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(54) **Calcium intercalated boronated carbon fibre.**

(57) A mesophase pitch derived carbon fibre having a diameter of less than 30 microns and which has been boronated and intercalated with calcium and a method of producing a mesophase pitch derived carbon fibre comprising the steps of boronating and intercalating with calcium a carbon fibre having a diameter of less than 30 microns and derived from a mesophase pitch having a mesophase content of at least about 70% by weight mesophase.

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DESCRIPTION

"CALCIUM INTERCALATED BORONATED CARBON FIBRE"

The invention relates to a mesophase pitch derived carbon fibre and particularly to a carbon fibre which has been boronated and intercalated with calcium.

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 rather than isotropic pitch for producing the carbon fibres because the mesophase pitch derived carbon fibre possesses excellent mechanical properties. Furthermore, it is preferable to use a mesophase pitch having a meshophase content of at least about 70% by weight for the process.

Carbon fibres have found a wide range of commercial uses. In certain uses, it is desirable to use carbon fibres which possess both excellent mechanical properties and good electrical conductivity. The electrical conductivity is usually described in terms of resistivity. Typically, a mesophase pitch derived carbon fibre which has been carbonized to a temperature of about 2500°C has a resistivity of about 7 microohm-metres and a Young's modulus of about 413.6 GPa. The same carbon fibre heat treated to about 3000°C has a resistivity of about 3.3 microohm-metres.

The cost for obtaining temperatures of 2500°C and particularly 3000°C is very high. Not only is it closely to expend the energy to reach the high temperatures, but the equipment needed to reach such high temperatures is costly and deteriorates rapidly due to the elevated temperatures.

The present invention allows the production of a mesophase pitch derived carbon fibre having a resistivity

of less than about 2 microohm-metres, and preferably about 1 microohm-metre, with a maximum heat treating temperature of from about 2000°C to about 2300°C.

The present invention relates to a mesophase pitch derivated carbon fibre which has been boronated and intercalated with calcium.

In the preferred embodiment there is a calcium to boron weight ratio of about 2:1 in the carbon fibre.

In the absence of boron, the calcium does not intercalate into the carbon fibre very well. Even very small amounts of boron enhance the intercalation of the calcium. Generally, 0.1% by weight boron or even less is sufficient to improve substantially the intercalation of calcium into the carbon fibres.

For any given amount of boron in a carbon fibre, the resistivity generally increases as the amount of intercalated calcium increases at the low end, below a calcium to boron weight ratio of 2:1. It is believed that the boron acts as an acceptor and the calcium acts as an electronic donor. The interaction between the boron and the calcium is such that a maximum resistivity is reached and then the resistivity is reduced until a minimum is reached for a calcium to boron weight ratio of about 2:1. Apparently high conductivity is associated with the donor state. As the amount of calcium increases so that the ratio is greater than 2:1, the resistivity increases because a multiple phase condition exists.

Generally, if one were to boronate a carbon fibre in the absence of calcium, the maximum amount of boron which could be introduced into the carbon fibre is about 1.2% by weight. The presence of the intercalcated calcium, however, substantially increases the maximum amount of boron. It is expected that about 10% by weight or more of boron can be introduced into the carbon fibre in the presence of the intercalated calcium. In addition,

it is expected that as much as 20% by weight of calcium can be intercalated into the carbon fibre in the presence of the boron.

Surprisingly, the boron and calcium can be introduced into the carbon fibre without chemically reacting with the carbon fibre so that a single phase is maintained. Heat treatments at elevated temperatures can result in the formation of new phase, calcium borographite.

It is believed that the presence of the intercalated calcium results in cross-linking between layer planes in the carbon fibre and improved mechanical properties are obtained. Excellent values for tensile strength and Young's modulus are obtained for the calcium intercalated boronated fibres even though relatively low process temperatures are used. For example, a carbon fibre according to the invention which has been produced using a process temperature of about 2000°C possesses mechanical properties comparable to a conventional mesophase pitch derived carbon fibre which has been subjected to a process temperature of 3000°C. In addition, the carbon fibre according to the invention possesses much lower resistivity compared to the conventional carbon fibre.

