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(54) Boronated mesophase pitch derived carbon fibres.

(57) A mesophase pitch derived carbon fibre having a diameter of less than 30 microns and having at least about 0.1% by weight boron diffused in the lattice of the fibre and a method for producing a mesophase pitch derived carbon fibre comprising contacting a mesophase pitch derived fibre having a diameter of less than 30 microns with a boron compound, and subjecting the fibre to heat treatment in an inert atmosphere at a maximum temperature of about 2000°C to about 2400°C to form the carbon fibre.

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DESCRIPTION

BORATED MESOPHASE PITCH DERIVED CARBON FIBRES

The invention relates to boronated mesophase pitch derived carbon fibres and to a method for producing mesophase pitch derived carbon fibres.

It is well known to spin a mesophase pitch into a fibre, thermoset the pitch fibre by heating it in air, and carbonize the thermoset pitch fibre by heating the thermoset pitch fibre in an inert gaseous environment to an elevated temperature.

It is preferable to use mesophase pitch in carrying out this process rather than isotropic pitch because the carbon fibre obtained using mesophase pitch exhibits excellent mechanical properties.

The present invention is directed to mesophase pitch derived carbon fibres which have diameters less than about 30 microns.

In a process for producing a mesophase pitch derived carbon fibre, it is well known that a relatively high Young's modulus of greater than about 517 G Pa requires a carbonizing temperature in the order of 3000°C. It is also well known that such elevated temperatures are costly to produce and the equipment to produce such temperatures deteriorate rapidly due to the intense heat.

In addition, it has been found that even though a high Young's modulus can be obtained using carbonizing temperatures of 3000°C or higher, there tends to be a degradation in the compressive strength of the mesophase pitch derived carbon fibres for higher values of Young's modulus and this is undesirable.

The process of the present invention overcomes the problems of the prior art and enables the carbonizing temperature to be considerably lower for producing a mesophase pitch derived carbon fibre having a relatively high Young's modulus. Furthermore, the carbon fibre produced by the present invention possesses a higher compressive strength as compared to the prior art mesophase pitch derived carbon fibres having comparable Young's moduli.

According to the present invention a mesophase pitch derived carbon fibre is provided having a diameter of less than 30 microns and having at least about 0.1% by weight boron diffused in the lattice of the fibre.

The invention includes a method for producing a mesophase pitch derived carbon fibre comprising contacting a mesophase pitch derived fibre with a boron compound, and subjecting the fibre to heat treatment at a maximum temperature of about 2000°C to about 2400°C to form the carbon fibre.

The steps of contacting and heat treating can be simultaneous or in tandem in time.

The mesophase pitch derived fibre of the invention preferably has 0.6% by weight boron diffused in the lattice of the fibre.

Preferably, a solution such as a boric acid solution with a concentration of about 2% by weight should be used.

Preferably, a thermoset mesophase pitch derived fibre which has been carbonized to 1300°C is wound on a mandrel and immersed in a 2% by weight boric acid aqueous solution for at least 24 hours, dried at a temperature of about 300°C for 17 hours, and thereafter subjected to a heat treatment at a temperature of about 2000°C in an inert atmosphere such as an argon atmosphere.

In carrying out the invention, a "yarn" or bundle of filaments is used rather than a single fibre. Typically, a commercial yarn has about 2000 filaments.

It has been found that the presence of oxygen in and around a fibre being treated to establish the boronating can degrade the resulting carbon fibre. Thus, it is preferable to use a carbonized fibre which has both good handling capabilities and has lost the oxygen which was introduced during the thermosetting.

A thermoset mesophase pitch derived yarn can be boronated. This yarn must be handled more carefully than the carbonized yarn due to the relatively weak mechanical properties.

For completeness, it is pointed out that U.S. Patent No. 3,723,605 to Ram is directed to a process of using a boron compound to reduce the temperature for graphitizing an amorphous carbon. The patent is directed to carbon fibres derived from organic polymeric fibrous materials such as, for example, acrylic polymer, a cellulosic polymer, a polyamide, a polybenzimidazole or polyvinyl alcohol. That is, the patent teaches away from mesophase pitch derived fibres.

In any event, the disclosure of the patent is incorporated into the instant disclosure.

Further objects and advantages of the invention will be set forth in part in the following specification and in part will be obvious therefrom without being specifically referred to, the same being realized and attained as pointed out in the claims hereof.

In carrying out the best mode, a mesophase pitch derived yarn having 2,000 filaments was used. The yarn was thermoset and carbonized to 1300°C. Each filament has a diameter of about 10 microns. A mandrel or spool made of graphite and having a diameter of about 7cm and a height of about 12.7 cm was wrapped with a layer of carbon felt having a thickness of 0.64 cm and approximately 42.7 cm of the mesophase pitch derived yarn was wrapped on this layer. The yarn made about four layers. A second layer of carbon felt was wrapped around the layers of the yarn to define a mandrel assembly.

