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(54) Title: CARBON-CARBON COMPOSITE MATERIAL

(57) Abstract

Method for the manufacture of a carbon-carbon composite by providing an assembly of carbon fibre and carbonisable carbonaceous material, subjecting the assembly to heat and pressure to consolidate the assembly and heating to carbonise the carbonaceous material, wherein the assembly of carbon fibre and carbonisable carbonaceous material is provided by a process comprising wetting carbon fibre with a liquid medium carrying carbonisable carbonaceous material and then removing the liquid medium to deposit a coating of the carbonaceous material on the carbon fibre. Uses of the product include aircraft brake friction discs.

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CARBON-CARBON COMPOSITE MATERIAL

This invention relates to carbon-carbon composites, especially to a method for the manufacture of such composites and to products of the method.

It is known to produce carbon-carbon composites by providing a composition of carbon fibres and carbonisable carbonaceous material and then carbonising the material, or by depositing carbon from a gaseous phase onto a carbon fibre substrate. One known method comprises applying a molten pitch to a preform of carbon fibres, often at a high pressure, and then carbonising the pitch.

Usually the current methods for manufacturing carbon-carbon composites are slow and costly and have other shortcomings, especially in the manufacture of products such as aircraft brake discs.

An object of the present invention is the provision of an efficient economic method for the manufacture of carbon-carbon composites having a uniform high density, and graphitised versions of such composites suitable for applications requiring high thermal conductivity, for instance in aircraft brakes.

The present invention provides a method for the manufacture of a carbon-carbon composite by providing an assembly of carbon fibre and carbonisable carbonaceous material, subjecting the assembly to heat and pressure to consolidate the assembly and heating to carbonise the carbonaceous material: wherein the assembly of carbon fibre and carbonisable carbonaceous material is provided by a process comprising wetting carbon fibre with a liquid medium carrying carbonisable carbonaceous material and then removing the liquid medium to deposit a coating of the carbonaceous material on the carbon fibre.

According to a further aspect of the invention there is provided a moulding compound comprising an assembly of carbon fibre having a coating of carbonisable carbonaceous material deposited from a

solution and/or suspension of the material in a liquid medium. The assembly may be at least partially consolidated.

The present invention also provides products of the aforementioned method.

The carbon fibre may be of any kind normally employed for the manufacture of carbon-carbon composites. Staple and/or continuous length fibre may be employed. Preferably the carbon fibre consists of or comprises fibres having a length of at least 10 mm, especially at least 25 mm. Examples of the form of the carbon fibre are continuous tow, non-woven fabric (needled or non-needled), woven fabric and knitted fabric.

The carbonisable carbonaceous material typically is a polymeric material, preferably a thermoplastic material. Advantageously for many applications of carbon-carbon composites, for instance in aircraft brakes, the carbonaceous material should be one which, when carbonised, yields high density carbon, preferably having a true density, i.e. the density excluding porosity, of greater than 1.7 $g.cm^{-3}$, which preferably also is capable of being at least partially converted into graphitic form, i.e. graphitised, on heating to a high temperature.

Advantageously also, the carbonaceous material is of the high-char type, especially one which is capable of yielding greater than 60% of its original weight as carbon when the material is carbonised. Preferably it yields carbon in an amount of at least 70%, more preferably at least 80%, based on its original weight.

A preferred carbonaceous material is a pitch, which may be natural or synthetic. Natural pitches are a range of materials derived from coal tars or petroleum distillate residues. They are mixtures of organic compounds having high aromaticity. Synthetic pitches may be produced by heat treatment of aromatic

hydrocarbons such as naphthalene and anthracene. One preferred form of pitch is a mesophase pitch. Such a pitch is described in 'Carbon' vol. 24 No.2 at page 247 (1986). Another example of a suitable pitch is that available as Ashland Aerocarb 80.

Other carbonaceous materials which may be employed include resins, especially thermoplastic resins. Employment of a thermoplastic material rather than a thermosetting (curable or hardenable) resin obviates a separate curing/hardening stage. Also, thermosetting resins usually are not suitable when graphitisation is required.

Advantageously the liquid medium is a solvent and the carbonaceous material is at least partially dissolved, preferably completely dissolved, in the liquid medium at normal (room) temperature. The liquid medium may be aqueous or non-aqueous. Examples of non-aqueous media are organic liquids such as toluene, benzene, pyridine, quinoline and tetrahydrofuran.

Suitably the viscosity of the liquid medium with the carbonaceous material and any other materials carried therein is up to 2,000, up to 1,000, up to 500, up to 100 or up to 10 $mN.sec.m^{-2}$ as measured at 20°C and atmospheric pressure. A suitable minimum viscosity may be at least 0.2, at least 0.5 or at least 1 $mN.sec.m^{-2}$ as measured at 20°C and atmospheric pressure.

Examples of means of application of the carbonaceous material in liquid medium to the carbon fibre are by immersion, spraying, vacuum impregnation, electrophoretic deposition and electrostatic deposition. The carbonaceous material in liquid medium may be applied to the carbon fibre at any stage prior to consolidation, such as to the carbon fibre in tow or sheet fabric form or to a preform.

