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[54] **PROCESS FOR MAKING CARBON FOAM**

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[51] Int. Cl.⁷ **B29C 67/20**; B32B 31/06; C01B 31/02

[52] U.S. Cl. **156/78**; 156/245; 264/29.6; 264/29.7; 264/42; 264/46.5; 264/85; 264/101

[58] Field of Search 264/29.6, 29.7, 264/42, 46.5, 85, 101; 156/78, 245

[56] **References Cited**

U.S. PATENT DOCUMENTS

32,319	12/1986	Korb et al.	423/445
3,558,276	1/1971	Otani	264/29.6 X
3,914,392	10/1975	Klett	264/29
3,979,196	9/1976	Frank et al.	65/25
4,025,689	5/1977	Kobayashi et al.	428/402
4,096,097	6/1978	Yan	252/510
4,125,676	11/1978	Maricle et al.	429/38
4,225,463	9/1980	Unger et al.	252/445
4,272,356	6/1981	Stiller et al.	208/8
4,276,246	6/1981	A. Bonzom, et al.	264/53
4,303,431	12/1981	Torobin	65/21.4
4,311,682	1/1982	Miyazaki et al.	423/448
4,318,824	3/1982	Turner	252/421
4,439,349	3/1984	Everett et al.	502/180
4,442,165	4/1984	Gebhardt et al.	428/307.7
4,487,687	12/1984	Simo et al.	208/56
4,518,483	5/1985	Dickkian	208/44
4,525,492	6/1985	Rastall et al.	521/181
4,550,015	10/1985	Korb et al.	423/445
4,637,906	1/1987	Fukuda et al.	264/29.1
4,659,624	4/1987	Yaeger et al.	428/408
4,775,655	10/1988	Edwards et al.	502/416
4,782,586	11/1988	Joo et al.	29/623.5
4,832,881	5/1989	Arnold, Jr. et al.	264/29.7
4,873,071	10/1989	Yamada et al.	423/448
4,873,218	10/1989	Pekala	502/418
4,892,783	1/1990	Brazel	428/282
4,917,835	4/1990	Lear et al.	264/29.1
4,934,657	6/1990	Dodson	251/214
4,978,649	12/1990	Surovikin et al.	502/416
4,992,254	2/1991	Kong	423/449
4,999,385	3/1991	McCullough, Jr. et al.	521/149
5,019,164	5/1991	Tomita et al.	106/22
5,047,225	9/1991	Kong	423/447.2
5,053,148	10/1991	von Bonin	252/8.05
5,071,631	12/1991	Takabatake	423/445
5,076,845	12/1991	Seo et al.	106/284.4
5,114,635	5/1992	Sohda et al.	264/29.2
5,217,701	6/1993	Sakata et al.	423/447.1
5,232,772	8/1993	Kong	428/312.2

5,248,705	9/1993	McGuigan et al.	521/149
5,300,272	4/1994	Simandl et al.	423/445
5,384,193	1/1995	Suh et al.	423/375
5,437,927	8/1995	Ross et al.	428/367
5,487,946	1/1996	McGinniss et al.	428/413
5,540,903	7/1996	Romine	423/445
5,556,892	9/1996	Pekala	521/181
5,578,255	11/1996	Okuyama et al.	264/29.5
5,580,500	12/1996	Muramatsu et al.	264/29.1
5,582,781	12/1996	Hayward	264/28
5,614,134	3/1997	Sohda et al.	264/29.1
5,695,816	12/1997	Iwashita et al.	427/228
5,705,106	1/1998	Kolesnikov et al.	264/29.1
5,709,914	1/1998	Hayes	428/35.1
5,733,484	3/1998	Uchida et al.	264/29.1
5,770,127	6/1998	Abrams et al.	264/29.1
5,888,469	3/1999	Stiller et al.	423/445

FOREIGN PATENT DOCUMENTS

WO 98/27023 6/1998 WIPO .

OTHER PUBLICATIONS

Dan D. Edie, "Pitch And Mesophase Fibers", (1990) pp. 1-30.

Shih, Wei, "Development of Carbon-Carbon Composites for Electronic Thermal Management Applications," IDA Workshop, May 3-5, 1994, pp. III-119-III-136.

A.R. Phillips Laboratory Contract No. F29601-93-C-0165 and Engle, G.B., "High Thermal Conductivity C/C Composites for Thermal Management," IDA Workshop, May 3-5, 1994, pp. III-137-III-148.

Hager, Joseph W. and Max L. Lake, "Novel Hybrid Composites Based on Carbon Foams," Mat. Res. Soc. Symp., Materials Research Society, 270:29-34 (1992).

Sandhu, S.S. and J.W. Hager, "Formulation of a Mathematical Process Model Process Model for the Foaming of a Mesophase Carbon Precursor," Mat. Res. Soc. Symp., Materials Research Society, 270:35-40 (1992).

Gibson, L.J. and M.F. Ashby, "Cellular Solids: Structure & Properties," pp. 1-277, Pergamon Press, New York (1988).

Gibson, L.J., "Modeling the Mechanical Behavior of Cellular Materials", Mat. Sci. and Eng. A110, pp. 1-36 (1989).

Knippenberg, W.F. and B. Lersmacher, "Carbon Foam," Phillips Tech. Rev., pp. 93-103 (1976).

White, J.L. and P.M. Scheaffer, "Pitch-Based Processing of Carbon-Carbon Composites," Carbon, 27: pp. 697-707 (1989).

(List continued on next page.)

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[57] **ABSTRACT**

The process obviates the need for conventional oxidative stabilization. The process employs mesophase or isotropic pitch and a simplified process using a single mold. The foam has a relatively uniform distribution of pore sizes and a highly aligned graphic structure in the struts. The foam material can be made into a composite which is useful in high temperature sandwich panels for both thermal and structural applications.

38 Claims, 10 Drawing Sheets

OTHER PUBLICATIONS

- Hager, Joseph W., "Idealized Strut Geometries for Open-Cell Foams," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:41-46 (1992).
- Aubert, J.W., MRS Symposium Proceedings, "Microcellular Foams Prepared from Demixed Polymer Solutions," 207:117-127 (1991).
- Cowlard, F.C. and J.C. Lewis, "Vitreous Carbon—A New Form of Carbon," *J. of Mat. Sci.* 2:507-512 (1967).
- Noda, T., M. Inagaki and S. Yamada, "Glass-like Carbons," *J. of Non-Crystalline Solids*, 1:285-302 (1969).
- Davies, G.J. and Zhen, Shu "Review: Metallic Foams: Their Production, Properties and Applications," *J. of Mat. Sci.* 18: pp. 1899-1911 (1983).
- Rajeev Mehta et al., "Graphite Carbon Foams: Processing and Characterization", 21st Biennial Conference on Carbon, Conf. Proceedings, American Carbon Society, Buffalo, New York, pp. 104-105, 1993, no month.
- Hexcel Product Data Sheet (1997).
- Kearns, Kris, Graphitic Carbon Foam Processing, 21st Annual Conference on Composites, Materials, and Structures, Jan. 26-31, 1997, Cocoa Beach, FL, pp. 835-847 (1997).
- Lake, Max L., Simple Process Produces High Modulus Carbon Fibers at Much Lower Cost, *Mat. Tech.*, 11 (4), pp. 137-139 (1996).
- Jones, S. P., Fain, C. C., and Edie, D. C., Structural Development in Mesophase Pitch Based Carbon Fibers Produced from Naphthalene, 35 (10), pp. 1533-1543 (1997).
- Amoco Product Literature (1997).
- Steiner, K., Banhart, J., Baumeister, J. and Weber, M., Production and Properties of Ultra-Lightweight Aluminum Foams for Industrial Applications, Proceeding from the 4th International Conference on Composites Engineering, Edited by David Hui, pp. 943-944 (1997).
- Inoue, K., Application of laser flash method of penetrative materials for measurement of thermal diffusivity, *High Temp. Tech.*, 8 (1), pp. 21-26 (1990).
- Cowan, R. D., Pulse Method of Measuring Thermal Diffusivity at High Temperatures, *J. of App. Phys.*, 34 (4), pp. 926-927 (1962).
- Ohlhorst, C., Vaughn, W., Ransone, P., and Tsou, H., Thermal Conductivity Database of Various Structural Carbon-Carbon Composite Materials, Japan Welding Soc., 561, pp. 38-42 (1987).



