A carbon or carbonizable fibrous structure (1) is disclosed such as is particularly, though not exclusively, applicable to the manufacture of preforms for use in the production of friction products and to hollow, heat-resistant structures. The structure (1) comprises a layered tube including an innermost layer (2), an outer layer (3) and at least one intermediate layer (4). The intermediate layer (4) is formed from a material (5) comprising carbon yarn or precursor carbon yarn in the form of a substrate (6) with a pile (7; 10) projecting from at least one side thereof. Preferably, the substrate (6) is woven and has piles (7; 10) projecting from both sides thereof. Preferably also, the pile (7; 10) has been raised from the substrate (6) by fracturing the yarns making up the substrate (6), for example by needling, carding or abrading the substrate (6). A method of manufacturing such a structure (1) is also disclosed.

Fig. 7

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A CARBON OR CARBONIZABLE FIBROUS STRUCTURE AND A METHOD OF MANUFACTURING SAME

The present invention relates to a carbon or carbonizable fibrous structure and to a method of manufacturing such a fibrous structure. The invention is particularly, though not exclusively, applicable to the manufacture of preforms that are used to produce friction products such as discs for use in brake mechanisms, and hollow, heat-resistant structures such as cones, nozzles and the like for projectiles and aircraft.

Use of the term "fibrous" indicates that the structure is made from fibres that may be either loose fibres or fibres that have been spun into yarn which is then used to produce the structure. Such fibres or yarns may be made of carbon fibres or yarns or of precursor, carbonizable materials. Hence, use of the term 'carbonizable' indicates that fibrous structures in accordance with the present invention are heated in an autoclave in a methane or acetylene atmosphere at an appropriate temperature for an appropriate period of time in order to produce a hardened carbonaceous structure or carbon billet. This structure or billet is then further processed to produce the desired products. Suitable precursor carbonizable fibres for use in the manufacture of such a structure are well known to those in the art and are, for example, sold under the registered trade mark PANOX ®. These fibres comprise oxidized polyacrylonitrile fibers or precursors of polyacrylonitrile fibers of various types. They are converted to carbon fibres by the heat treatment and produce carbon particles which enter and fill voids in the preform to density the structure. Such fibres may be produced in a yarn form and comprise a large number of flexible filaments, for example between 3,000 and 25,000 filaments, in order that the preform can be manufactured using textile techniques, which in the present invention is weaving.

Conventional carbon or carbonizable fibrous structures are manufactured in various ways. Typically they are produced by felting or by needling punching braided tapes or mats of loose fibre to produce a cylindrical stack. See, for example EP0748781 (B.F. Goodrich), W098/49382 (B. F. Goodrich), EP0232059 (P. G. Lawton Limited) and GB2428253 (P. G. Lawton (Industrial Semces) which all describe such methods. These structures are, in general, comprised of a loose accretion of fibres,
segments or tapes that are only held together by needle-punched fibres, which generally do not extend through all the layers of the structure. This can result in a stack or disc that has a propensity to fail owing to delamination. It can also be difficult to produce such structures with an homogeneous, optimum fibre fraction, which is a measure of the density of the structure. The fibre fraction is important as it affects the success of the carbonizing process. A homogeneous carbon fibre fraction of between 15% and 35% is required, and a fibre fraction between 15% and 20% is preferable.

The fibre fraction is calculated by measuring the volume and weight of a fabric sample and comparing it with the weight the sample would have been if that volume had been 100% carbon. For example, if the sample weighs 20 g and that volume of carbon would weigh 100 g, then the fibre fraction of the sample is 20%.

In our co-pending United Kingdom Patent Application No. 1004476.6 is described a fibrous structure comprising a tube made up of a plurality of layers of woven material wrapped around one another with an outer layer comprising a sheath in the form of a seamless woven tube. Such a structure, being made of woven material rather than via needle punching, is easier and more economical to produce than the needle-punched structures produced hitherto. It also has the advantage that it can be woven from carbon yarn rather than yarns made of carbonizable fibres. The former have the tendency to be brittle and unsuitable for use in needle punched structures. However, most woven fabrics have a fibre fraction of between 35% and 50%, with the rest being trapped air. Such a fibre fraction is too high for a carbon or carbonizable fibrous structure for use in the manufacture of preforms that are used to produce friction products. In addition, the carbon fibre that makes up the woven material is around 50% denser than normal textile fibres. The high fibre fraction of fibrous structures made from layers of woven material is a significant disadvantage and a desired fibre fraction required can only be achieved by a careful combination of the choice of yarns used to make the woven material and an appropriate method of construction of the structure.