Surprisingly, the carbon fibre according to the invention possesses a relatively high interlayer spacing as compared to the typical interlayer spacing of 3.37 Angstroms of a carbon fibre which has been subjected to a heat treatment of about 3000°C. According to the prior art, one would expect a deterioration of mechanical properties for larger values of interlayer spacing for the carbon fibres. The maximum interlayer spacing occurs for a calcium to boron weight ratio of about 2:1 as in the case for the minimum resistivity.

Generally, about 0.5% by weight boron and about 1% by weight calcium provides a good quality carbon fibre according to the invention.

The present invention also relates to a method of producing a meshophase pitch derived carbon fibre having a low resistivity and excellent mechanical properties, and comprises the steps of boronating and intercalating with calcium,a carbon fibre having a diameter of less than 30 microns and derived from a mesophase pitch having a mesophase content of at least about 70% by weight mesophase.

The steps for boronating and intercalating can be carried out simultaneously or consecutively, boronating being first.

The preferred embodiment is to carry out the method to produce a calcium intercalated boronated carbon fibre having a calcium to boron weight ratio of about 2:1.

The boronating can be carried out with elemental boron, boron compounds, or a gaseous boron compound. A calcium compound such as for example CaNCN can be used. Oxygen-containing compounds of calcium are less desirable because of the possible detrimental effect of the oxygen on the carbon fibre.

Boronating up to about 1.2% by weight maintains a single phase in the carbon fibre. Greater amounts of boron tend to produce boron carbide, B_4C.

In carrying out the present invention, the carbon fibre has a diameter of less than 30 microns and preferably about 10 microns.

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

Illustrative, non-limiting Examples of the practice of the invention are set out below. Numerous other examples can readily be evolved in the light of the guiding principles and teachings contained herein. The examples given herein are intended to illustrate the invention and not in any sense limit the manner in which the invention can be practiced.

The Examples were carried out using mesophase pitch derived carbon fibres having diameters of about 8 microns. The mesophase pitch used to produce the fibres had a mesophase content of about 80% by weight.

The carbon fibres were produced using conventional methods and were carbonized to about 1700°C. Lower or higher carbonizing temperatures could have been used. The use of carbon fibres made the handling of the fibres simple because of the mechanical properties exhibited by carbon fibres.

The best mode used in the Examples simultaneously boronated and calcium intercalated the carbon fibres. This does not preclude the advantage of consecutive treatments for commercial operations. The method used is as follows.

Finely ground graphite, so-called graphite flour, was blended with elemental boron powder. The weight percentage of boron was selected to about the desired weight percentage for the carbon fibres. This mixture amounted to about 600 grams and was roll-milled for about 4 hours to mix and grind the graphite and boron thoroughly. The mixture was then calcined in an argon atmosphere at a temperature of about 2500°C for about one hour. Any inert atmosphere would have been satisfactory.

The boronated graphte flour was blended with CaNCN powder having particles less than about 44 microns to form a treatment mixture. The amount of

CaNCN is determined by the amount of calcium to be intercalated.

The weight of the carbon fibres being treated as compared to the amount of the treatment mixture used is very small. As a result, the weight percentage of the boron in the treatment mixture is about the same for the combination of the carbon fibres and the treatment mixture. This simplifies the selection of a predetermined weight percentage of boronating for the carbon fibres.

The amount of calcium intercalation must be determined experimentally by varying the amount of the calcium compound used and the treatment time.

It should be recognized that the vapour pressure of the boron is much lower than the calcium. The boronation is a result of atomic diffusion whereas the intercalation of calcium is a result of vapour diffusion.

For each Example, six carbon fibres were used and each fibre had a length of about 10 cm. Each of the carbon fibres was suspended inside a graphite container using a graphite form. The graphite form maintained the carbon fibre in a preselected position while the treatment mixture was added to the graphite container. The treatment mixture was vibrated around each carbon fibre to obtain a uniform and packed arrangement.