Additional advantages may be achieved wherein one or more materials additional to the primary carbonaceous material are carried by the liquid medium,

for instance to increase solution viscosity, carbon yield, carbon density, oxidation resistance, friction, wear resistance and/or graphitisation efficiency.

If desired, more than one carbonaceous material may be applied in the liquid medium and deposited on the carbon fibre. One or more carbonaceous materials may be in solution in the liquid medium and one or more carbonaceous materials may be in the form of fine particles suspended in the liquid medium. The suspended carbonaceous materials may be particles of carbon (e.g. amorphous carbon, colloidal graphite powder or carbon black) or particles of carbonisable material (e.g. microbeads of mesophase pitch).

Additionally to the carbonaceous material(s), the liquid medium may carry one or more modifying materials, for instance a catalyst to promote graphitisation (e.g. to achieve graphitisation at a faster rate and/or at a lower temperature) or an antioxidant. Such materials suitably may be in particulate form suspended in the liquid medium and are deposited with the carbonaceous material(s) upon removal of the liquid medium. Examples of suitable particulate non-carbonaceous materials are boron, which may act as a graphitisation catalyst, and ceramic materials, which may improve properties such as oxidation resistance, friction and wear resistance. The particles suitably are in fine powder form, preferably of diameter less than 10 microns.

An advantageous particulate antioxidant may be a substance which combines with oxygen selectively at temperatures in excess of 500°C to produce a protective layer between the carbon-carbon composite and the atmosphere, thereby to improve the overall oxidation resistance of the composite.

Additionally or alternatively to application of particles as a suspension in the liquid medium, particles may be applied in dry powder form after application of a solution of carbonaceous material

in the liquid medium and preferably while the applied solution is in a tacky state, e.g. after partial evaporation of the liquid medium.

After application of the liquid medium carrying the carbonaceous material(s) and any other materials, the liquid medium is removed. A suitable means of removal is by evaporation, in which case the vapour pressure of the liquid medium preferably should be significantly higher than that of the carbonaceous material(s) and any other materials carried by the liquid medium so that substantially only the liquid medium evaporates. If desired, the evaporated liquid may be recovered for re-use.

The resulting coated-fibre assembly may be further subjected to treatment with carbonaceous material in a liquid medium to build up the deposited coating of carbonaceous material if required.

If desired, the coated fibres may be fragmented, such as by cutting or chopping, to provide a moulding-compound.

The assembly for consolidation may comprise more than one coated-fibre sub-assembly. For instance, two or more coated-fibre sub-assemblies may be stacked in a multi-ply arrangement.

The assembly may be in the form of a shaped preform, for instance a needled stack of fabric sheets. Preferably the assembly is self-supporting (i.e. it does not require the aid of a supporting jig) during the consolidation process.

If desired an assembly of coated fibres may be wound to form a hollow cylindical preform prior to consolidation.

Consolidation of the assembly is achieved by hot-pressing, usually at a temperature up to about 500°C, for instance at about 300°C.

The consolidation process may be carried out using isostatic pressure but more usually uniaxial pressure is employed. If desired, when uniaxial

pressure is used, restraining means may be employed to restrain outward deformation of the assembly in at least one direction transversely of the pressure application direction. Alternatively, uniaxial pressure may be applied without transverse restraint; this could allow greater retention of fibre orientation.

The assembly may be moulded or shaped prior to and/or during consolidation. The consolidated assembly may be in a form for moulding and subjection to carbonisation or it may be cut into shape or smaller lengths (e.g. when the assembly is based on a long tow of carbon fibre) prior to moulding or carbonisation.

Carbonisation of the consolidated assembly (composite) may be achieved by heating, in the substantial absence of air or other oxidising environment, at a higher temperature than that employed for consolidation. The carbonisation temperature typically is at least 600°C and more usually at least 1,000°C. The temperature may be selected to enable the assembly to exhibit plastic behaviour and thereby to enable further consolidation and/or moulding, if desired, prior to complete carbonisation.

The level of pressure employed for consolidation of the assembly usually is not necessary during carbonisation. However, it may be advantageous to maintain some, relatively low, usually uniaxial, compression pressure during carbonisation in order to minimise the risk of delamination. Means may be provided to maintain substantially atmospheric pressure and vent means may be provided to ensure that gases evolved during carbonisation do not cause an undesirable increase of gas pressure. Alternatively the by-products of carbonising may be removed, for example by a vacuum system.

If required, the carbonised assembly may be subjected to further application of carbonaceous material in a liquid medium followed by removal of liquid medium and by further carbonisation.

Additionally or alternatively, carbon may be deposited on the assembly by a carbon vapour deposition technique.

For some purposes it is advantageous for the product to be in graphitic form, especially when thermal conductivity is desirable. Graphitisation may be attained by heating the carbonised assembly to a higher temperature such as at least 1500°C and often at least 2,000°C. The temperature preferably should not exceed that at which the carbon starts to vaporise and accordingly usually it will not exceed about 3,000°C.

