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(54) Title: IMPROVEMENTS IN OR RELATING TO BRAKE AND CLUTCH DISCS

(57) Abstract: Carbon fibre-reinforced ceramic brake and clutch discs are manufactured by siliconising incompletely densified carbon-carbon fibre preforms produced by only a single liquid infiltration step. Such use of only a single step to densify the preform substantially reduces processing times and costs whilst yielding highly effective siliconised end products, which may optionally then be subjected to a further carbon impregnation step, e.g. by a single chemical vapour or liquid infiltration step, to optimise their structural and frictional properties, particularly in terms of stability at high temperatures.



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Improvements in or relating to brake and clutch discs

5 This invention relates to a method for manufacturing brake and clutch discs, e.g. for motorised land vehicles or for aircraft, and to novel brake and clutch discs which are obtainable thereby. More particularly it concerns brake and clutch discs comprising carbon fibre-reinforced ceramic material such as may be obtained by using a liquid infiltration technique to generate a carbon matrix around the
10 reinforcing carbon fibres, and thereafter impregnating the carbon matrix with molten silicon.

 Much interest has been shown in the use of carbon fibre-reinforced ceramic brake discs, in particular siliconised carbon-carbon fibre composites, because of their high strength, their ability to maintain excellent physical and frictional
15 properties at high operating temperatures, and their low weight compared to conventional metal discs, for example permitting a weight reduction of 50-60% relative to a standard cast iron disc. Such weight reduction is important in improving performance and fuel economy; by reducing the unsprung weight of a vehicle it may also improve the road holding, handling and comfort of the vehicle.
20 Motor vehicles may likewise benefit from the use of such low weight high friction materials in clutch discs.

 Existing commercially available siliconised carbon fibre-reinforced ceramic brake discs are mainly prepared by a "resin char" method in which the reinforcing carbon fibres and a carbonisable resin (e.g. pitch or a phenolic resin) are hot
25 moulded together to approximately the desired shape, and the resulting moulded preform is carbonised (e.g. by heating to *ca.* 1000°C under an inert atmosphere or *in vacuo*), and optionally graphitised (e.g. by heating to $\geq 2000^{\circ}\text{C}$). The resulting green bodies may then be shaped and/or joined together as appropriate, and are siliconised, for example by at least partial immersion in a bath of molten silicon or
30 by a hot isostatic pressure treatment involving encapsulation with excess silicon in an evacuated container which is then subjected to high temperature and isostatic pressure.

Resin char procedures have the advantage of being relatively simple to operate, but do suffer a number of disadvantages. Thus the mould is normally filled with randomly oriented short carbon fibres, typically having an average length of less than 30 mm, more commonly less than 25 mm. The fibres may, for example, be
5 chopped from matchstick-like aggregates of carbon fibres which have been preimpregnated with resin; alternatively dry fibres chopped from a carbon fibre fabric such as a felt may be used, in which case resin is separately injected into the mould. It will be appreciated that the random orientation of the short carbon fibres necessarily limits the reproducibility of products obtained using resin char
10 procedures.

Another disadvantage is that the resin tends to shrink away from and expose some of the carbon fibre content during carbonisation. The integrity of such exposed fibres may be damaged by reaction with silicon in the subsequent siliconisation step.

15 The need to use a mould also puts practical limitations on the procedure, since any desired changes to the shape of the product will necessitate potentially expensive retooling.

It is known in the art that chemical vapour infiltration may be used as an alternative to resin char processing in order to form carbon-carbon fibre composites,
20 although it is generally considered to be unduly complicated and too expensive for more than highly specialised uses such as the manufacture of carbon-carbon fibre composite brake discs for aircraft. The manufacture of such discs typically involves generation of an initial carbon fibre preform which is then subjected to a sequence of chemical vapour infiltration steps, for example using methane as the source of
25 pyrolytic carbon. A sequence of steps is needed because the depositing carbon tends to block the pores between the reinforcing fibres, thereby halting carbon uptake. Initial saturation typically occurs after 10-14 days; by this time the preform may have a density of the order of $1.4\text{--}1.5\text{ g/cm}^3$ and will not yet have sufficient strength or integrity for use as a brake disc. It is therefore normal practice to remove the
30 partially densified preform from the furnace and machine its surfaces in order to reopen the blocked pores, whereafter chemical vapour infiltration may be resumed. At least one further machining step and a third chemical vapour infiltration stage are

normally required in order to obtain a disc with an acceptable density of around 1.8-1.9 g/cm³; the total processing time is typically of the order of 150 days. U.S. Patent No. 6,878,331 confirms that chemical vapour infiltration generally has to be repeated three to five times before the desired density is achieved.