FIG. 1

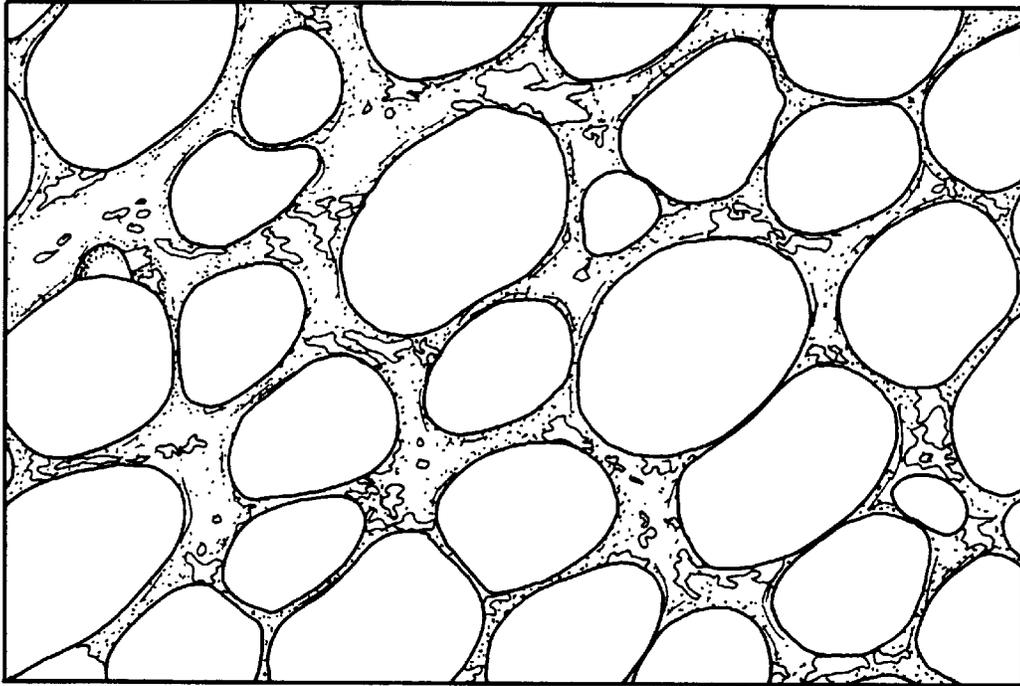


FIG. 2

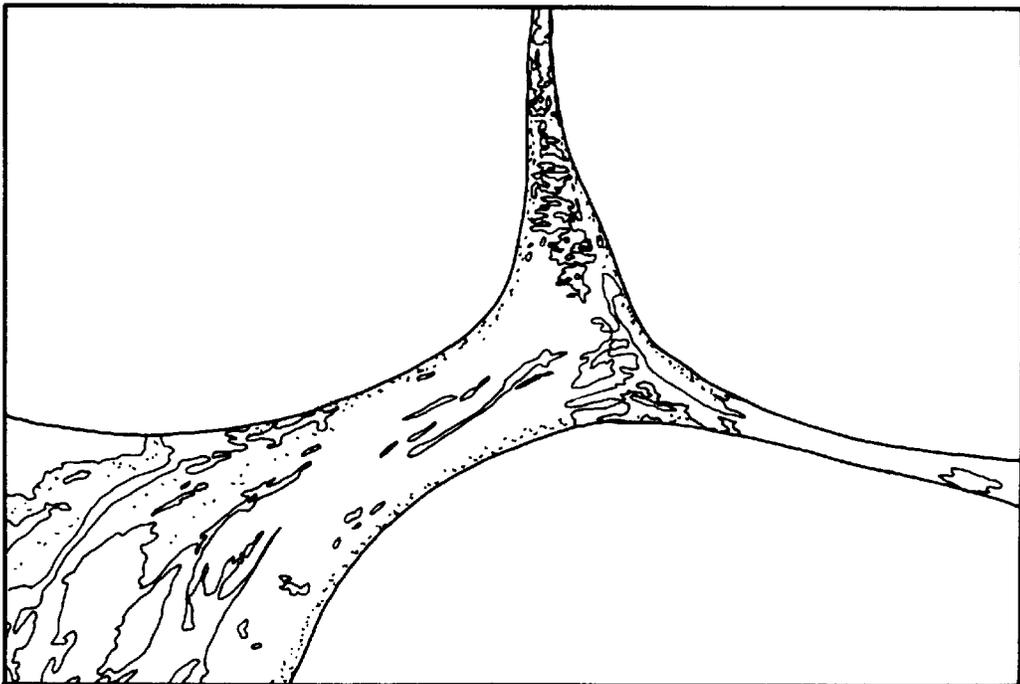


FIG. 3

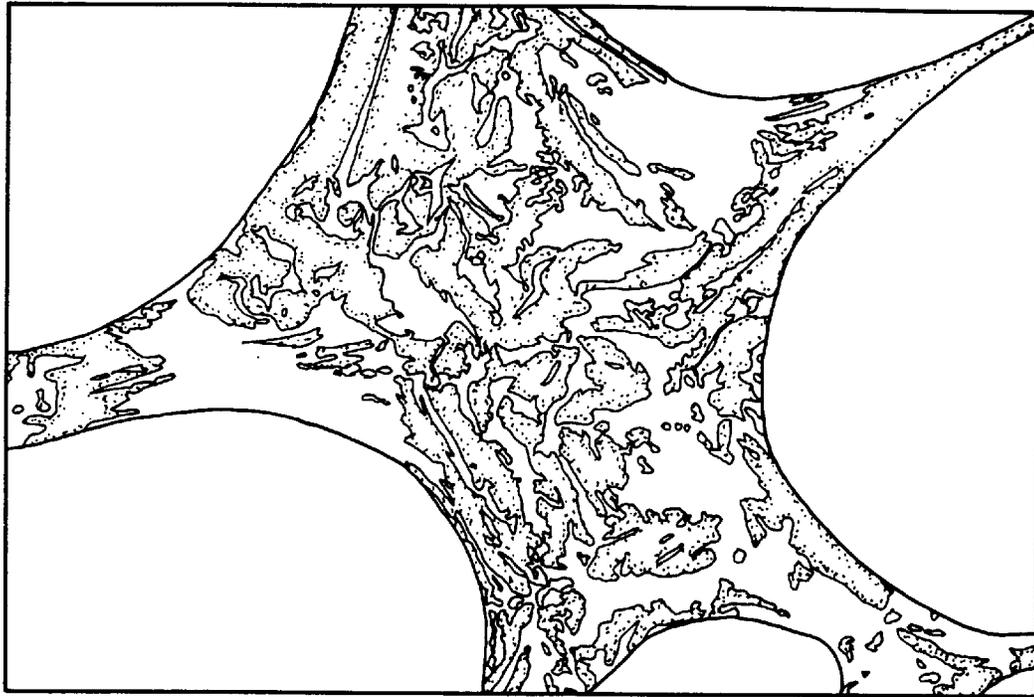


FIG. 4

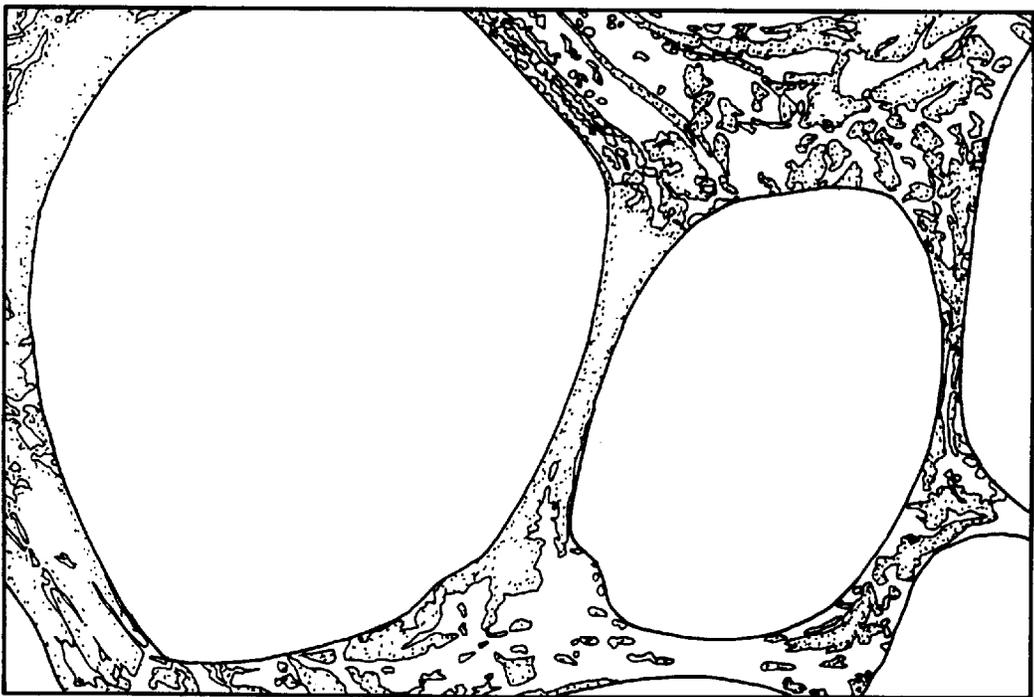


FIG. 5

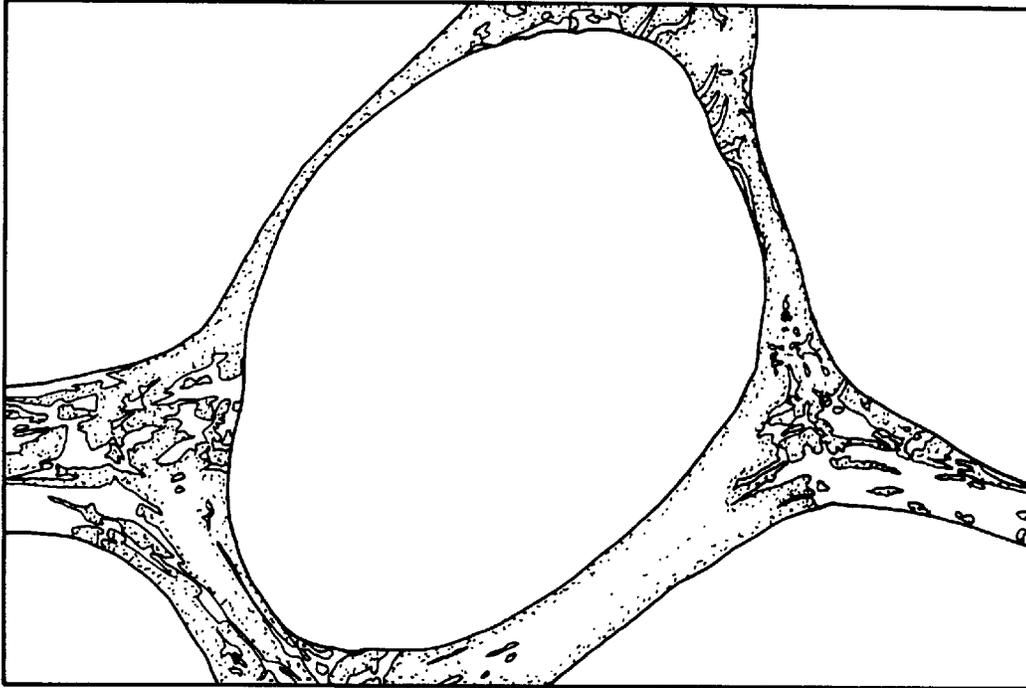


FIG. 6

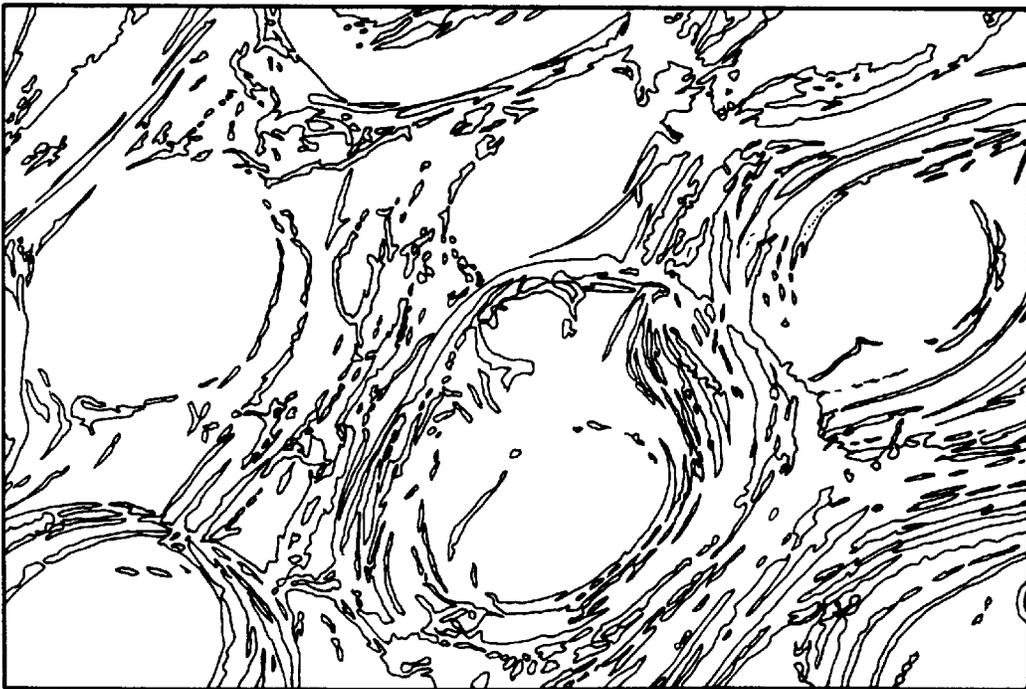


FIG. 7

