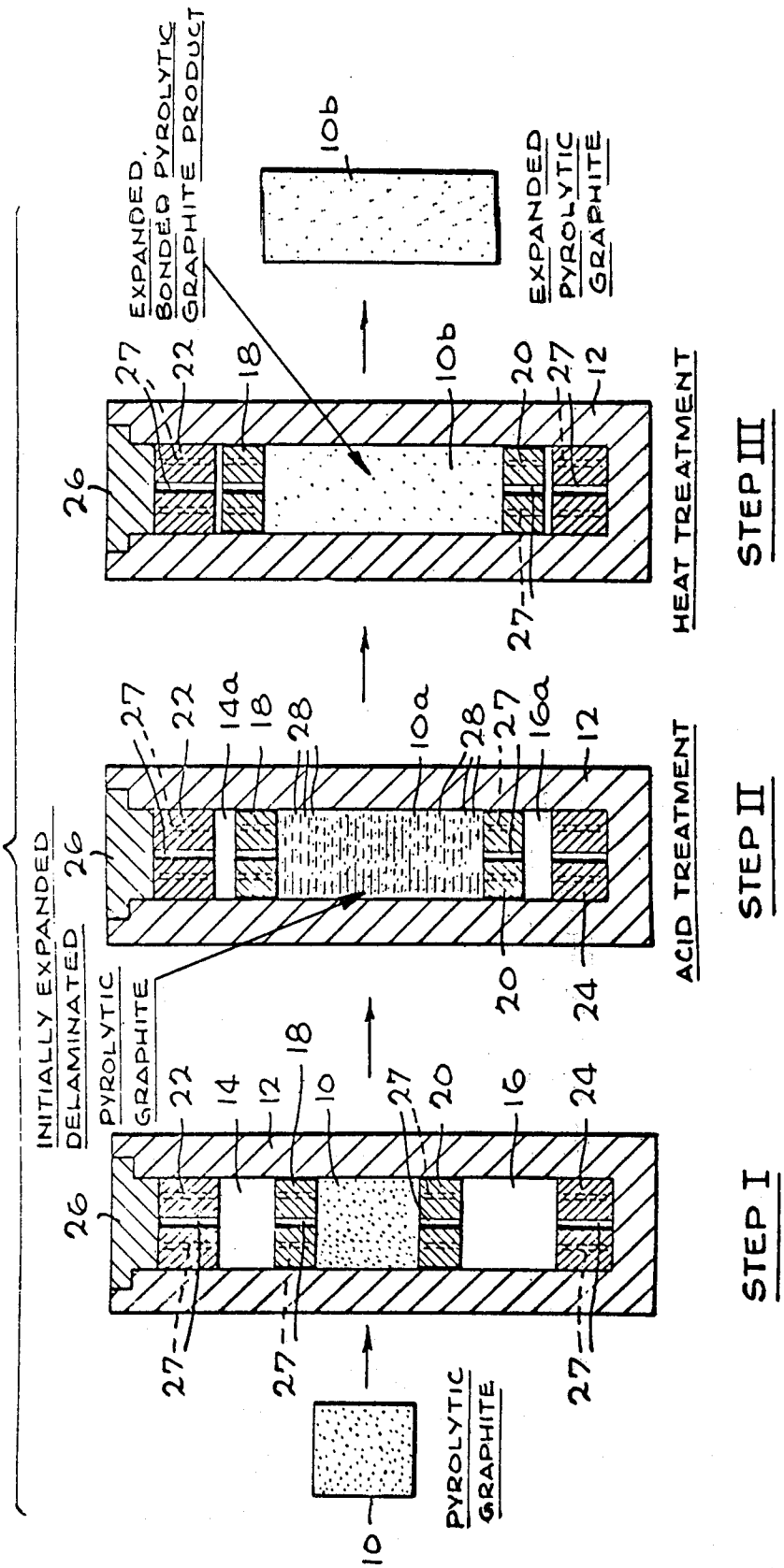
[57] **ABSTRACT**

Improved uniformly expanded pyrolytic graphite, useful particularly as insulation material, e.g. heat insulator or heat shield, by a process comprising treating pyrolytic graphite with an intercalating agent, preferably a mixture of nitric and sulfuric acids, to cause the pyrolytic graphite to expand in a controlled manner only in the direction normal to the deposition surface (the c-direction) and continuing such treatment for a period sufficient to substantially completely delaminate the expanded pyrolytic graphite, and heating such delaminated expanded pyrolytic graphite under conditions constraining movement in the direction parallel to the deposition surface (the a-b direction) and permitting movement in the c-direction, to cause the delaminated expanded pyrolytic graphite to expand further to a controlled extent in the c-direction, forming an integral bonded expanded pyrolytic graphite expanded, e.g. from about 1 to about 10 times or more its original dimension in the c-direction.