The six graphite containers were placed in a graphite susceptor and heated inductively to a predetermined maximum temperature for about 15 minutes. The furnace chamber was evacuated to about 5×10^{-5} Torr prior to the heat treatment and then purged with argon during the heating cycle. An inert gas other than argon could be used.

The process could be carried out using BCl_3, boranes or water-soluble salts such as H_3BO_3. In addition, $CaCl_2$ could have been used. Of course, a wide range of other compounds for supplying boron and calcium could be realized easily experimentally in accordance with the criteria set forth herein.

Examples 1 to 18:

Examples 1 to 18 were carried out to obtain about 0.5% by weight of boron in the carbon fibres and varying amounts of intercalated calcium. The maximum temperature for the heat treatment was 2050°C.

Table 1 shows the results of Examples 1 to 18. The amount of the intercalated calcium varied from about 0.5% to about 3.6% by weight. The Young's modulus for each of the carbon fibres was extremely high and the tensile strength was also very good. The resistivity showed a minimum of about 1.8 microohm-metres for about 1% by weight calcium the interlayer spacing, Co/2 was about a maximum for that value.

TABLE 1

Example	0.5% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 A
1	0.5	2.9	2.28	448	3.4176
2	0.8	3.8	1.80	551	3.4217
3	1.0	1.8	1.33	489	3.4224
4	0.5	3.5	1.90	545	3.4091
5	0.6	2.7	1.80	593	3.4158
6	0.7	3.6	1.88	558	3.4174
7	0.7	4.3	1.69	648	3.4219
8	0.6	4.7	1.66	489	3.4229
9	0.8	2.9	1.58	586	3.4248
10	0.9	1.8	1.28	614	3.4198
11	0.9	1.8	1.58	724	3.4133
12	0.9	2.0	1.43	641	3.4147
13	1.2	1.5	1.32	634	3.4205
14	2.3	2.1	1.84	738	3.4174
15	2.0	2.3	1.48	684	3.4141
16	2.6	1.6	1.44	662	3.4062
17	2.8	1.4	1.25	662	3.4082
18	3.6	1.8	0.79	600	3.4035

Examples 19 to 40

Examples 19 to 40 were carried out to obtain about 1.0% by weight of boron in the carbon fibres and varying amounts of intercalated calcium. The maximum temperature for the heat treatment was 2050°C.

Table 2 shows the results of Examples 19 to 40. By interpolation, it can be seen that as in Examples 1 to 18, a calcium to boron weight ratio of 2:1 results in the lowest resistivity, about 1.1 microohm-metres, and a large value for the interlayer spacing.

TABLE 2

Example	1% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 A
19	1.5	4.8	1.89	641	3.4381
20	0.4	4.3	2.07	476	3.4120
21	0.5	2.3	1.98	779	3.3833
22	1.3	4.3	2.53	786	3.4348
23	1.1	3.3	1.85	692	3.4265
24	1.5	2.8	1.63	745	3.4638
25	1.6	3.4	1.92	669	3.4564
26	1.8	5.0	1.96	717	3.4534
27	1.8	4.4	2.12	689	3.4610
28	1.6	2.3	2.14	758	3.4540
29	1.8	3.0	1.52	717	3.4571
30	2.2	1.4	1.33	627	3.4559
31	1.9	1.7	0.89	448	3.4488
32	1.9	1.1	1.54	586	3.4520
33	3.2	2.0	0.58	340	3.4549
34	2.5	1.5	1.15	558	3.4461
35	4.7	2.3	0.41	358	3.4288
36	4.3	2.4	0.39	338	3.4388
37	6.2	2.6	0.50	290	3.4394
38	5.4	2.0	0.50	352	3.4452
39	6.5	1.7	0.56	462	3.4486
40	8.9	2.2	0.70	552	3.4392

Examples 41 to 58:

Examples 41 to 58 were carried out to obtain about 2.0% by weight of boron in the carbon fibres and varying amounts of intercalated calcium. The maximum temperature for the heat treatment was 1600°C.