The mandrel assembly was then immersed in a 2% by weight aqueous solution of boric acid for at least 24 hours and then dried at a temperature of about 300°C for about 17 hours. Immediately after drying, the mandrel assembly was charged in a graphite susceptor and placed in an induction vacuum furnace. The furnace was evacuated to 10^{-5} Torr prior to purging the system with argon and an argon atmosphere was maintained throughout the heating cycle.

In separate tests, yarns were heat treated at 2050°C, 2300°C, and 2500°C for 0, 15 and 30 minutes in each case. The 0 minute hold procedure consisted of reaching the designated peak temperature and then turning the furnace power off. The heating rate was such that the time required to reach 2050°C was about ten minutes while the time to reach 2500°C was about fifteen minutes.

Table 1 shows the Young's modulus for each boronated mesophase pitch derived carbon fibre according to the present invention and control mesophase pitch derived carbon fibres which were carried through the same heat treatment but were not boronated. In each case, the boronated carbon fibres had a higher Young's modulus and the improvement in the boronated fibres was particularly evident for the heat treatment of 2050°C.

The Young's modulus was measured using yarn specimens. The yarn was embedded in an epoxy resin and loaded at the rate of 1.27 cm per minute and the modulus was obtained using an extensometer.

TABLE 1

Holding Time (Min)	Maximum Temperature 2050°C Boronated/ Control G Pa	2300°C Boronated/ Control G Pa	2500°C Boronated/ Control G Pa
0	462/359	621/503	635/662
15	724/531	703/628	745/669
30	510/428	586/566	572/572

For high modulus fibres, the compressive strength of the boronated carbon fibres was greater than the prior art carbon fibres.

The process of contacting the mesophase pitch derived fibres with boron compounds can be carried out continuously by having the thermoset pitch yarn contacted with a boron solution prior to a heat treatment such as carried out in accordance with the invention. Preferably, the thermoset pitch yarn should be carbonized to about 1300°C and then contacted with a boron solution and carbonized according to the invention.

Tests have shown that if a thermoset fibre yarn is used in connection with the mandrel, then a subsequent heat treatment while the thermoset fibre remains on the mandrel results in a deterioration of mechanical properties. It is believed that this deterioration arises from the oxygen released from the thermoset fibres being maintained in the vicinity of the fibres by the carbon felt which surrounds the fibres on the mandrel.

Generally, the boron which enters the lattice of the carbon fibres amounts to up to about 1.2% by weight. At least about 0.1% by weight boron is needed in the lattice in order to produce an appreciable improvement.

CLAIMS

1. A mesophase pitch derived carbon fibre having a diameter of less than 30 microns and having at least about 0.1% by weight boron diffused in the lattice of the fibre.

2. A mesophase pitch according to claim 1, wherein the maximum amount of boron is about 1.2%.

3. A mesophase pitch derived carbon fibre according to claim 1 or 2, wherein said fibre has a Young's modulus of at least about 517 G Pa.

4. A method for producing a mesophase pitch derived carbon fibre, comprising contacting a mesophase pitch derived fibre having a diameter of less than 30 microns with a boron compound, and subjecting the fibre to heat treatment in an inert atmosphere at a maximum temperature of about 2000°C to about 2400°C to form the carbon fibre.

5. A method according to claim 4, wherein the mesophase pitch derived fibre is a thermoset fibre.

6. A method according to claim 4 or 5, wherein the mesophase pitch derived fibre is a carbonized fibre.

7. A method according to claim 6, wherein the carbonized fibre has been subjected to a temperature of about 1300°C

8. A method according to any of claims 4 to 7, wherein the boron compound is boric acid in the form of an aqueous solution.

9. A method according to claim 8, wherein the mesophase pitch derived fibre is contacted with the boric acid solution and dried before the heat treatment.

10. A method according to claim 8 or 9, wherein the concentration of the solution is about 2% by weight boric acid.

11. A method according to any of claims 4 to 10, wherein the heat treatment occurs simultaneously with, or subsequent to, the contacting step.

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EUROPEAN SEARCH REPORT

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Application number

EP 82 30 3176

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	FR-A-2 424 240 (STACK POLE CARBON) * Claims; page 1, lines 20-38 *	1,8-11	D 01 F 9/14 D 01 F 11/10

A	DE-A-1 949 830 (NATIONAL RESEARCH) * Claims *	1,8-10	

A	GB-A-1 295 289 (EZEKIEL) * Claims; page 2, lines 16-25; page 2, line 6 - page 3, line 20 *	1,8-10	

			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			D 01 F C 01 B C 10 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-10-1982	HELLEMANS W.J.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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