



***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<b>AT</b> Austria	<b>GA</b> Gabon	<b>MR</b> Mauritania
<b>AU</b> Australia	<b>GB</b> United Kingdom	<b>MW</b> Malawi
<b>BB</b> Barbados	<b>HU</b> Hungary	<b>NL</b> Netherlands
<b>BE</b> Belgium	<b>IT</b> Italy	<b>NO</b> Norway
<b>BG</b> Bulgaria	<b>JP</b> Japan	<b>RO</b> Romania
<b>BR</b> Brazil	<b>KP</b> Democratic People's Republic of Korea	<b>SD</b> Sudan
<b>CF</b> Central African Republic	<b>KR</b> Republic of Korea	<b>SE</b> Sweden
<b>CG</b> Congo	<b>LI</b> Liechtenstein	<b>SN</b> Senegal
<b>CH</b> Switzerland	<b>LK</b> Sri Lanka	<b>SU</b> Soviet Union
<b>CM</b> Cameroon	<b>LU</b> Luxembourg	<b>TD</b> Chad
<b>DE</b> Germany, Federal Republic of	<b>MC</b> Monaco	<b>TG</b> Togo
<b>DK</b> Denmark	<b>MG</b> Madagascar	<b>US</b> United States of America
<b>FI</b> Finland	<b>ML</b> Mali	
<b>FR</b> France		

CARBON FIBRILS, METHOD FOR PRODUCING SAME,  
AND COMPOSITIONS CONTAINING SAME

BACKGROUND OF THE INVENTION

5

This invention relates to the production of graphitic carbon fibrils having high surface area, high Young's modulus of elasticity and high tensile strength. More specifically, it relates to such fibrils grown catalytically from inexpensive, readily available carbon precursors without the need for usual and expensive graphitizing temperatures (approximately 2900°C).

10

Fiber-reinforced composite materials are becoming increasingly important because their mechanical properties, notably strength, stiffness and toughness, are superior to the properties of their separate components or of other non-composite materials. Composites made from carbon fibers excel in strength and stiffness per unit weight, hence are finding rapid acceptance in aerospace and sporting goods applications. Their high cost, however, inhibits their wider use.

15

20

Carbon fibers are currently made by controlled pyrolysis of continuous filaments of precursor organic polymers, notably cellulose or polyacrylonitrile, under carefully maintained tension, needed to insure good orientation of the anisotropic sheets of carbon atoms in the final filaments. Their high cost is a consequence of the cost of the preformed organic fibers, the weight loss in carbonization, the slow rate of carbonization in expensive equipment and the careful handling necessary to avoid breaks in the continuous filaments.

25

30

35

There has been intense development of methods of spinning

-2-

and carbonizing hydrocarbon pitch fiber to reduce precursor filament cost and weight loss. So far, the pitch pre-treatment, spinning conditions and post-treatments needed to insure correct orientation of the sheets of carbon atoms in the final products have been nearly as expensive as the previously noted method involving organic polymers. Both methods require use of continuous filaments to achieve high orientation and best properties. There is a practical lower limit of fiber diameter, 6 to 8 micrometers, below which fiber breakage in spinning and post-treatments becomes excessive.

An entirely distinct approach to carbon fiber formation involves the preparation of carbon filaments through the catalytic decomposition at metal surfaces of a variety of carbon containing gases, e.g., CO/H<sub>2</sub>, hydrocarbons, and acetone. These filaments are found in a wide variety of morphologies (e.g., straight, twisted, helical, branched) and diameters (e.g., ranging from tens of angstroms to tens of microns). Usually, a mixture of filament morphologies is obtained, frequently admixed with other, non-filamentous carbon (cf. Baker and Harris, Chemistry and Physics of Carbon, Vol. 14, 1978). Frequently, the originally formed carbon filaments are coated with poorly organized thermal carbon. Only relatively straight filaments possessing relatively large graphitic domains oriented with their c-axes perpendicular to the fiber axis and possessing little or no thermal carbon overcoat will impart the properties of high strength and modulus required in reinforcement applications.

Most reports that cite formation of filamentous carbon do not document the particular type of filaments formed, so that it is impossible to determine whether the filaments are suitable for reinforcement applications. For example,

Baker et al., in British Patent 1,499,930 (1977), disclose that carbon filaments are formed when an acetylene or diolefin is decomposed over catalyst particles at 675-775°C. No description of the structure of these filaments is given, however. In European Patent Application EP 56,004 (1982), Tates and Baker describe the formation of filamentous carbon over  $\text{FeO}_x$  substrates, but again do not disclose any information concerning the structure of the carbon filaments formed. Bennett et al., in United Kingdom Atomic Energy Authority Report AERE-R7407, describe the formation of filamentous carbon from catalytic decomposition of acetone, but also fail to give any indication of the morphology, and hence suitability for reinforcement applications, of the carbon formed.