Table 3 shows the results of Examples 41 to 58.

The values of the resistivity are not as good as in Examples 1 to 40. The lowest resistivity is for a calcium to boron weight ratio of about 2:1. The value for the Young's modulus for each carbon fibre is fairly high.

TABLE 3

Example	2% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 Å
41	0.2	7.5	2.62	400	3.4202
42	0.2	7.6	2.62	365	3.4242
43	0.3	7.7	2.48	338	3.4324
44	0.7	7.3	2.59	393	3.4283
45	1.2	6.8	2.29	407	3.4179
46	1.8	5.8	1.98	420	3,4209
47	2.3	7.1	1.86	427	3.4238
48	2.6	5.6	2.03	427	3,4383
49	2.6	4.0	2.38	414	3.4368
50	3.3	4.2	1.97	400	3.4291
51	4.0	3.8	2.15	427	3.4483
52	5.1	3.8	1.96	434	3.4491
53	5.1	3.8	1.27	400	3.4444
54	6.4	4.0	1.32	448	3,4559
55	6.8	4.2	1.63	455	3.4326
56	8.0	4.7	1.13	420	3.4486
57	8.5	3.5	1.16	510	3.4381
58	12.5	4.2	1.23	786	3.4338

Examples 59 to 75:

Examples 59 to 75 were carried out to obtain about 2.0% by weight of boron in the carbon fibres as in Examples 41 to 58 except that the maximum temperature for the heat treatment was 2050°C.

Table 4 shows the results of Examples 59 to 75.

Examples 59 to 75 produced much lower values for resistivity than Examples 41 to 58. The lowest resistivity and highest interlayer spacing can be interpolated to be at a calcium to boron weight ratio of about 2:1. The Young's modulus and tensile strength for each of the carbon fibres is excellent.

TABLE 4

Example	2% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 A
59	0	2.8	2.25	689	3.381
60	0.7	2.5	1.60	593	3.4003
61	3.5	2.9	1.31	689	3,5390
62	0.4	2.8	2.06	641	3.3964
63	0.6	2.9	2 12	620	3.4050
64	0.9	2.6	2.07	738	3.4302
65	1.8	2.6	1.68	662	3.4489
66	2.9	2.8	1.60	551	3.4717
67	3.1	2.6	2.11	586	3.4957
68	3.2	3.4	1.37	627	3.5077
69	3.5	2.5	1.73	579	3.5136
70	3.6	2.0	1.48	579	3.5222
71	4.8	1.5	0.99	510	3.5293
72	4.5	1.8	1.25	476	3,5349
73	5.1	1.5	1.52	565	3.5027
74	5.1	1.5	1.80	634	3.4930
75	6.6	1.8	0.97	551	3.4886

Examples 76 to 93:

Examples 76 to 93 were carried out to obtain about 2.0% by weight of boron in the carbon fibres as in Examples 41 to 75 except that the maximum temperature for the heat treatment was about 2300°C.

Table 5 shows the results of Examples 76 to 93.

Examples 76 to 93 compare well with Examples 59 to 75.

TABLE 5

Example	2% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 A
76	1.0	2.3	1.82	551	3.4385
77	2.5	2.5	1.15	510	3.4585
78	1.1	2.3	0.86	420	3.3896
79	1.1	2.6	1.70	572	3.4410
80	1.4	2.4	1.63	558	3.4339
81	1.5	2.5	1.69	724	3.4462
82	1.5	2.3	2.34	538	3.4405
83	1.4	2.3	2.29	524	3.4312
84	2.5	2.3	2.37	696	3.4681
85	2.5	2.4	2.30	682	3.4671
86	2.5	2.3	2.30	724	3.4667
87	2.4	2.2	2.54	731	3.4752
88	2.9	2.6	1.93	662	3.4913
89	5.1	1.2	1.90	772	3.5074
90	6.1	1.4	1.91	689	3.4992
91	5.7	1.2	1.99	800	3,5232
92	7.0	1.2	1.69	558	3,4954
93	8.2	1.5	1.14	517	3.5159

While a maximum temperature for the heat treatment can exceed 2300°C, there is a reduction of mechanical properties of the fibres when the maximum temperature exceeds 2500°C.