10 Claims, 3 Drawing Figures


INITIALLY EXPANDED DELAMINATED PYROLYTIC GRAPHITE
PYROLYTIC GRAPHITE
EXPANDED, BONDED PYROLYTIC GRAPHITE PRODUCT
EXPANDED PYROLYTIC GRAPHITE
ACID TREATMENT
HEAT TREATMENT
STEP I
STEP II
STEP III

PROCESS FOR EXPANDING PYROLYTIC GRAPHITE

This invention relates to production of improved expanded pyrolytic graphite, and is particularly concerned with procedure for producing uniformly expanded pyrolytic graphite by controlled expansion employing intercalating agents for initially expanding and delaminating the pyrolytic graphite, and further treating such expanded and delaminated pyrolytic graphite under controlled conditions to bond the delaminated layers together into an integral uniformly expanded pyrolytic graphite, and with the resulting improved uniformly expanded pyrolytic graphite product thus formed.

Pyrolytic graphite is produced by the pyrolytic deposition process wherein at a suitable pressure, a hydrocarbon gas, e.g. methane, natural gas or benzene, is thermally decomposed at the surface of a substrate of suitable shape, size and material, e.g. graphite heated for example by induction or resistance means to temperatures ranging from between about 1500°C and 3000°C. Under these conditions, as the hydrocarbon gas is thermally decomposed, pure carbon atoms are deposited layer by layer on the substrate. As the carbon atoms are deposited they link up to form layer planes of hexagonal arrays or networks of carbon atoms. These layer planes of hexagonally arranged carbon atoms are oriented so as to be parallel to each other and to the surface of the substrate upon which they are deposited. The sheets or layers of carbon atoms, usually referred to as basal planes, are linked or bonded together, the number and sizes of basal planes increasing as the deposition temperature increases.

The pyrolytic graphite material thus formed is spectroscopically pure carbon, approaches theoretical density, i.e. 2.266, is monolithic, free of voids or pores, is gas impervious, has a tensile strength of about 1200 psi and is anisotropic. Pyrolytic graphite may be characterized as a laminated structure of graphite composed of parallel basal planes of carbon atoms in hexagonal arrays, the basal planes also tending to be oriented parallel to the substrate or surface of deposit. In considering the pyrolytic graphite structure, two directions are usually noted, i.e. the "a" or "a-b" direction which is parallel to the deposition surface, and the "c" direction, which is normal or perpendicular to the deposition surface.

Although pyrolytic graphite prepared under normal conditions has a high degree of preferred crystallite orientation, it often exhibits disorder or random orientation between the carbon hexagon networks or layers which lie parallel to one another. For example, such interlayer disorder may comprise layer stacking defects. Additionally, pyrolytic graphite may exhibit some rotational disorder, e.g. the continuous atomic planes, though parallel to each other, may be wrinkled or buckled. Pyrolytic graphite can be treated to eliminate such defects to produce pyrolytic graphite having a well ordered structure, by utilizing higher deposition temperatures or by converting or transforming it to a more perfect graphite structure by heat treating or annealing for a period of time of from about 1 to about 5 hours at a temperature, e.g. between 2500°C and about 3600°C.

The bonding forces holding the parallel layer planes of pyrolytic graphite together are only small or weak van der Waals forces. It has heretofore been found that the weak bonding forces between the parallel layer planes can be attached so that without affecting complete separation of layers, spacing between layers can be appreciably opened up to provide a marked expansion in the direction perpendicular to the layers, that is, in the c-direction, and thus form an expanded coherent pyrolytic graphite structure in which the laminar or lamellar character is substantially retained. Thus, as described in British Pat. No. 991,581, pyrolytic graphite may be expanded so as to produce expanded structures having a thickness or c-direction dimension which can range from 2 times to 125 times the original dimension. The resulting expanded pyrolytic graphite retains or possesses anisotropic features.

Expanded pyrolytic graphite has substantial utility. Thus, it can be employed as insulation material, e.g. bulk insulation material. It can be employed for low temperature or cryogenic insulation or as a heat insulator, e.g. as a heat shield. The expanded low density pyrolytic graphite has particular utility as a light weight bulk heat insulator, e.g. in aeronautical applications, and in high temperature furnace structures such as heat treating or annealing furnaces and metal producing furnaces. Expanded pyrolytic graphite can also be utilized in producing various composite structures.