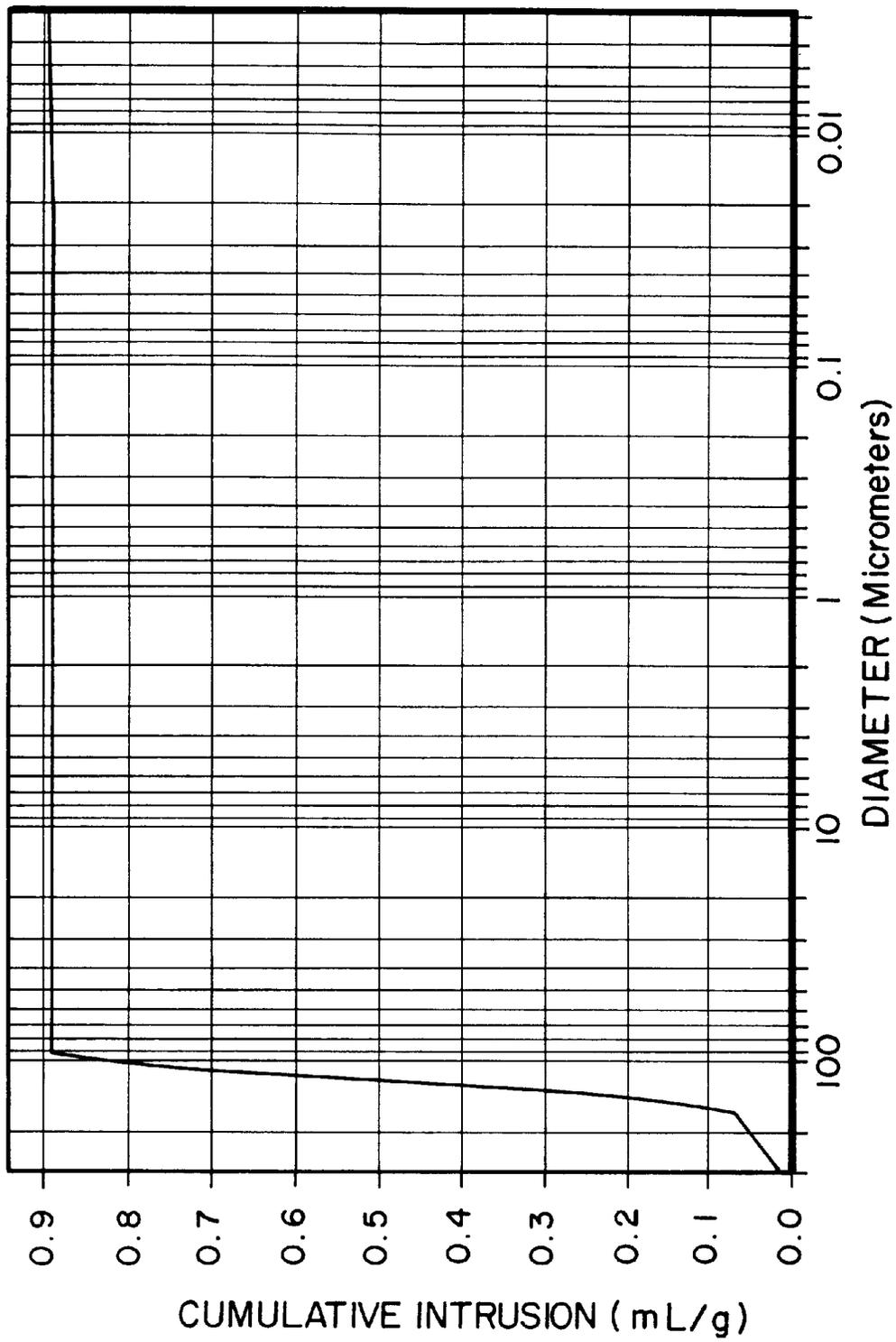


FIG. 8

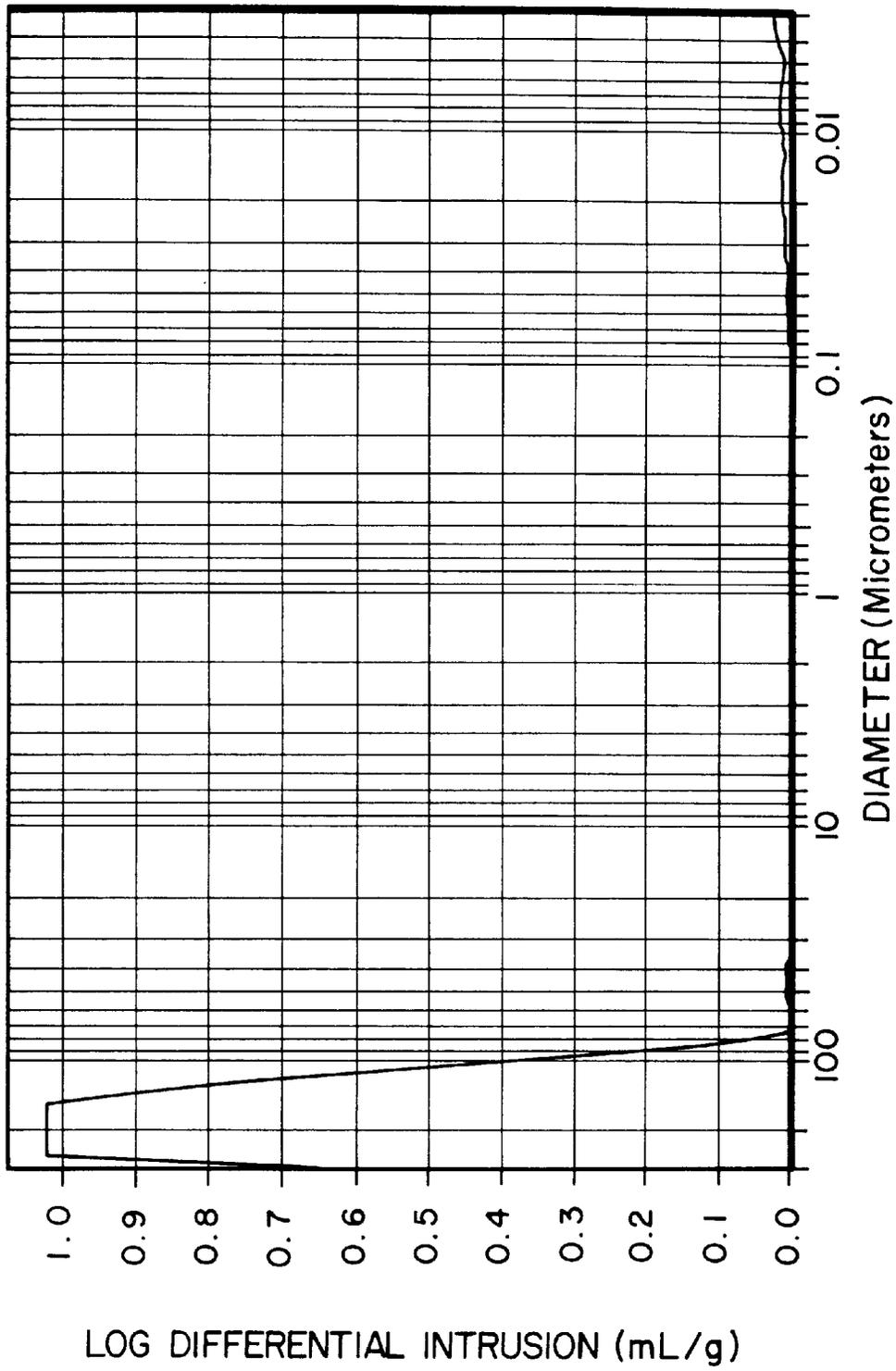


FIG. 9

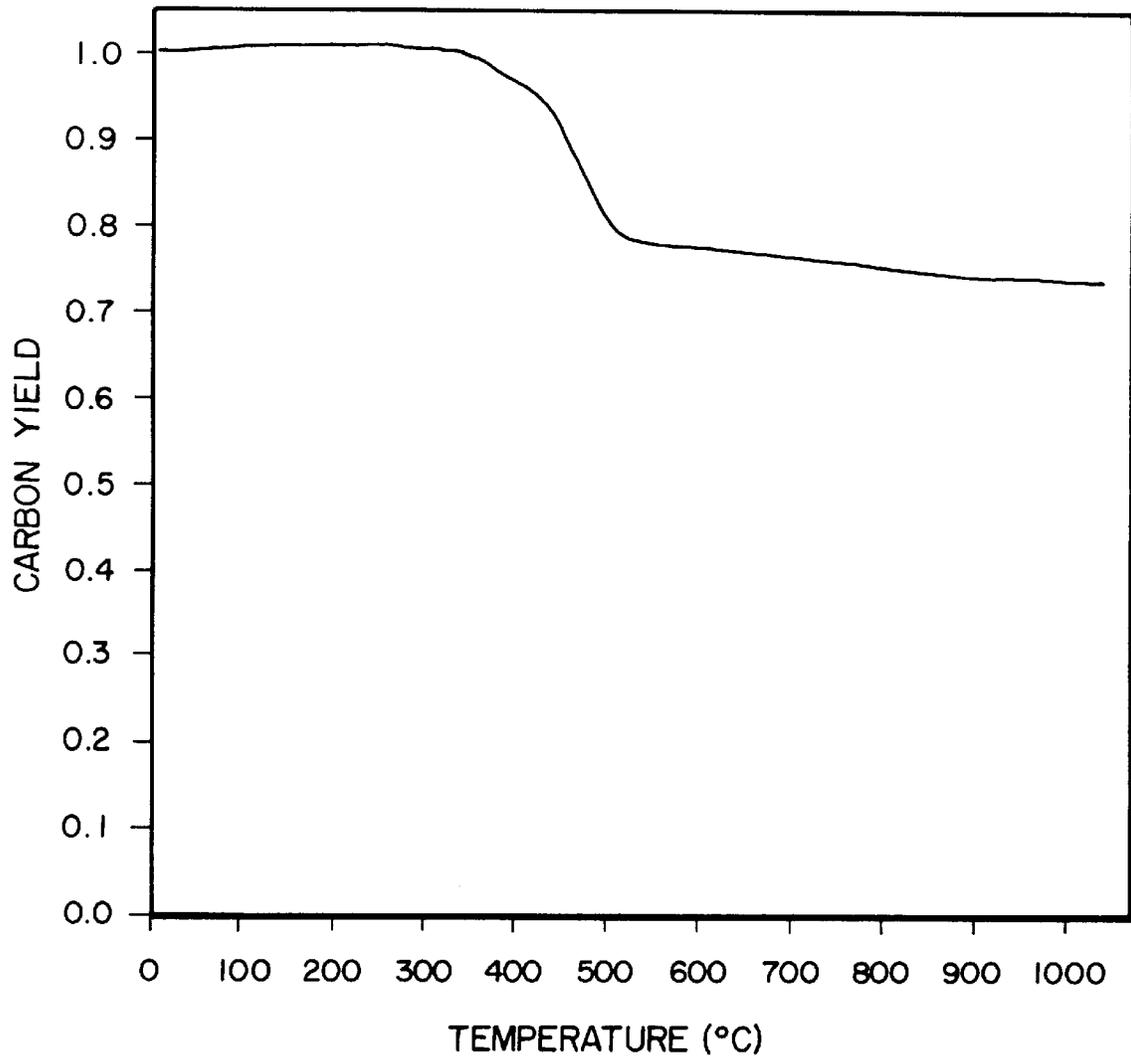


FIG. 10

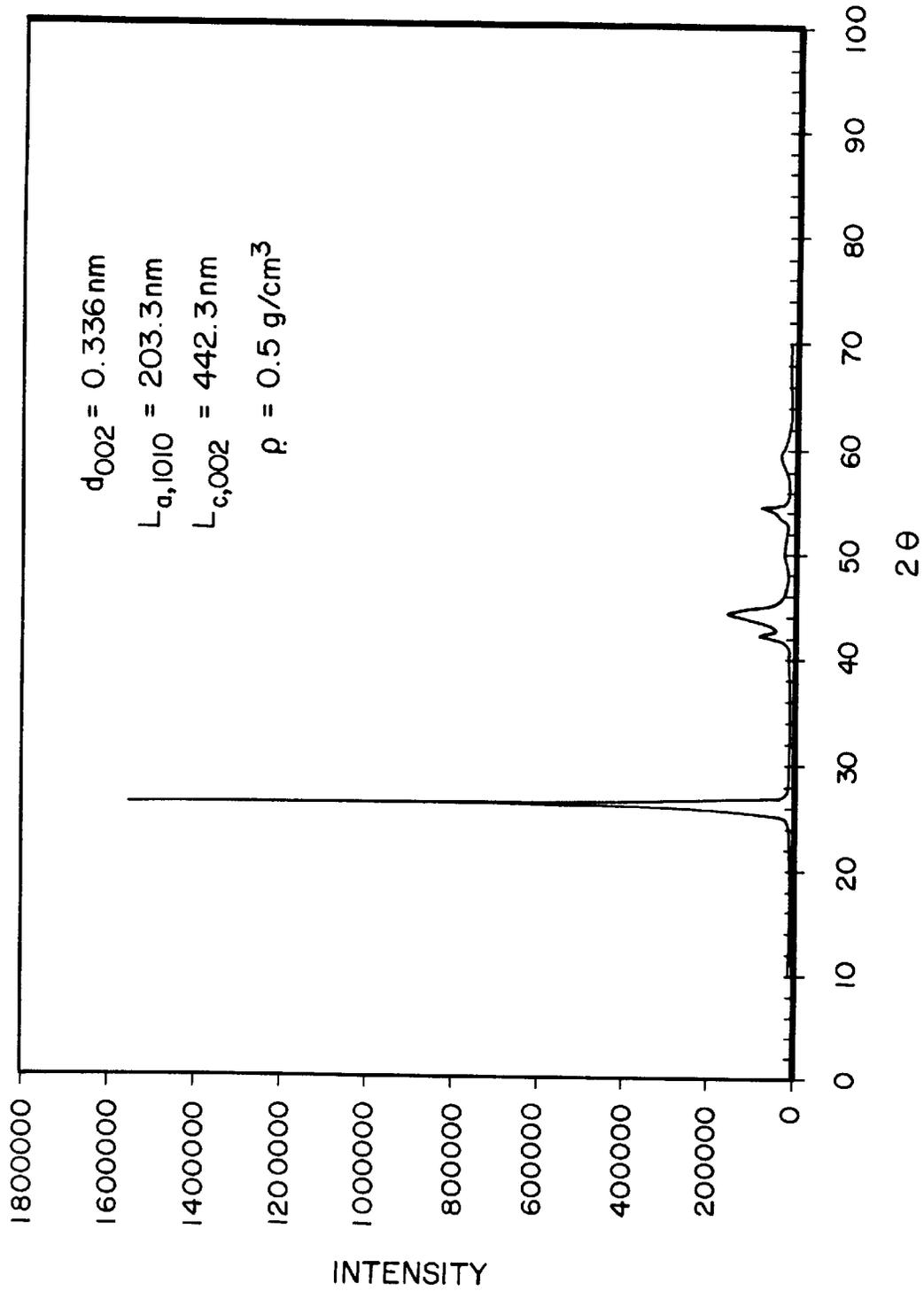
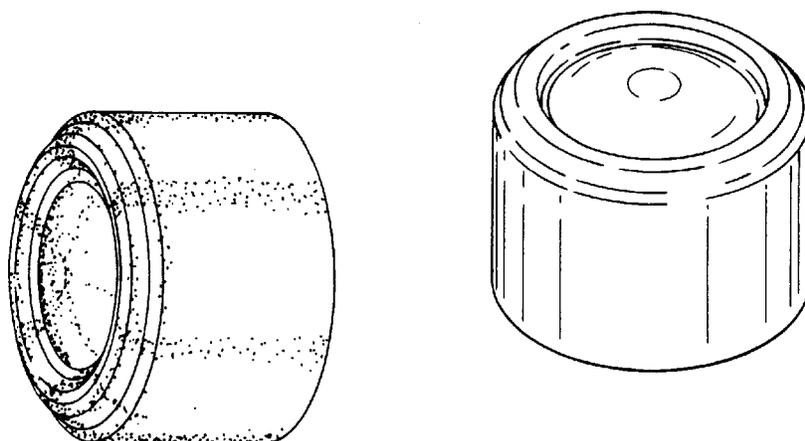
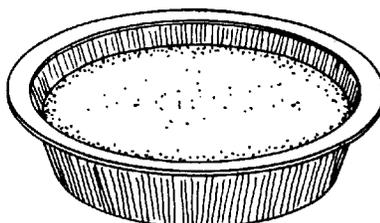


FIG. 11



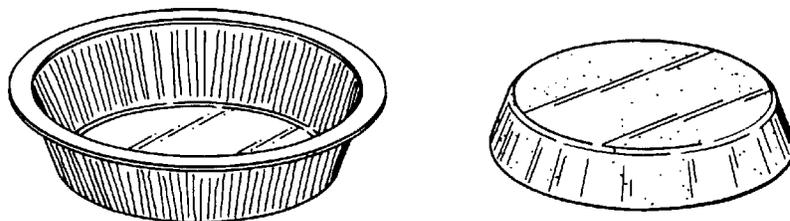