5 Discs obtaining in this way are not siliconised, and function well as aircraft brakes. They are, however, inappropriate for use in land vehicles, since they exhibit poor frictional properties at ambient temperatures and so cannot be used to provide occasional light braking.

It has hitherto been thought that even chemical vapour infiltration-generated
10 discs which are intended to be siliconised require at least two stages of infiltration to be performed. Thus it is noted in U.S. Patent No. 6,030,913 that if chemical vapour infiltration is used only once per process, then microcracks remain in the deposited pyrocarbon layer and permit unwanted penetration of silicon during siliconisation. It is observed that multistage infiltration to overcome this problem is very costly.

15 Whilst U.S. Patent No. 6,110,535 describes a technique for delivering a molten silicon composition into porous substrates of carbon composite material which may be obtained by densification using chemical vapour infiltration, this is normally the first step of a two stage densification process and is followed by a resin char densification so as to form grains of coke in the pores of the residual pore space
20 remaining after the chemical vapour infiltration.

A further route to carbon-carbon fibre composite materials is the wetting monomer infiltration process described in, for example, WO-A-9964361 and U.S. Patent No. 6,756,112. In this process the carbon fibre preform is impregnated with one or more liquid monomers, for example polynuclear aromatic hydrocarbons such
25 as naphthalene, preferably together with a polymerisation catalyst such as a Lewis acid. The impregnated preform is then heated to promote polymerisation of the monomer(s), and the resulting polymer is then carbonised by further heating.

This sequence of liquid monomer impregnation, polymerisation and carbonisation steps is generally repeated several times in order to achieve the desired
30 degree of densification. Thus a total of four cycles conducted over 4-5 days is typically employed to provide carbon-carbon fibre composites with densities of the order of 1.8 g/cm³; a representative density after the first cycle is around 1.4 g/cm³.

The products are said to compare favourably with composites prepared by multistage chemical vapour infiltration procedures carried out over a total period of 6-8 months.

In our International Patent Application No. PCT/GB2006/002815, the contents of which are incorporated herein by reference, we describe our unexpected finding that highly effective siliconised carbon-carbon fibre composite brake and clutch discs may in fact be manufactured by siliconisation of incompletely densified preforms which have undergone densification by only a single chemical vapour infiltration step. It is therefore possible to reduce the chemical vapour infiltration processing time from around 150 days to as little as, for example, seven days or less; this greatly reduces process operating costs and permits the manufacture of brake and clutch discs with highly advantageous properties at costs comparable to those of procedures using resin char processing. The reduced operating costs make the products commercially viable for application to motorised land vehicles, including both road going and racing cars and motorbikes, as well as vans, lorries, buses and coaches, military vehicles and railway engines, coaches and trucks.

The present invention is based on our finding that advantageous products may be obtained in particularly economical manner by siliconisation of incompletely densified preforms which have undergone initial densification by carbonisation involving only a single liquid infiltration step.

Thus according to one aspect of the invention there is provided a method for the manufacture of a carbon fibre-reinforced ceramic brake or clutch disc which comprises preparing a carbon fibre preform having dimensions which substantially correspond to those of the desired disc, densifying said preform with carbon using only a single liquid infiltration step, and siliconising said densified preform by reaction with molten silicon.

A major advantage of the process of the invention is that, by avoiding the use of moulds, minimal constraints are placed on the shape of the carbon fibre preform, which may be varied as required without the need for major retooling, thereby rendering the manufacturing process highly versatile.

There are similarly no constraints on the length of the carbon fibres which may be used. The preforms may therefore advantageously consist essentially of

long fibres, for example having an average length of at least 50 mm, preferably at least 75, 100, 125 or 150 mm, since long fibres enhance the strength and integrity of the product. Without wishing to be bound by theoretical considerations, it may be that the presence of long fibres is beneficial in ensuring that the products remain free from structural defects such as microcracks in contrast to the single stage chemical vapour infiltration-generated prior art products discussed in the aforementioned US Patent No. 6,030,913.

It is particularly preferred that the reinforcing carbon fibres are essentially continuous, i.e. that the average fibre length is equal to or exceeds the radial distance between the inner and outer peripheries of the disc. A particularly simple method of preparing such a continuous fibre preform is to cut it from a continuous sheet or cylinder of carbon fibre fabric, for example a woven fabric or a non-woven felt comprising alternating layers of carbon fibres laid at different angles, e.g. 0° and 90°.