Expanded pyrolytic graphite can be produced by first forming a lamellar compound of pyrolytic graphite as by treatment with various intercalation agents such as halogens, metal halides or an acidic mixture of sulfuric and nitric acids, and following intercalation, heat treating the resulting lamellar compound of pyrolytic graphite.

In conventional processes for producing expanded pyrolytic graphite by procedure of the type described briefly above, and which do not provide suitable constraint in order to obtain controlled expansion, such procedure depends critically on the quality of pyrolytic graphite starting material and the time lapse period during chemical treatment, e.g. with the above noted intercalating agent. If the pyrolytic graphite is highly oriented it will delaminate within a few minutes upon treatment with the intercalating agent. However, if the pyrolytic graphite has relatively poor orientation properties, a greater time period of the order of several minutes of chemical treatment may be necessary for this purpose. Since pyrolytic graphite quality varies substantially from one material to another, prior art procedure for producing consistent uniformly expanded pyrolytic graphite becomes highly complex and impractical, requiring the use of only certain types of pyrolytic graphite in which the degree of orientation is restricted to be within a certain maximum and a certain minimum value. Regardless as to the care in selecting a suitable pyrolytic graphite, in prior art processes wherein treatment with the intercalating agent is permitted to proceed so as to obtain only partial delamination, prior to heat treating, inconsistent results in the nature of a non-uniformly expanded pyrolytic graphite product, whose density is difficult to control, is obtained.

According to the present invention, a basically simple process is provided which yields consistent results in producing uniformly expanded pyrolytic graphite of good quality and of controlled density, and which is relatively independent of the quality of the initial pyrolytic graphite starting material. As a particular feature of the present process, the chemical reaction between the pyrolytic graphite and the intercalating agent is per-

mitted to continue until the pyrolytic graphite has delaminated to the maximum extent, that is, until the pyrolytic graphite is substantially completely delaminated. By such procedure, it is not required to exercise great care regarding the duration of treatment with the intercalating agent, e.g. acid treatment employing a mixture of sulfuric and nitric acids. In the present process, expanded pyrolytic graphite is consistently produced which is uniformly expanded and with the desired density, without the above noted stringent restrictions with respect to the nature and properties of the pyrolytic graphite starting material. Thus, the present invention provides a simplified and more practical procedure for producing uniformly expanded pyrolytic graphite. The process of the present invention permits reproducible results to be consistently obtained, and the product, expanded pyrolytic graphite, can be produced with a variety of densities, has highly anisotropic properties, has relatively good strength, and is stable to temperatures above 2000°C.

Briefly, the invention accordingly provides a process for expanding pyrolytic graphite, which comprises treating the pyrolytic graphite with an intercalating agent to cause the pyrolytic graphite to expand in the direction normal to the deposition surface (the c-direction) while constraining movement in the direction parallel to the deposition surface (the a-b direction), and continuing such treatment for a period sufficient to substantially completely delaminate the expanded pyrolytic graphite, and heating the delaminated expanded pyrolytic graphite while permitting movement of said expanded pyrolytic graphite in the direction normal to the deposition surface and constraining movement in the direction parallel to the deposition surface, to cause said delaminated expanded pyrolytic graphite to expand further in the c-direction.

As previously noted, it is preferred for obtaining most consistent results, to employ as starting material pyrolytic graphite which has been annealed at temperatures between about 2500° and about 3600°C, preferably at about 3100°C or higher. However, it is understood that pyrolytic graphite which has not been annealed can also be employed in the invention process for producing the improved expanded pyrolytic graphite thereof.

Various intercalating agents can be employed for treatment and expansion of the pyrolytic graphite. Examples of some of the atomic and molecular species that intercalate pyrolytic graphite are Na, K, Rb, Cs, F, Cl, Br and I; $CuCl_2$, $CuBr_2$, $AuCl_3$; chlorides of B, Fe, Cr, Co, Ru, Al, Ga, In and Tl; $AlBr_3$, $ZrCl_4$, $CoCl_4$, $RuCl_4$, $HfCl_4$, $SbCl_5$, $TaCl_5$, $MoCl_5$, WCl_6, UCl_4, $ReCl_4$, CrO_2F_2 and UO_2Cl_2; Tl_2S, Sb_2S_5, CuS, FeS_2, and CrO_3. It is accordingly seen from the above exemplary intercalating agents, that interlayer attack can be accomplished, for example, by means of intercalating agents such as halogens and metal halides, e.g. those exemplified above, including metal chlorides, iodides or bromides, generally in the form of solutions. Also acids and oxidizing agents can be employed to effect interlayer attack and to open up or spread apart the layers of pyrolytic graphite by such chemical treatment, including in addition to various chlorates such as potassium chlorate, also, for example, nitric acid, permanganates such as potassium permanganate, dichromates, phosphoric acid and chromic acid.