FOAM PRODUCED IN BOTTOM OF SODA CAN.

FIG. 12A



FOAM PRODUCED IN ALUMINUM WEIGHING DISH.

FIG. 12B



FOAM REMOVED FROM ALUMINUM WEIGHING DISH AND
TURNED OVER, EXPOSING SMOOTH INTEGRATED SURFACE (FACE)

FIG. 12C

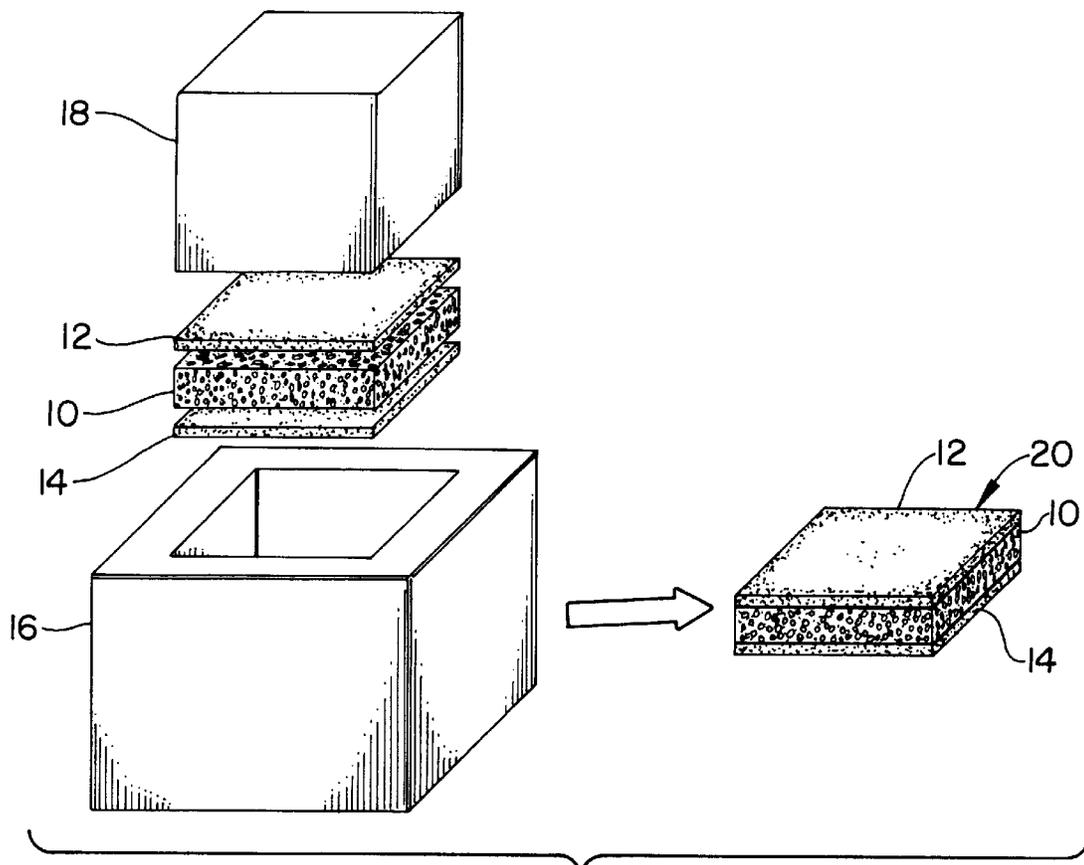


FIG. 13A

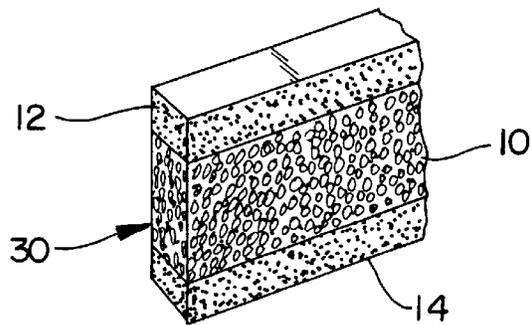


FIG. 13B

PROCESS FOR MAKING CARBON FOAM

STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT

The United States Government has rights in this invention pursuant to contract No. DE-AC05-96OR22464 between the United States Department of Energy and Lockheed Martin Energy Research Corporation.