The liquid infiltration step may be effected using wetting monomer infiltration as described in the aforementioned WO-A-9964361 and U.S. Patent No. 6,756,112, the contents of which are incorporated herein by reference.

Wetting monomers which may be used include furfural and polynuclear aromatic hydrocarbons, for example containing a total of 2-4 fused benzene rings, a portion of which may be hydrogenated, and optionally carrying one or more ring substituents such as C₁₋₄ alkyl (e.g. methyl or ethyl) groups. Representative examples of such hydrocarbons include naphthalene, methylnaphthalene, tetrahydronaphthalene, phenanthrene, anthracene and pyrene; the use of naphthalene may be advantageous for reasons of its ease of handling and relatively low cost. It will be appreciated that monomers having a relatively low melting point, for example not exceeding 225°C, preferably not exceeding 175°C, may facilitate processing in order to impregnate the preform. The use of partially hydrogenated hydrocarbons such as 1,2,3,4-tetrahydronaphthalene which are liquid at ambient temperature may likewise be advantageous.

Impregnation may be effected by dipping or immersing the preform in liquid (including molten) monomer(s) until the desired amount of monomer(s) has passed into or been taken up through capillary attraction into the preform. Impregnation

times of 2-10 hours, for example 1-5 hours, may be appropriate, depending on factors such as the dimensions of the preform and the nature and temperature of the monomer(s).

Polymerisation of the impregnated monomer may be effected by heating, for example to a temperature in the range 300-500°C; reaction times of about 2-6 hours, for example *ca.* 4 hours, may be appropriate. The resulting polymer matrix may then be carbonised by further heating, for example to a temperature in the range 700-1400°C, e.g. over a period of 6-24 hours, such as 10-18 hours. The total processing time for the wetting monomer infiltration process, i.e. comprising the impregnation, polymerisation and carbonisation steps, is advantageously about 12-36 hours, preferably 20-30 hours, more preferably about 24 hours.

Alternatively the preform may be directly impregnated with a liquid (including molten) polymer or resin, preferably having a low molecular weight (for example less than 5,000, preferably less than 3,000 or 2,500 and correspondingly low viscosity, which is then carbonised by heating as described above.

The density of the preforms following liquid infiltration and carbonisation may conveniently be in the range 0.9-1.4 g/cm³.

If desired, the partially densified preforms may be graphitised prior to siliconisation, for example by heat treatment at *ca.* 2000°C or above, e.g. up to 2400°C, under non-oxidising conditions, e.g. under an inert gas such as argon or *in vacuo*, for example for a period of about 96 hours at peak temperature.

Siliconisation may be effected in any appropriate manner such as is known in the art. For ease of operability a dip process in which the optionally graphitised partially densified preform is at least partially immersed in a bath of molten silicon or a hot isostatic pressing procedure may be preferred. The density of the siliconised product may, for example, be 1.9-2.4 g/cm³, e.g. about 2.0 g/cm³.

The product may be machined to its desired final dimensions either before or after siliconisation. The former option may be preferred since the presiliconisation intermediate product is less hard and therefore more readily machinable than the siliconised end product.

If desired the siliconised product may be subjected to a further carbon impregnation step. Such treatment may be particularly advantageous in enhancing

the lifetime and performance of aircraft brake discs, for example their wear resistance and frictional performance. Such brake discs may reach extremely high operating temperatures during landing, on occasions exceeding the melting point of silicon (1410°C). Under such conditions free silicon within a siliconised carbon-
5 carbon fibre composite disc may melt in the region of the disc surface, where it may either react to form silicon carbide or solidify as a thin film. The former possibility may lead to increased wear of cooperating brake components by virtue of the highly abrasive nature of silicon carbide, whilst the latter may compromise the frictional properties of the disc.

- 10 Carbon impregnation of the siliconised partially densified preform may obviate this problem by reacting with and/or coating residual free silicon or otherwise providing a reserve of carbon within the disc structure to react with such free silicon should the disc temperature exceed the melting point of silicon during use. It may also be used to control the carbon/silicon and carbon/silicon carbide
15 ratios so as to provide an optimal balance between hardness, wear resistance and abrasive properties.

Such carbon impregnation is preferably effected in a single step, either by chemical vapour or liquid infiltration as hereinbefore described.