The preferred intercalating agent for initial expansion and delamination of pyrolytic graphite is a mixture of sulfuric acid and an oxidizing agent, particularly nitric acid, although other oxidizing agents such as chromic acid, perchloric acid, potassium chlorate or potassium dichromate, or mixtures thereof, can be employed. Thus, the preferred intercalating agent is a mixture of sulfuric acid and nitric acid, an exemplary mixture of this type being an acid solution having a ratio of about 3 parts sulfuric acid and about 1 part nitric acid, by volume. Generally such mixed acid is diluted with water to form an aqueous solution containing a ratio of about 100 parts of such mixed acids or mixed concentrated acids, to about 0.5 to about 50, preferably to about 1 to about 20, parts of water, by volume. However, the ratio of sulfuric acid to oxidizing agent, particularly nitric acid, can range, e.g. from about 9 to 1 or higher, to about 1 to 1. Also aqueous acid solutions having various sulfuric and nitric acid concentrations can be employed, e.g. each of such acids being from about 0.1 normal up to about 10 normal.

Upon treating pyrolytic graphite with a mixture of sulfuric acid and an oxidizing agent such as nitric acid, graphite bisulfate is formed.

Initial expansion and delamination of the pyrolytic graphite can also be accomplished by subjecting it to electrolytic or anodic oxidation. In this mode of procedure pyrolytic graphite is employed as the anode in an electrolytic bath containing, e.g. sulfuric acid, a mixture of sulfuric acid and nitric acid, phosphoric acid or an aqueous solution of ferric chloride. The electrolyte bath can be maintained at between ambient temperature and about 125°C, with current ranging, e.g. from about 100 ma (milliamps) to about 5 amperes, with the period of electrolytic treatment ranging, e.g. from about 1 to about 120 minutes. The term "treating the pyrolytic graphite with an intercalating agent" as employed in the specification and claims is accordingly intended to include the above described electrolytic treatment of the pyrolytic graphite with suitable solutions of acids or salts, such as those noted above, as electrolytic baths or intercalating agents.

In carrying out the invention process in accordance with preferred procedure, the initial pyrolytic graphite starting material, preferably employing pyrolytic graphite which has previously been annealed, as noted above, is placed in a chamber in which all lateral movement, i.e. in the a-b direction parallel to the deposition surface, is constained, the chamber permitting movement or expansion of the pyrolytic graphite material only in the c-direction, i.e. normal to the deposition surface.

The pyrolytic graphite material in the chamber is then treated with any of the intercalating agents noted above, preferably a mixture of sulfuric and nitric acids, e.g. by immersing the chamber containing the pyrolytic graphite into the intercalating solution. The treatment with the intercalating agent is carried out for a period of time, e.g. of the order of about 10 to about 60 minutes, usually about 15 to about 30 minutes, to cause the pyrolytic graphite to expand in the c-direction only, to the desired extent, e.g. 2 to 3 times, usually more than 2 times, its original length or dimension in the c-direction. Temperature of treatment with the intercalating agent can vary, e.g. from ambient or room temperature to substantially elevated temperature. Employing a mixture os sulfuric acid and an oxidizing agent, particularly nitric acid, temperature can range

from about ambient to about 125°C, depending on the concentration of the acid solution.

Of particular significance and as an essential feature of the invention, such treatment with the intercalating agent is continued for a period sufficient to form a lamellar compound of pyrolytic graphite with the intercalating agent, e.g. graphite bisulfate where a mixture of sulfuric and nitric acids is the intercalating agent, which is thoroughly delaminated or substantially completely delaminated. The resulting lamellar and expanded pyrolytic graphite consists essentially of a large number of parallel planes stacked in tandem. When the intercalating reaction is completed, excess intercalating agent, e.g. excess sulfuric-nitric acid solution, is removed from the chamber.