CROSS-REFERENCE TO RELATED
APPLICATIONS

Not Applicable

BACKGROUND OF THE INVENTION

The present invention relates to carbon foam and composites, and more particularly to a process for producing them.

The extraordinary mechanical properties of commercial carbon fibers are due to the unique graphitic morphology of the extruded filaments. See Edie, D. D., "Pitch and Mesophase Fibers," in *Carbon Fibers, Filaments and Composites*, Figueiredo (editor), Kluwer Academic Publishers, Boston, pp. 43-72 (1990). Contemporary advanced structural composites exploit these properties by creating a disconnected network of graphitic filaments held together by an appropriate matrix. Carbon foam derived from a pitch precursor can be considered to be an interconnected network of graphitic ligaments or struts, as shown in FIG. 1. As such interconnected networks, they represent a potential alternative as a reinforcement in structural composite materials.

Recent developments of fiber-reinforced composites has been driven by requirements for improved strength, stiffness, creep resistance, and toughness in structural engineering materials. Carbon fibers have led to significant advancements in these properties in composites of various polymeric, metal, and ceramic matrices.

However, current applications of carbon fibers has evolved from structural reinforcement to thermal management in application ranging from high density electronic modules to communication satellites. This has simulated research into novel reinforcements and composite processing methods. High thermal conductivity, low weight, and low coefficient of thermal expansion are the primary concerns in thermal management applications. See Shih, Wei, "Development of Carbon-Carbon Composites for Electronic Thermal Management Applications," IDA Workshop, May 3-5, 1994, supported by AF Wright Laboratory under Contract Number F33615-93-C-2363 and AR Phillips Laboratory Contract Number F29601-93-C-0165 and Engle, G. B., "High Thermal Conductivity C/C Composites for Thermal Management," IDA Workshop, May 3-5, 1994, supported by AF Wright Laboratory under Contract F33615-93-C-2363 and AR Phillips Laboratory Contract Number F29601-93-C-0165. Such applications are striving towards a sandwich type approach in which a low density structural core material (i.e. honeycomb or foam) is sandwiched between a high thermal conductivity facesheet. Structural cores are limited to low density materials to ensure that the weight limits are not exceeded. Unfortunately, carbon foams and carbon honeycomb materials are only available materials for use in high temperature applications (>1600° C.). High thermal conductivity carbon honeycomb materials are extremely expensive to manufacture compared to low conductivity honeycombs, therefore, a performance penalty is

paid for low cost materials. High conductivity carbon foams are also more expensive to manufacture than low conductivity carbon foams, in part, due to the starting materials.

In order to produce high stiffness and high conductivity carbon foams, invariably, a pitch must be used as the precursor. This is because pitch is the only precursor which forms a highly aligned graphitic structure which is a requirement for high conductivity. Typical processes utilize a blowing technique to produce a foam of the pitch precursor in which the pitch is melted and passed from a high pressure region to a low pressure region. Thermodynamically, this produces a "Flash," thereby causing the low molecular weight compounds in the pitch to vaporize (the pitch boils), resulting in a pitch foam. See Hagar, Joseph W. and Max L. Lake, "Novel Hybrid Composites Based on Carbon Foams," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:29-34 (1992), Hagar, Joseph W. and Max L. Lake, "Formulation of a Mathematical Process Model Process Model for the Foaming of a Mesophase Carbon Precursor," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:35-40 (1992), Gibson, L. J. and M. F. Ashby, *Cellular Solids: Structures & Properties*, Pergamon Press, New York (1988), Gibson, L. J., *Mat. Sci. and Eng A110*, 1 (1989), Knippenberg and B. Lersmacher, *Phillips Tech. Rev.*, 36(4), (1976), and Bonzom, A., P. Crepau and E. J. Moutard, U.S. Pat. No. 4,276,246, (1981). Then, the pitch foam must be oxidatively stabilized by heating in air (or oxygen) for many hours, thereby, cross-linking the structure and "setting" the pitch so it does not melt during carbonization. See Hagar, Joseph W. and Max L. Lake, "Formulation of a Mathematical Process Model Process Model for the Foaming of a Mesophase Carbon Precursor," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:35-40 (1992) and White, J. L., and P. M. Shaeffer, *Carbon*, 27:697 (1989). This is a time consuming step and can be an expensive step depending on the part size and equipment required. The "set" or oxidized pitch is then carbonized in an inert atmosphere to temperatures as high as 1100° C. Then, graphitization is performed at temperatures as high as 3000° C. to produce a high thermal conductivity graphitic structure, resulting in a stiff and very thermally conductive foam.

Other techniques utilize a polymeric precursor, such as phenolic, urethane, or blends of these with pitch. See Hagar, Joseph W. and Max L. Lake, "Idealized Strut Geometries for Open-Celled Foams," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:41-46 (1992), Aubert, J. W., (MRS Symposium Proceedings, 207:117-127 (1990), Cowlard, F. C. and J. C. Lewis, *J. of Mat. Sci.*, 2:507-512 (1967) and Noda, T., Inagaki and S. Yamada, *J. of Non-Crystalline Solids*, 1:285-302, (1969). High pressure is applied and the sample is heated. At a specified temperature, the pressure is released, thus causing the liquid to foam as volatile compounds are released. The polymeric precursors are cured and then carbonized without a stabilization step. However, these precursors produce a "glassy" or vitreous carbon which does not exhibit graphitic structure and, thus, has low thermal conductivity and low stiffness. See Hagar, Joseph W. and Max L. Lake, "Idealized Strut Geometries for Open-Celled Foams," *Mat. Res. Soc. Symp.*, Materials Research Society, 270:41-46 (1992).

In either case, once the foam is formed, it is then bonded in a separate step to the facesheet used in the composite. This can be an expensive step in the utilization of the foam.

The process of this invention overcomes these limitations, by not requiring a "blowing" or "pressure release" technique to produce the foam. Furthermore, an oxidation stabilization step is not required, as in other methods used to produce

pitchbased carbon foams with a highly aligned graphitic structure. This process is less time consuming, and therefore, will be lower in cost and easier to fabricate.

Lastly, the foam can be produced with an integrated sheet of high thermal conductivity carbon on the surface of the foam, thereby producing a carbon foam with a smooth sheet on the surface to improve heat transfer.

SUMMARY OF THE INVENTION

The general object of the present invention is to provide carbon foam and a composite from a mesophase or isotropic pitch such as synthetic, petroleum or coal-tar based pitch.

Another object is to provide a carbon foam and a composite from pitch which does not require an oxidative stabilization step.

These and other objectives are accomplished by a method of producing carbon foam wherein an appropriate mold shape is selected and preferably an appropriate mold release agent is applied to walls of the mold. Pitch is introduced to an appropriate level in the mold, and the mold is purged of air such as by applying a vacuum. Alternatively, an inert fluid could be employed. The pitch is heated to a temperature sufficient to coalesce the pitch into a liquid which preferably is of about 50° C. to about 100° C. above the softening point of the pitch. The vacuum is released and an inert fluid applied at a static pressure up to about 1000 psi. The pitch is heated to a temperature sufficient to cause gases to evolve and foam the pitch. The pitch is further heated to a temperature sufficient to coke the pitch and the pitch is cooled to room temperature with a simultaneous and gradual release of pressure.

In another aspect, the previously described steps are employed in a mold composed of a material such that the molten pitch does not wet.

In yet another aspect, the objectives are accomplished by the carbon foam product produced by the methods disclosed herein including a foam product with a smooth integral facesheet.

In still another aspect a carbon foam composite product is produced by adhering facesheets to a carbon foam produced by the process of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a micrograph illustrating typical carbon foam with interconnected carbon ligaments and open porosity.

FIGS. 2-6 are micrographs of pitch-derived carbon foam graphitized at 2500° C. and at various magnifications.

FIG. 7 is a SEM micrograph of the foam produced by the process of this invention.

FIG. 8 is a chart illustrating cumulative intrusion volume versus pore diameter.

FIG. 9 is a chart illustrating log differential intrusion volume versus pore diameter.

FIG. 10 is a graph illustrating the temperatures at which volatiles are given off from raw pitch.

FIG. 11 is an X-ray analysis of the graphitized foam produced by the process of this invention.

FIGS. 12A-C are photographs illustrating foam produced with aluminum crucibles and the smooth structure or face sheet that develops.

FIG. 13A is a schematic view illustrating the production of a carbon foam composite made in accordance with this invention.

FIG. 13B is a perspective view of the carbon foam composite of this invention.