Several groups of workers have disclosed the formation of straight carbon filaments through catalytic decomposition of hydrocarbons. Oberlin, Endo, and Koyama have reported that aromatic hydrocarbons such as benzene are converted to carbon fibers with metal catalyst particles at temperatures of around 1100°C, Carbon 14:133 (1976). The carbon filaments contain a well ordered, graphitic core of approximately the diameter of a catalyst particle, surrounded by an overcoat of less organized thermal carbon. Final filament diameters are in the range of 0.1 to 80 microns. The authors infer that the graphitic core grows rapidly and catalytically, and that thermal carbon subsequently deposits on it, but state that the two processes cannot be separated "because they are statistically concomitant". Journal of Crystal Growth 32:335 (1976). The native fibers, coated with thermal carbon, possess low strength and stiffness, and are not useful as a reinforcing filler in composites. An additional high temperature treatment at 2500-3000°C is necessary to convert the entire filament to highly ordered graphitic carbon. While this procedure may be an im-

5  
10  
15  
20  
25  
30  
35

provement on the difficult and costly pyrolysis of preformed organic fibers under tension, it suffers from the drawback that a two step process of fiber growth and high temperature graphitization is required. In addition, the authors state nothing regarding deliberate catalyst preparation, and catalyst particles appear to be adventitious. In more recent work, preparation of catalytic particles is explored, but the two processes of catalytic core growth and thermal carbon deposition are again not separated, Extended Abstracts, 16th Biennial Conference on Carbon: 523 (1983).

15  
20  
25  
30  
35

Tibbetts has described the formation of straight carbon fibers through pyrolysis of natural gas in type 304 stainless steel tubing at temperatures of 950-1075°C, Appl. Phys. Lett. 42(8):666 (1983). The fibers are reported to grow in two stages similar to those seen by Koyama and Endo, where the fibers first lengthen catalytically and then thicken by pyrolytic deposition of carbon. Tibbetts states that these stages are "overlapping", and is unable to grow filaments free of pyrolytically deposited carbon. In addition, Tibbetts's approach is commercially impracticable for at least two reasons. First, initiation of fiber growth occurs only after slow carbonization of the steel tube (typically about ten hours), leading to a low overall rate of fiber production. Second, the reaction tube is consumed in the fiber forming process, making commercial scale-up difficult and expensive.

30  
35

It has now unexpectedly been found that it is possible to catalytically convert hydrocarbon precursors to carbon filaments substantially free of pyrolytically deposited thermal carbon, and thereby to avoid the thickening stage reported in the prior art as "overlapping" and "concomitant" with the filament lengthening stage. This ability allows the direct formation of high strength fibrils useful in the

-5-

reinforcement of matrices, in the preparation of electrode materials of very high surface area, and in the shielding of objects from electromagnetic radiation.

5

10

15

20

25

30

35

SUMMARY OF THE INVENTION

5 This invention concerns an essentially cylindrical discrete carbon fibril characterized by a substantially constant diameter between about 3.5 and about 70 nanometers, e.g. between about 7 and 25 nanometers, length greater than about  $10^2$  times the diameter, an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core region, each of the layers and core disposed substantially concentrically about the cylindrical axis of the fibril. Preferably the entire fibril is substantially free of thermal carbon overcoat.

10 The inner core of the fibril may be hollow or may contain carbon atoms which are less ordered than the ordered carbon atoms of the outer region, which are graphitic in nature.

15 The fibril of this invention may be produced by contacting for an appropriate period of time and at a suitable pressure a suitable metal-containing particle with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particle being at least about 100:1.

20 The contacting of the metal-containing particle with the carbon-containing compound may be carried out in the presence of a compound, e.g. CO<sub>2</sub>, H<sub>2</sub> or H<sub>2</sub>O, capable of reaction with carbon to produce gaseous products.

25 Suitable carbon-containing compounds include hydrocarbons, including aromatic hydrocarbons, e.g. benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof; non-aromatic hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene or acetylene or mixtures thereof; and oxygen-con-

30

35

-7-

taining hydrocarbons, e.g. formaldehyde, acetaldehyde, acetone, methanol, or ethanol or mixtures thereof; and include carbon monoxide.

5 The suitable metal-containing particle may be an iron-, cobalt-, or nickel-containing particle having a diameter between about 3.5 and about 70 nanometers.

10 Such particles may be supported on a chemically compatible, refractory support, e.g., a support of alumina, carbon, or a silicate, including an aluminum silicate.

15 In one embodiment the surface of the metal-containing particle is independently heated, e.g. by electromagnetic radiation, to a temperature between about 850°C and 1800°C, the temperature of the particle being higher than the temperature of the gaseous, carbon-containing compound.

20 In a specific embodiment, the metal-containing particle is contacted with the carbon-containing compound for a period of time from about 10 seconds to about 180 minutes at a pressure of from about one-tenth atmosphere to about ten atmospheres. In this embodiment, the metal-containing particle is an iron-containing particle, the gaseous carbon-containing compound is benzene, the reaction temperature is between 900°C and 1150°C and the ratio of carbon-containing compound to metal-containing particle is greater than about 1000:1. The contacting may be carried out in the presence of gaseous hydrogen. Additionally, the iron-containing particle may be supported on a chemically compatible, refractory support of, e.g., alumina or carbon.

35 In addition to the above-mentioned method and carbon fibril produced thereby this invention also concerns a method for producing a substantially uniform plurality of essentially cylindrical, discrete carbon fibrils which comprises con-

-8-

tacting for an appropriate period of time and at a suitable pressure, suitable metal-containing particles with a suitable gaseous, carbon-containing compound, at a temperature between about 850°C and 1200°C, the ratio on a dry weight basis of carbon-containing compound to metal-containing particles being at least about 100:1. Preferably, each of the fibrils so produced has a diameter substantially equal to the diameter of each other fibril. In one embodiment the metal-containing particles are pre-formed.

The fibrils are useful in composites having a matrix of e.g., an organic polymer, an inorganic polymer or a metal. In one embodiment the fibrils are incorporated into structural materials in a method of reinforcement. In other embodiments the fibrils may be used to enhance the electrical or thermal conductivity of a material, to increase the surface area of an electrode or an electrolytic capacitor plate, to provide a support for a catalyst, or to shield an object from electromagnetic radiation.