The completely delaminated lamellar expanded pyrolytic graphite, still contained in the chamber, is then heated at temperture ranging, e.g. from about 300° to about 700°C, usually from about 400° to about 600°C, and most desirably of the order of about 500°C, for a period of time such as to cause such delaminated expanded pyrolytic graphite to expand further to a controlled extent only in the c-direction, i.e. the direction normal to the deposition surface, while still constrained from movement in the a-b direction, i.e. the direction parallel to the deposition surface. Generally this period of heat treatment ranges from about 5 to about 60 minutes, e.g. a period of about 10 to about 30 minutes. During this heat treatment, the intercalating agent or additive between the crystallite planes or layers of the expanded pyrolytic graphite is removed, e.g. "boiled off" when employing for example a mixture of sulfuric and nitric acid as intercalating agent. As a result, the pyrolytic graphite expands further in the *c*-direction, i.e. the direction normal to the deposition surface, and during such heating process the pyrolytic graphite not only expands, but the carbonaceous planes bond together to produce an integral expanded pyrolytic graphite.

According to the invention procedure, expansion ratios for the expanded pyrolytic graphite of the order of 10:1 or more can be achieved, e.g. expansion ratios up to 50:1 to 100:1. That is, an expansion of the order of 10 times or more of the original length or dimension in the c-direction can be obtained. According to the present invention process, particularly where a mixture of sulfuric and nitric acid is employed as intercalating agent, expansion ratios from about 2:1 to about 5:1 are preferred. If it is desired to fabricate expanded pyrolytic graphite according to the invention process having an expansion ratio of 2, or less, usually the delaminated pyrolytic graphite, following treatment with the intercalating agent, e.g. the delaminated graphite bisulfate, must be compresses somewhat before heating is initiated, since the expansion occurring during treatment with the intercalating agent, e.g. during graphite bisulfate formation, usually is greater than 2.

In accordance with two of the main features of the invention, namely (1) controlling the expansion of the pyrolytic graphite so that expansion occurs only in the c-direction, normal to the deposition surface, and constrained in the a-b direction, parallel to the deposition surface, and (2) carrying out the intercalating reaction, that is reacting the intercalating agent or additive with pyrolytic graphite, to such an extent that a substantially completely delaminated lamellar compound of pyrolytic graphite is obtained, a uniformly expanded bonded pyrolytic graphite product of high quality and of controlled and desired density is obtained upon subsequent heat treatment, which is relatively independent of the quality of the initial pyrolytic graphite starting material, that is without stringent restrictions on the degree of orientation of the initial pyrolytic graphite material. This is in contrast to prior art processes for producing expanded pyrolytic graphite, e.g. as described in above British Pat. No. 991,581, wherein unrestricted expansion of the pyrolytic graphite is permitted to occur, without constraining the movement of the pyrolytic graphite in the a-b direction, i.e. parallel to the deposition surface, and wherein during treatment with intercalating agent or medium, this treatment is controlled so that "at most, only a partial delamination or exfoliation of layers or laminae is effected," such prior art process, as noted above, producing inconsistent results as contrasted to production of expanded pyrolytic graphite having uniform expansion and controlled density characteristics according to the present invention.

The electrical and thermal conductivities of expanded pyrolytic graphite produced according to the invention process are highly anisotropic, as in the case of the parent pyrolytic graphite material. Thus, the laminar structure of the original pyrolytic graphite is maintained in the expanded pyrolytic graphite product following expansion. As previously noted, the process of the invention is particularly adapted to produce expanded pyrolytic graphite having expansion ratios of about 2:1 to about 5:1.

The cross section of the pyrolytic graphite employed can be chosen as desired, and can be for example circular or rectangular or any other shape, and expanded pyrolytic graphite of corresponding cross section or shape obtained according to the invention. It will be understood that various sizes of expanded pyrolytic graphite with respect to the a-b dimension and the c-dimension of the expanded pyrolytic graphite can be produced according to the invention process.

The following are examples of practice of the invention, taken in connection with the accompanying drawing which illustrates schematically the invention process.

In the drawing there is illustrated Step I showing placement of pymolytic graphite in a suitable chamber,

Step II showing acid treatment of the pyrolytic graphite in the chamber, and

Step III showing heat treatment of the pyrolytic graphite in the chamber following acid treatment and final production of the expanded pyrolytic graphite.

EXAMPLE 1

Pyrolytic graphite of rectangular cross section and which has been annealed at temperature of the order of about 3100°C, is cut with its end faces parallel to each other and to the deposition surface.