Examples 94 to 109:

Examples 94 to 109 were carried out to obtain about 5% by weight of boron in the carbon fibres.

The maximum temperature for the heat treatment was about 2050°C.

Table 6 shows the results of Examples 94 to 109.

Examples 94 to 109 do not include the preferred calcium to boron weight ratio but the trend of resistivity versus calcium content shows the characteristic increase in resistivity for a calcium to boron weight ratio less than 2:1. In addition, the interlayer spacing increases from a calcium content of about 3.8% to 8.5% by weight and would be expected to be a maximum at about 10% by weight in accordance with the invention.

TABLE 6

Example	5% Boron Ca in Fibre %	Resistivity μ-Ω-m	Tensile strength G Pa	Young's Modulus G Pa	Co/2 A
94	0.6	2.5	1.43	531	3.3928
95	2.0	2.6	1.70	462	3.4435
96	3.2	2.6	1.27	446	3.5160
97	2.8	2.6	1.58	572	3.4830
98	3.8	2.8	1.40	531	3.4822
99	4.3	2.8	1.61	503	3.5089
100	2.5	2.9	2.20	689	3.5134
101	3.2	3.0	1.57	600	3.5134
102	3.9	3.3	2.21	558	3.5473
103	4.5	3.3	1.46	579	3.5306
104	4.8	3.4	0.88	517	3.5367
105	6.7	3.0	0.37	317	3.5316
106	7.7	3.0	0.34	290	3.5614
107	8.0	3.6	0.29	241	3.5721
108	8.0	3.4	0.49	324	3.5834
109	8.5	6.0	0.33	186	3.6007

CLAIMS

1. A mesophase pitch derived carbon fibre having a diameter of less than 30 microns and which has been boronated and intercalated with calcium.

2. A carbon fibre according to claim 1 wherein the calcium to boron weight ratio in the fibre is about 2:1.

3. A carbon fibre according to claim 1 or 2 wherein said fibre contains at least about 0.1% by weight boron.

4. A carbon fibre according to claim 1, 2 or 3 wherein the resistivity of the fibre is about one microohm-metre.

5. A carbon fibre according to any of claims 1 to 4 wherein the fibre contains up to about 10% by weight boron and up to about 20% by weight calcium.

6. A method of producing a mesophase pitch derived carbon fibre comprising the steps of boronating and intercalating with calcium a carbon fibre having a diameter of less than 30 microns and derived from a mesophase pitch having a mesophase content of at least about 70% by weight mesophase.

7. A method according to claim 6 wherein the boronating and intercalating steps are carried out simultaneously, or the intercalating step is carried out subsequent to the boronating step.

8. A method according to claim 6 or 7 wherein the boronating and intercalating steps are carried out to produce a calcium to boron weight ratio of about 2:1 in said fibre.

9. A method according to claim 8 wherein the fibre contains at least about 0.1% by weight boron.

10. A method according to any of claims 6 to 9 wherein the boronating step is carried out with

elemental boron, $BC1_3$, a borane or a water-soluble compound of boron.

11. A method according to any of claims 6 to 10, wherein the intercalating step is carried out using CaNCN or $CaC1_2$.

European Patent Office

EUROPEAN SEARCH REPORT

0068752
Application number

EP 82 30 3177

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	US-A-3 692 577 (EVANS) *Claims; column 2, lines 20-44*	1	D 01 F 9/14 D 01 F 11/10
A	DE-A-2 946 414 (NICKL) *Claims*	1	
A	FR-A-2 424 240 (STACK POLE CARBON) *Claims*	1,3,7, 9,10	

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
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