- Carbon fibre-reinforced ceramic brake and clutch discs obtainable in
20 accordance with the method of the invention are new and useful products and constitute a feature of the invention in their own right. Unlike products obtained using conventional resin char processing, the carbon matrix of the present products exhibits particularly high levels of adherence to the reinforcing fibres. The fibres are therefore well protected against unwanted interaction with silicon during
25 siliconisation, and the products exhibit substantially enhanced strength and integrity compared to those of the prior art.

- In siliconised discs subjected to a final carbon impregnation stage any free silicon content is effectively locked into the discs as a result of this impregnation treatment and may thus limit migration of silicon to the disc surface at operating
30 temperatures which exceed the melting point of silicon.

This according to a further feature of this embodiment of the invention there is provided a siliconised carbon-carbon fibre composite brake or clutch disc

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characterised in that it contains impregnated carbon which overlies the silicon content.

- 5 Whereas the carbon matrix in resin char products of the prior art predominantly comprises amorphous glassy carbon, the matrix carbon content of the present products is comparatively more ordered, generally being in an isotropic, rough laminar or smooth laminar form. This is advantageous in that it permits more even and controlled interactions with silicon during siliconisation, permitting the manufacture of more uniform and reproducible products.

Claims

1. A method for the manufacture of a carbon fibre-reinforced ceramic brake or clutch disc which comprises preparing a carbon fibre preform having dimensions
5 which substantially correspond to those of the desired disc, densifying said preform with carbon using only a single liquid infiltration step, and siliconising said densified preform by reaction with molten silicon.
2. A method as claimed in claim 1 wherein the average length of the carbon
10 fibres within the preform is at least 50 mm.
3. A method as claimed in claim 1 where the average length of the carbon fibres within the preform is equal to or exceeds the radial distance between the inner and outer peripheries of the disc.
15
4. A method as claimed in any of claims 1 to 3 wherein the preform is cut from a continuous sheet or cylinder of carbon fibre fabric.
5. A method as claimed in claim 4 wherein said continuous sheet is a non-
20 woven felt.
6. A method as claimed in any of claims 1 to 5 wherein the initial preform has a density of 0.3-0.6 g/cm³.
- 25 7. A method as claimed in any of claims 1 to 6 wherein the densified preform has a density of 0.9-1.4 g/cm³.
8. A method as claimed in any of claims 1 to 7 wherein the preform is densified by a single wetting monomer infiltration step carried out over a total of 12-36 hours.
30
9. A method as claimed in claim 8 wherein the said infiltration step is carried out over a total of about 24 hours.

10. A method as claimed in any of claims 1 to 9 wherein the densified preform is machined to the dimensions of the desired disc prior to the reaction with molten silicon.

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11. A method as claimed in any of claims 1 to 10 wherein the reaction with molten silicon is carried out by at least partially immersing the densified preform in a bath of molten silicon or by encapsulation with excess silicon in an evacuated container which is subjected to high temperature and isostatic pressure.

10

12. A method as claimed in any of claims 1 to 11 wherein the siliconised densified preform has a density of 1.9-2.4 g/cm³.

13. A method as claimed in any of claims 1 to 12 wherein the siliconised
15 densified preform is machined to the dimensions of the desired disc.

14. A method as claimed in any of claims 1 to 13 wherein the siliconised densified preform is subjected to a further carbon impregnation step.

20 15. A method as claimed in claim 14 wherein said further carbon impregnation step is a single stage chemical vapour or liquid infiltration step.

16. A method as claimed in claim 15 wherein said chemical vapour infiltration is carried out for a total of 7-14 days.

25

17. A method as claimed in claim 15 wherein said liquid infiltration is a wetting monomer infiltration which is carried out over a total of 12-36 hours.

18. A method as claimed in claim 17 wherein said wetting monomer infiltration
30 is carried out over a total of about 24 hours.

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19. A carbon fibre-reinforced ceramic brake or clutch disc obtainable by a process as claimed in any of claims 1 to 18.
20. A siliconised carbon-carbon fibre composite brake or clutch disc
- 5 characterised in that it contains impregnated carbon which overlies the silicon content.

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2008/000308

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J5/14 C04B35/573 C04B35/80 F16D65/12 F16D69/02

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)

C04B 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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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E	EP 1 908 740 A (MITSUBISHI CHEMICAL FUNCTIONAL [JP]) 9 April 2008 (2008-04-09) paragraph [0063]; example 1; table 1	1,11,19
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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