The pyrolytic graphite starting material, indicated at **10** in the drawing, is then placed in a chamber **12** having dimensions such that all lateral movement of the pyrolytic graphite material **10**, i.e. in the a-b direction parallel to the deposition, surface, is constrained. However, the chamber **12** is of sufficient internal vertical dimension to provide space above and below the sample **10**, as indicated at **14** and **16**, to permit movement or expansion of the pyrolytic graphite sample **10**, only in the c-direction, that is the direction normal to the deposition surface, which is in the vertical direction view-

ing the chamber **12** shown in the drawing. Movable spacers indicated at **18** and **20** are placed in the chamber adjacent to the upper and lower faces of the pyrolytic graphite samples (parallel to the deposition surface) to provide restraining forces which prevent the expansion process from occurring too rapidly and to thus aid in producing uniformly expanded pyrolytic graphite. Additional fixed spacers **22** and **24** are provided at the top and bottom within chamber **12,** to control maximum expansion of the pyrolytic graphite sample **10** within the chamber. This is illustrated at "Step I" in the drawing.

As illustrated in Step II of the drawing, the pyrolytic graphite starting material **10** within chamber **12** is then subjected to treatment with an acid solution in the form of a mixture having a ratio of 3 parts sulfuric acid and 1 part nitric acid by volume, such mixed acid being diluted with water in a ratio of 100 parts of such mixed acids to 17 parts of water, by volume, said solution having a temperature of about 40°C. Such treatment is carried out by removing the cover **26** of the chamber **12** and immersing the chamber and the pyrolytic graphite sample **10** into the sulfuric acid-nitric acid solution. The spacers **18, 20, 22** and **24** are constructed, e.g. of stainless steel slabs containing holes **27** to permit passage of the acid treating solution therethrough, and in contact with the pyrolytic graphite sample **10.** If desired, during such acid treatment the chamber lid **26** can be replaced by a screen (not shown) so that the expansion of the pyrolytic graphite during the acid treating process can be observed.

Acid treatment is permitted to continue for a period of about 15 minutes, during which the pyrolytic graphite sample **10** expands about 2.5 times its original length or dimension in the c-direction, that is in the vertical direction as seen at **10***a* in the drawing, which is normal to the deposition surface. When the acid reaction has been completed, the chamber **12** containing the sample **10** is removed from the sulfuric-nitric acid solution and the excess acid is drained from the chamber, and the cover **26** is replaced.

As illustrated in Step II of the drawing, following treatment with the sulfuric-nitric acid solution and initial expansion of the pyrolytic graphite sample **10,** the pyrolytic graphite sample which has thus been expanded only in the c-direction, as indicated at **10***a*, is thoroughly delaminated, and essentially is composed of a large number of vertically stacked planes or plates, as illustrated at **28.** Enough space is left in the interior of the chamber **12,** as indicated at **14***a* and **16***a*, such that the pyrolytic graphite which has been initially expanded as a result of the above described acid treatment, can be further expanded to the desired extent.

Such further expansion is carried out by heating chamber **12** containing the initially expanded pyrolytic graphite sample **10***a* at temperature of 500°C for a period of about **10** minutes. Such heat treatment, illustrated in Step III of the drawing, causes further expansion of the expanded pyrolytic graphite **10***a* again only in the c-direction (that is the direction normal to the deposition surface), while the side walls of the chamber constrain any expansion or movement of the expanded pyrolytic graphite **10***a* in th lateral direction, that is the direction parallel to the deposition surface. In such heating process, the initially expanded pyrolytic graphite sample **10***a* not only expands, but the delaminated planes or plates **28** formed during initial expansion with the above acid intercalating agent, are bonded together such that an integral expanded pyrolytic graphite product having the desired degree of expansion in the c-direction, of 3 times the original dimension of the initial pyrolytic graphite sample indicated at **10,** is obtained, as illustrated at **10***b* in Step III of the drawing. Following cooling of the chamber **12** containing the expanded pyrolytic graphite product **10***b*, cover **26** is removed, and the expanded pyrolytic graphite product **10***b* is removed, together with the spacers **18** and **22,** to recover the expanded pyrolytic graphite product **10***b*.

The resulting uniformly expanded pyrolytic graphite product **10***b* produced by a three-fold expansion of the initial pyrolytic graphite material **10,** has a controlled density of 0.76 gm per cc. Electrical and thermal conductivities of the expanded pyrolytic graphite product **10***b* are denoted by the symbols σ and k, respectively, in the table below. The subscript a-b and c indicate directions parallel to the deposition surface and normal to the deposition surface, respectively. The ultimate shear strength of the expanded pyrolytic graphite product **10***b* is also given in the table.