DETAILED DESCRIPTION OF THE INVENTION

In order to illustrate the carbon foam product and composite of this invention, the following Examples are set forth. They are not intended to limit the invention in any way.

EXAMPLE I

Pitch powder, granules, or pellets are placed in a mold with the desired final shape of the foam. These pitch materials can be solvated if desired. In this Example Mitsubishi ARA-24 mesophase pitch was utilized. A proper mold release agent or film is applied to the sides of the mold to allow removal of the part. In this case, Boron Nitride spray and Dry Graphite Lubricant were separately used as a mold release agent. If the mold is made from pure aluminum, no mold release agent is necessary since the molten pitch does not wet the aluminum and, thus, will not stick to the mold. Similar mold materials may be found that the pitch does not wet and, thus, they will not need mold release. The sample is evacuated to less than 1 torr and then heated to a temperature approximately 50 to 100° C. above the softening point. In this case where Mitsubishi ARA24 mesophase pitch was used, 300° C. was sufficient. At this point, the vacuum is released to a nitrogen blanket and then a pressure of up to 1000 psi is applied. The temperature of the system is then raised to 800° C., or a temperature sufficient to coke the pitch which is 500° C. to 1000° C. This is performed at a rate of no greater than 5° C./min. and preferably at about 2° C./min. The temperature is held for at least 15 minutes to achieve an assured soak and then the furnace power is turned off and cooled to room temperature. Preferably the foam was cooled at a rate of approximately 1.5° C./min. with release of pressure at a rate of approximately 2 psi/min. Final foam temperatures for three product runs were 500° C., 630° C. and 800° C. During the cooling cycle, pressure is released gradually to atmospheric conditions. The foam was then heat treated to 1050° C. (carbonized) under a nitrogen blanket and then heat treated in separate runs to 2500° C. and 2800° C. (graphitized) in Argon.

Carbon foam produced with this technique was examined with photomicrography, scanning electron microscopy (SEM), X-ray analysis, and mercury porosimetry. As can be seen in the FIGS. 2-7, the interference patterns under cross-polarized light indicate that the struts of the foam are completely graphitic. That is, all of the pitch was converted to graphite and aligned along the axis of the struts. These struts are also similar in size and are interconnected throughout the foam. This would indicate that the foam would have high stiffness and good strength. As seen in FIG. 7 by the SEM micrograph of the foam, the foam is open cellular meaning that the porosity is not closed. FIGS. 8 and 9 are results of the mercury porosimetry tests. These tests indicate that the pore sizes are in the range of 90-200 microns.

A thermogravimetric study of the raw pitch was performed to determine the temperature at which the volatiles are evolved. As can be seen in FIG. 11, the pitch loses nearly 20% of its mass fairly rapidly in the temperature range between about 420° C. and about 480° C. Although this was performed at atmospheric pressure, the addition of 1000 psi pressure will not shift this effect significantly. Therefore, while the pressure is at 1000 psi, gases rapidly evolved during heating through the temperature range of 420° C. to 480° C. The gases produce a foaming effect (like boiling) on the molten pitch. As the temperature is increased further to

temperatures ranging from 500° C. to 1000° C. (depending on the specific pitch), the foamed pitch becomes coked (or rigid), thus producing a solid foam derived from pitch. Hence, the foaming has occurred before the release of pressure and, therefore, this process is very different from previous art.

Samples from the foam were machined into specimens for measuring the thermal conductivity. The bulk thermal conductivity ranged from 58 W/m·K to 106 W/m·K. The average density of the samples was 0.53 g/cm³. When weight is taken into account, the specific thermal conductivity of the pitch derived foam is over 4 times greater than that of copper. Further derivations can be utilized to estimate the thermal conductivity of the struts themselves to be nearly 700 W/m·K. This is comparable to high thermal conductivity carbon fibers produced from this same ARA24 mesophase pitch.

X-ray analysis of the foam was performed to determine the crystalline structure of the material. The x-ray results are shown in FIG. 11. From this data, the graphene layer spacing (d_{002}) was determined to be 0.336 nm. The coherence length (La, 1010) was determined to be 203.3 nm and the stacking height was determined to be 442.3 nm.

The compression strength of the samples were measured to be 3.4 MPa and the compression modulus was measured to be 73.4 MPa. The foam sample was easily machined and could be handled readily without fear of damage, indicating a good strength.

It is important to note that when this pitch is heated in a similar manner, but under only atmospheric pressure, the pitch foams dramatically more than when under pressure. In fact, the resulting foam is so fragile that it could not even be handled to perform tests.

EXAMPLE II

An alternative to the method of Example I is to utilize a mold made from aluminum. In this case two molds were used, an aluminum weighing dish and a sectioned soda can. The same process as set forth in Example I is employed except that the final coking temperature was only 630° C., so as to prevent the aluminum from melting.

FIGS. 12 A–C illustrate the ability to utilize complex shaped molds for producing complex shaped foam. In one case, shown in FIG. 12 A the top of a soda can was removed and the remaining can used as a mold. No release agent was utilized. Note that the shape of the resulting part conforms to the shape of the soda can, even after graphitization to 2800° C. This demonstrates the dimensional stability of the foam and the ability to produce near net shaped parts.

In the second case, as shown in FIGS. 12 B and C employing an aluminum weight dish, a very smooth surface was formed on the surface contacting the aluminum. This is directly attributable to the fact that the molten pitch does not wet the surface of the aluminum. This would allow one to produce complex shaped parts with smooth surfaces so as to improve contact area for bonding or improving heat transfer. This smooth surface will act as a face sheet and, thus, a foam-core composite can be fabricated in-situ with the fabrication of the face sheet. Since it is fabricated together and an integral material no interface joints result, thermal stresses will be less, resulting in a stronger material.

The following examples illustrate the production of a composite material employing the foam of this invention.

EXAMPLE III

Pitch derived carbon foam was produced with the method described in Example I. Referring to FIG. 13A the carbon

foam **10** was then machined into a block 2"×2"×½". Two pieces **12** and **14** of a prepreg comprised of Hercules AS4 carbon fibers and ICI Fibirite Polyetheretherketone thermoplastic resin also of 2"×2"×½" size were placed on the top and bottom of the foam sample, and all was placed in a matched graphite mold **16** for compression by graphite plunger **18**. The composite sample was heated under an applied pressure of 100 psi to a temperature of 380° C. at a rate of 5° C./min. The composite was then heated under a pressure of 100 psi to a temperature of 650° C. The foam core sandwich panel generally **20** was then removed from the mold and carbonized under nitrogen to 1050° C. and then graphitized to 2800° C., resulting in a foam with carbon—carbon facesheets bonded to the surface. The composite generally **30** is shown in FIG. 13B.

EXAMPLE IV

Pitch derived carbon foam was produced with the method described in Example I. It was then machined into a block 2"×2"×½". Two pieces of carbon—carbon material, 2"×2"×½", were coated lightly with a mixture of 50% ethanol, 50% phenolic Durez© Resin available from Occidental Chemical Co. The foam block and carbon—carbon material were positioned together and placed in a mold as indicated in Example III. The sample was heated to a temperature of 150° C. at a rate of 5° C./min and soaked at temperature for 14 hours. The sample was then carbonized under nitrogen to 1050° C. and then graphitized to 2800° C., resulting in a foam with carbon—carbon facesheets bonded to the surface. This is also shown generally at **30** in FIG. 13B.

EXAMPLE V

Pitch derived carbon foam was produced with the method described in Example I. The foam sample was then densified with carbon by the method of chemical vapor infiltration for 100 hours. The density increased to 1.4 g/cm³, the flexural strength was 19.5 MPa and the flexural modulus was 2300 MPa. The thermal conductivity of the raw foam was 58 W/m·K and the thermal conductivity of the densified foam was 94 W/m·K.

EXAMPLE VI

Pitch derived carbon foam was produced with the method described in Example I. The foam sample was then densified with epoxy by the method of vacuum impregnation. The epoxy was cured at 150° C. for 5 hours. The density increased to 1.37 g/cm³ and the flexural strength was measured to be 19.3 MPa.

It is obvious that other materials, such as metals, ceramics, plastics, or fiber reinforced plastics could be bonded to the surface of the foam of this invention to produce a foam core composite material with acceptable properties. It is also obvious that ceramics, or glass, or other materials could be impregnated into the foam for densification.

Based on the data taken to date from the carbon foam material, several observations can be made and the important features of the invention are:

1. Pitch-based carbon foam can be produced without an oxidative stabilization step, thus saving time and costs.
2. High graphitic alignment in the struts of the foam is achieved upon graphitization to 2500° C., and thus high thermal conductivity and stiffness will be exhibited by the foam, making them suitable as a core material for thermal applications.
3. High compressive strengths should be achieved with mesophase pitch-based carbon foams, making them suitable as a core material for structural applications.