The bulk density of the carbon-carbon composites preferably is at least 1.7, more preferably at least 1.8 and even more preferably at least 1.9 $g.cm^{-3}$.

The carbon-carbon composites, particularly the graphitised composites, are suitable for applications requiring high thermal conductivity and/or high thermal diffusivity. Examples of applications are in brake friction discs (especially for aircraft), friction pads, protective tiles and linings in thermonuclear fusion apparatus, thermal protection material for spacecraft, protective surfaces for hypersonic aircraft, and high temperature components in gas turbines.

CLAIMS:-

1. Method for the manufacture of a carbon-carbon composite by providing an assembly of carbon fibre and carbonisable carbonaceous material, subjecting the assembly to heat and pressure to consolidate the assembly and heating to carbonise the carbonaceous material, wherein: the assembly of carbon fibre and carbonisable carbonaceous material is provided by a process comprising wetting carbon fibre with a liquid medium carrying carbonisable carbonaceous material and then removing the liquid medium to deposit a coating of the carbonaceous material on the carbon fibre.

2. Method according to Claim 1 wherein the liquid medium is a solvent for the carbonaceous material and the carbonaceous material is at least partially dissolved therein at normal temperature.

3. Method according to Claim 2 wherein the carbonaceous material is completely dissolved therein at normal temperature.

4. Method according to Claim 2 or 3 wherein the carbonaceous material comprises a pitch.

5. Method according to any one of the preceding Claims wherein the liquid medium carries one or more additional materials which are deposited on the carbon fibre when the liquid medium is removed.

6. Method according to Claim 5 wherein the liquid medium carries carbonisable carbonaceous material dissolved therein and one or more additional materials in the form of particles suspended therein.

7. Method according to Claim 6 wherein the suspended particles are of size less than 10 microns diameter.

8. Method according to Claim 6 or 7 wherein the suspended particles comprise carbonaceous material selected from carbon and carbonisable material.

9. Method according to Claim 8 wherein the suspended carbonisable material comprises a pitch.

10. Method according to any one of Claims 5 to 9 wherein the one or more additional materials comprise

a graphitisation catalyst and/or an antioxidant.

11. Method according to any one of Claims 5 to 10 wherein the one or more additional materials comprise boron and/or ceramic material.

12. Method according to any one of the preceding Claims wherein the or each carbonisable carbonaceous material is one which, when carbonised, yields carbon having a true density greater than 1.7 $g.cm^{-3}$.

13. Method according to any one of the preceding Claims wherein the or each carbonisable carbonaceous material is of the high-char type.

14. Method according to any one of the preceding Claims wherein the carbonisable carbonaceous material is one which, when carbonised, yields greater than 60% by weight of carbon.

15. Method according to any one of the preceding Claims wherein the liquid medium with the carbonisable carbonaceous material and any additional materials carried thereby has a viscosity in the range 0.5 to 500 $mN.sec.m^{-1}$ as measured at 20°C and atmospheric pressure.

16. Method according to Claim 15 wherein said viscosity is in the range 1 to 10 $mN.sec.m^{-1}$ as measured at 20°C and atmospheric pressure.

17. Method according to any one of the preceding Claims wherein, after wetting the carbon fibre with the liquid medium, at least one further material in dry powder form is applied to the assembly while the liquid medium on the carbon fibre is in a tacky state.

18. Method according to any one of the preceding Claims wherein the liquid medium is removed from the carbon fibre by evaporation.

19. Method according to any one of the preceding Claims wherein the coated fibre assembly is consolidated by uniaxial compression at up to 500°C.

20. Method according to any one of the preceding Claims wherein, after consolidation, the coated fibre assembly is heated to graphitise the carbonisable

carbonaceous material.

21. Method according to Claim 1 and substantially as described herein.

22. Carbon-carbon composite manufactured by a method according to any one of the preceding Claims.

23. Carbon-carbon composite according to Claim 22 having a bulk density of at least 1.7 $g.cm^{-3}$.

24. Aircraft brake friction disc comprising carbon-carbon composite according to Claim 22 or 23.

25. Moulding compound comprising an assembly of carbon fibre having a coating of carbonisable carbonaceous material deposited from a solution and/or suspension of the material in a liquid medium.

26. Moulding compound according to Claim 25 and substantially as described herein.

27. Carbon-carbon composite manufactured from a moulding compound according to Claim 25 or 26.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/00242

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C04B 35/52, D01F 11/14, F16D 69/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C04B, D01F, F16D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP, A2, 0307968 (PETOCA LTD.), 22 March 1989 (22.03 89), abstract, example 1	1-27
X	EP, A2, 0335736 (NIPPON OIL CO., LTD.), 4 October 1989 (04.10.89), column 4, line 40 - line 46, examples 6 and 7	1-27
A	EP, A2, 0238790 (ALLIED CORPORATION), 30 Sept 1987 (30.09.87), abstract, examples	1,24

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

31/03/93

International application No.
PCT/GB 93/00242

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