TABLE 1

MATERIAL PROPERTIES OF EXPANDED PYROLYTIC GRAPHITE PRODUCED ABOVE AT ROOM TEMPERATURE AND EXPANSION RATIO OF 3:1

k_{ab}	k_c	σ_{ab}	σ_c	Ultimate Shear Strength (psi)
$\frac{\text{watts}}{\text{cm}-°K}$	$\frac{\text{watts}}{\text{cm}-°K}$	$\text{ohm}^{-1}\text{cm}^{-1}$	$\text{ohm}^{-1}\text{cm}^{-1}$	
5.3	0.01	10^3	1	30

It is seen from the above table that the pyrolytic graphite produced according to the invention process has highly anisotropic electrical and thermal conductivities.

The electrical and thermal conductivities parallel to the deposition planes (a-b-direction) and normal or perpendicular to such planes (c-direction) are dependent upon the density.

It will be understood that the drawing is only illustrative of one type of apparatus which can be used in carrying out the invention process. Thus, alternatively, the sides of chamber **12** adjacent pyrolytic graphite **10** can contain holes to permit passage of aqueous acid treating solution into the chamber, and one of such perforated sides of the chamber can function as a cover in place of cover **26.**

EXAMPLE 2

The procedure of Example 1 is repeated, except that the delaminated graphite bisulfate product **10***a* is compressed somewhat before heating is initiated, and expansion of the resulting compressed initially expanded and delaminated pyrolytic graphite is controlled by heating at 500°C for about 15 minutes to fabricate an integral bonded expanded pyrolytic graphite product **10***b* having an expansion ratio of 2:1, that is an expanded pyrolytic graphite product which is expanded

2 times the original dimension of the pyrolytic graphite starting sample **10.**

EXAMPLE 3

The procedure of Example 1 is repeated, except that the intercalating agent is an acid solution of 90% by volume 1 normal sulfuric acid and 10% by volume 1 normal nitric acid, at about ambient temperture, and the period of acid treatment is continued for a time such that the pyrolytic graphite expands to 3 times its original dimension in the c-direction.

Further, in the present example, heating is carried out at a temperature of about 500°C for a period of about 30 minutes, so as to produce a uniformly expanded integrally bonded pyrolytic graphite product which is expanded 8 times its original dimension in the c-direction.

EXAMPLE 4

The procedure of Example 1 is repeated, except that in place of employing the sulfuric acid-nitric acid mixture as intercalating agent, there is employed a solution of bromine in sulfuric acid.

An expanded pyrolytic graphite product similar to that of Example 1 is obtained.

EXAMPLE 5

The procedure of Example 1 is repeated except that in place of the sulfuric acid-nitric acid intercalating acid solution, there is employed solution of chromic acid or a solutin of potassium dichromate.

An expanded pyrolytic graphite product of improved properties similar to that of Example 1 is obtained.

EXAMPLE 6

The procedure of Example 1 is repeated, except in place of the sulfuric acid-nitric acid intercalating acid solution, the pyrolytic graphite is treated with $FeCl_3$ vapor at 1 torr (1 mm of Hg) vapor pressure and at about 200°C.

An expanded pyrolytic graphite product is obtained again having the improved properties similar to the expanded pyrolytic graphite product of Example 1.

EXAMPLE 7

The procedure of Example 1 is repeated, except in place of the sulfuric acid-nitric acid intercalating acid solution, the pyrolytic graphite is treated with cesium vapor at 1 torr vapor pressure and at about 300°C.

An expanded pyrolytic graphite product of improved properties similar to that of Example 1 is obtained.

EXAMPLE 8

The procedure of Example 1 is substantially repeated, except employing pyrolytic graphite in the shape of a cylindrical sleeve in which the a-b plane or direction is parallel to the cylindrical axis and the c-direction is radial, that is perpendicular to the cylindrical axis.

During treatment according to the procedure of Example 1, expansion of the pyrolytic graphite sleeve radially outward in the c-dirction only is permitted, while expansion radially inward is constained and axial expansion in the a-b direction is constrained.

The resulting uniformly radially expanded pyrolytic graphite sleeve has the same axial dimension and the same inner radial dimension of the interior wall of the sleeve, as the original pyrolytic graphite sleeve, but has an increased outer radial dimension in the c-direction.

From the foregoing, it is seen that the invention provides an improved procedure for expanding pyrolytic graphite in a controlled manner, including particularly the features of controlling the expansion to permit expansion in the c-direction only while constaining any expansion in the a-b direction, and producing in the initial expansion of the pyrolytic graphite obtained on treatment with an intercalating agent, a substantially completely delaminated lamellar pyrolytic graphite, so that upon further heating, a uniformly expanded integrally bonded pyrolytic graphite of controlled density is obtained.

While we have described particular embodiments of our invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, and hence the invention is not to be taken as limited except by the scope of the appended claims.