4. Foam core composites can be fabricated at the same time as the foam is generated, thus saving time and costs.
5. Rigid monolithic preforms can be made with significant open porosity suitable for densification by the Chemical Vapor Infiltration method of ceramic and carbon infiltrants.
6. Rigid monolithic preforms can be made with significant open porosity suitable for activation, producing a monolithic activated carbon.
7. It is obvious that by varying the pressure applied, the size of the bubbles formed during the foaming will change and, thus, the density, strength, and other properties can be affected.

The following alternative procedures and products can also be effected by the process of this invention:

1. Fabrication of preforms with complex shapes for densification by CVI or Melt Impregnation.
2. Activated carbon monoliths.
3. Optical absorbent.
4. Low density heating elements.
5. Firewall Material
6. Low secondary electron emission targets for high-energy physics applications.

It will thus be seen that the present invention provides for the manufacture of pitch-based carbon foam for structural and thermal composites. The process involves the fabrication of a graphitic foam from a mesophase or isotropic pitch which can be synthetic, petroleum, or coal-tar based. A blend of these pitches can also be employed. The simplified process utilizes a high pressure high temperature furnace and thereby, does not require an oxidative stabilization step. The foam has a relatively uniform distribution of pore sizes (≈ 100 microns), very little closed porosity, and density of approximately 0.53 g/cm^3 . The mesophase pitch is stretched along the struts of the foam structure and thereby produces a highly aligned graphitic structure in the struts. These struts will exhibit thermal conductivities and stiffness similar to the very expensive high performance carbon fibers (such as P-120 and K1100). Thus, the foam will exhibit high stiffness and thermal conductivity at a very low density ($\approx 0.5 \text{ g/cc}$). This foam can be formed in place as a core material for high temperature sandwich panels for both thermal and structural applications, thus reducing fabrication time.

By utilizing an isotropic pitch, the resulting foam can be easily activated to produce a high surface area activated carbon. The activated carbon foam will not experience the problems associated with granules such as attrition, channeling, and large pressure drops.

What is claimed is:

1. A process of producing carbon foam comprising: selecting an appropriate mold shape; introducing pitch to an appropriate level in a mold; purging air from the mold; heating the pitch to a temperature sufficient to coalesce the pitch into a liquid; applying an inert fluid at a static pressure up to about 1000 psi; heating the pitch to a temperature sufficient to cause gases to evolve and foam the pitch; heating the pitch to a temperature sufficient to coke the pitch; and cooling the foam to room temperature with a simultaneous release of pressure to produce a carbon foam.
2. The process of claim 1 wherein the pitch is introduced as granulated pitch.

3. The process of claim 1 wherein the pitch is introduced as powdered pitch.

4. The process of claim 1 wherein the pitch is introduced as pelletized pitch.

5. The process of claim 1 wherein the pitch is a synthetic mesophase or isotropic pitch.

6. The process of claim 1 wherein the pitch is a petroleum derived mesophase or isotropic pitch.

7. The process of claim 1 wherein the pitch is a coal-derived mesophase or isotropic pitch.

8. The process of claim 1 wherein the pitch is a blend of pitches selected from the group consisting of synthetic mesophase or isotropic pitch, petroleum derived mesophase or isotropic pitch, and coal derived mesophase or isotropic pitch.

9. The process of claim 1 wherein the pitch is a solvated pitch.

10. The process of claim 1 wherein the purging is effected by a vacuum step.

11. The process of claim 1 wherein the purging is effected by an inert fluid.

12. The process of claim 10 wherein the vacuum is applied at less than 1 torr.

13. The process of claim 1 wherein nitrogen is introduced as the inert fluid.

14. The process of claim 1 wherein the pitch is heated to a temperature in the range of about 500° C. to about 1000° C. to coke the pitch.

15. The process of claim 1 wherein the pitch is heated to a temperature of about 800° C. to coke the pitch.

16. The process of claim 1 wherein the temperature to coke the pitch is raised at a rate of no greater than 5° C. per minute.

17. The process of claim 1 wherein the pitch is soaked at the coking temperature for at least 15 minutes to effect the coking.

18. The process of claim 1 wherein the pitch is heated to a temperature of about 630° C. to coke the pitch.

19. The process of claim 1 wherein the pitch is heated to a temperature of about 50° C. to about 100° C. to coalesce the pitch.

20. The process of claim 1 where the foam is cooled at a rate of approximately 1.5° C./min with the release of pressure at a rate of approximately 2 psi/min.

21. The process of claim 1 further including the step of densifying the foam.

22. A process of producing carbon foam comprising: selecting an appropriate mold shape and a mold composed of

a material that the molten pitch does not wet;

introducing pitch to an appropriate level in the mold;

purging the air from the mold;

heating the pitch to a temperature sufficient to coalesce the pitch into a liquid;

applying an inert fluid at a static pressure up to about 1000 psi;

heating the pitch to a temperature sufficient to coke the pitch; and

cooling the foam to room temperature with a simultaneous release of pressure to produce a carbon foam.

23. The process of claim 22 wherein the pitch is introduced as granulated pitch.

24. The process of claim 22 wherein the pitch is introduced as powdered pitch.

25. The process of claim 22 wherein the pitch is introduced as pelletized pitch.

- 26. The process of claim 22 where in the pitch is a synthetic mesophase or isotropic pitch.
- 27. The process of claim 22 where in the pitch is a petroleum-derived mesophase pitch.
- 28. The process of claim 22 where in the pitch is a coal-derived mesophase pitch. 5
- 29. The process of claim 22 wherein the mold is purged by a vacuum applied at less than 1 torr.
- 30. The process of claim 22 wherein the mold is purged by an inert fluid before heating. 10
- 31. A process of producing carbon foam core composite comprising:
 - selecting an appropriate mold shape;
 - introducing pitch to an appropriate level in a mold;
 - purging air from the mold; 15
 - heating the pitch to a temperature sufficient to coalesce the pitch into a liquid;
 - applying an inert fluid at a static pressure up to above 1000 psi; 20
 - heating the pitch to a temperature sufficient to cause gases to evolve and foam the pitch;
 - heating the pitch to a temperature sufficient to coke the pitch; 25
 - cooling the foam to room temperature with a simultaneous release of pressure;
 - placing facesheets on the opposite sides of the carbon foam; and
 - adhering the facesheets to the carbon foam to produce a carbon foam core. 30
- 32. The process of claim 31 wherein the adhering of the facesheets to the carbon foam is effected by a molding step.
- 33. The process of claim 31 wherein the adhering of the facesheets to the carbon foam is effected by a coating material. 35
- 34. A process for producing a carbon foam comprising:
 - providing pitch in a container;
 - heating said pitch in a non-oxidizing atmosphere at a pressure and temperature sufficient to coalesce said pitch to form a liquid of said pitch; 40
 - increasing said pressure of said non-oxidizing atmosphere in said container containing said liquid of said pitch

- from said pressure to an increased pressure having a range greater than said pressure to about 1000 psi; and heating said container containing said liquid of said pitch at said increased pressure to a temperature sufficient to form a carbon foam.
- 35. A process for producing a carbon foam in accordance with claim 34 wherein said container containing said liquid of said pitch at said increased pressure of about 1000 psi is heated to a temperature from about 420° C. to about 480° C.
- 36. A process for producing a thermally conductive essentially graphitic carbon foam comprising:
 - providing pitch in a container;
 - heating said pitch in a non-oxidizing atmosphere at a pressure to a temperature sufficient to coalesce said pitch to form a liquid of said pitch;
 - increasing said pressure of said non-oxidizing atmosphere in said container containing said liquid of said pitch from said pressure to an increased pressure having a range greater than said pressure to about 1000 psi;
 - heating said container containing said liquid of said pitch at said increased pressure to a temperature sufficient to form a carbon foam;
 - cooling said carbon foam and reducing said increased pressure to atmospheric pressure;
 - heating said carbon foam in a non-oxidizing atmosphere to a temperature sufficient to carbonize said carbon foam to form a carbonized carbon foam; and
 - heating said carbonized carbon foam in a non-oxidizing atmosphere to a temperature sufficient to form a thermally conductive essentially graphitic carbon foam.
- 37. A process for producing a carbon foam in accordance with claim 36 wherein said container containing said liquid of said pitch is heated to a temperature from about 420° C. to about 480° C., said carbon foam at atmospheric pressure is heated to a temperature from about 500° C. to about 1050° C. and said carbonized carbon foam is heated to a temperature equal to or greater than 2500° C.
- 38. A process for producing a thermal conducting essentially graphitic carbon foam in accordance with claim 36 wherein said graphitic carbon foam has a specific thermal conductivity greater than 109 W.cm³/m.K.g.

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