We claim:

1. A process for expanding pyrolytic graphite which comprises placing said pyrolytic graphite in a chamber having dimensions in which movement in the direction parallel to the deposition surface (the a-b direction) is constrained by the chamber side walls, but which allows movement only in the direction normal to the depostion surface (the c-direction), treating said pyrolytic graphite with an intercalating agent to cause said pyrolytic graphite to expand in the direction normal to the deposition surface (the c-direction) while constraining movement in the direction parallel to the deposition surface (the a-b direction) by the side walls of said chamber and continuing said treatment for a period of about 1 to about 120 minutes sufficient to substantially completely delaminate said expanded pyrolytic graphite, and heating from about 300° to about 700°C, said delaminated expanded pyrolytic graphite while permitting movement in the direction normal to the deposition surface and constraining movement of said delaminated pyrolytic graphite in the direction parallel to the deposition surface by the side walls of said chamber, to cause said delaminated expanded pyrolytic graphite to expand further in the direction normal to the deposition surface.

2. A process as defined in claim **1,** wherein said intercalating agent is a metal hsalide selected from the group consisting of metal chlorides, iodides and bromides.

3. A process as defined in claim **1,** wherein said intercalating agent is an acid selected from the group consisting of sulfuric acid and phosphoric acid, or an oxidizing agent selected from the group consisting of nitric acid, chromic acid and perchloric acid, permanganates, and dichromates.

4. A process as defined in claim **1,** wherein said intercalating agent is a mixture of sulfuric acid and an oxidizing agent selected from the group consisting of nitric acid, chromic acid, perchloric acid, potassium chlorate, potassium dichromate, and mixtures thereof, forming graphite bisulfate.

5. A process as defined in claim **4,** wherein said oxidizing agent is nitric acid.

6. A process as defined in claim **5,** employing as intercalating agent a mixture having a ratio of about 3 parts sulfuric acid to about 1 part nitric acid, by volume, diluted with water to form an aqueous solution

containing a ratio of about 100 parts of such mixed acids to about 0.5 to about 50 parts of water, by volume, at a temperature ranging from about ambient to about 125°C.

7. A process as defined in claim **5,** said heating being carried out at a temperature ranging from about 400°C to about 600°C for a period ranging from about 10 to about 30 minutes.

8. A process as defined in claim **5,** employing annealed pyrolytic graphite, said heating being carried out at a temperature of about 500°C, and expanding the pyrolytic graphite from in excess of 1 to about 10 times the original dimension in the c-direction.

9. A process for expanding pyrolytic graphite, which comprises placing said pyrolytic graphite in a chamber having dimensions in which movement in the direction parallel to the deposition surface (the a-b direction) is constrained by the chamber side walls, but which allows movement only in the direction normal to the deposition surface (the c-direction), treating the pyrolytic graphite with a mixture of sulfuric and nitric acids to form graphite bisulfate and to cause the pyrolytic graphite to expand only in the c-direction in said chamber, while constraining movement in the a-b direction by the side walls of said chamber, and continuing said acid treatment for a period of about 10 to about 60 minutes sufficient to substantially completely delaminate the expanded pyrolytic graphite and form a lamellar compound of pyrolytic graphite, graphite bisulfate, draining excess sulfuric acid-nitric acid solution from said chamber, heating the delaminated lamellar pyrolytic graphite at about 500°C to cause said delaminated pyrolytic graphite to expand further only in the c-direction to a predetermined extent while constraining movement in the a-b direction by the side walls of said chamber, thereby bonding the carbonaceous planes of the expanded pyrolytic graphite and forming an integral uniformly expanded pyrolytic graphite, the resulting expanded pyrolytic graphite being expanded from about 1 to about 10 times its dimension in the c-direction.

10. A process as defined in claim **9,** employing annealed pyrolytic graphite, and wherein said mixture of nitric acid and sulfuric acid comprises a ratio of about 3 parts sulfuric acid and about 1 part nitric acid, by volume, diluted with water to form an aqueous solution containing a ratio of about 100 parts of such mixed acids to about 1 to about 20 parts of water, by volume, said treatment with said aqueous acid solution being carried out at a temperature ranging from ambient to about 125°C, for a period ranging from about 15 to about 30 minutes, said graphite bisulfate formation being accompanied by expansion of the expanded pyrolytic graphite from 2 to 3 times its original dimension in the c-direction, said heating at about 500°C being carried out for about 10 to about 30 minutes, and providing uniformly expanded pyrolytic graphite expanded from about 1 to about 5 times its original dimension in the c-direction.

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