It is also widely thought that fibrous preforms wherein the fibres extend longitudinally (x direction), chordally (y direction) and radially (z direction) with respect
to one another increases the strength of the finished product. This is termed producing the stack on an 'xyz' principle.

It is an object of the present invention to provide a carbon or carbonizable fibrous structure that uses the 'xyz' principle.

It is a further object of the present invention to provide a method of manufacturing a carbon or carbonizable fibrous structure of the type under discussion that can more readily be produced with an homogeneous, optimum fibre fraction than many prior art methods.

According to a first aspect of the present invention there is provided a carbon or carbonizable fibrous structure comprising a layered tube including an innermost layer, an outer layer and at least one intermediate layer, said intermediate layer being formed from a material comprising carbon yarn or precursor carbon yarn in the form of a substrate with a pile projecting from at least one side thereof.

It will be appreciated that the use of a pile in the intermediate layer or layers of this structure means that it has fibres that extend longitudinally (x direction), chordally (y direction) and radially (z direction) with respect to one another so that it uses the 'xyz' principle, which also enables a more homogeneous low density woven structure to be produced.

Preferably, the substrate comprises a woven, nonwoven or knitted layer.

Preferably also, the pile has been raised from the substrate by fracturing the yarns making up the substrate.

It will be appreciated that various methods can be used to produce a fabric with a pile surface but tufting or velvet weaving constructions do not reduce and typically add yarn to the substrate thereby increasing its fibre fraction. However, raising of the pile in a material by fracturing the yarns making up the substrate of the material reduces
the density of the substrate and also increases the thickness of the resulting material. This can be done to a point where a desired fibre fraction can be achieved.

Advantageously, the fracturing has been carried out by needling of the substrate. Alternatively, the fracturing has been carried out by carding or by abrading the surface of the substrate.

All of these methods produce a material with a velvet like surface and therefore expose a majority of the surfaces of the individual fibres to easy access by chemicals in subsequent chemical treatment of the fibrous structure to produce a hardened carbonaceous structure or carbon billet. Preferably, however, the fracturing has been carried out by needling of the substrate as this minimizes distortion and restricts the quantity of airborne carbon particles produces.

Preferably also, the material comprises a substrate with piles projecting from both sides thereof. Alternatively, the material comprises two back-to-back layers of a substrate with piles projecting from one side thereof such that the material has piles projecting from both sides thereof. Preferably also, the back-to-back layers of the substrate are bonded together, for example by a thermoplastic bonding material applied to at least one of the layers in the form of a sheet or a net. Advantageously, the back-to-back layers of the substrate are formed by a single layer of the substrate that is folded over itself.

Preferably also, the innermost layer comprises a seamless woven tube. Advantageously, the outer layer comprises a sheath or band that is also in the form of a seamless woven tube. Preferably also, the structure comprises at least one intermediate layer that comprises a seamless woven tube.

Preferably also, the fibrous structure comprises at least two intermediate layers in the form of a substrate with a pile projecting from at least one side, the projecting pile of one of these layers intermeshing with the pile of at least one other of these layers.
Preferably also, at least regions of the structure are bonded or fused together by incorporation of a thermoplastic bonding medium into the material or between layers of the material prior to a heat treatment during manufacture of the structure. Advantageously, the thermoplastic bonding material is incorporated into the substrate or the pile in the form of a thermoplastic yarn.

Preferably also, the substrate comprises braided carbon yarn and/or braided precursor carbon yarn. Advantageously, the pile comprises carbon yarn or precursor carbon yarn in conjunction with yarns made of any or a mixture of polyether ether ketone (PEEK), polyphenylene sulphide (PPS), polyester, nylon 6-6 and nylon 6.

According to a second aspect of the present invention there is provided a method of manufacturing a preform fibrous structure for use in the manufacture of friction products comprising
- providing a former;
- locating a first web around the former to form an innermost layer of the structure;
- providing one or more sheets of material comprising carbon yarn or precursor carbon yarn in the form of a substrate with a pile projecting from at least one side thereof;
- wrapping said material around the innermost layer to form at least one intermediate layer of the structure;
- providing a tube or band with an inner diameter comparable to the outer diameter of the structure on the former;
- locating the tube or band over the structure on the former; and
- removing the former to leave a free-standing fibrous structure.

Preferably, the method comprises the additional initial steps of producing said one or more sheets of material by providing one or more sheets of a substrate and raising a pile on at least one surface of the sheet or sheets of substrate by fracturing the yarns making up the substrate.
Preferably also, the fracturing of the yarns making up the substrate is carried out by at least one of needling of the substrate, carding one or both surfaces of the substrate and abrading one or both surfaces of the substrate.

Preferably also, the method comprises the additional step of folding said sheet or sheets of material over itself prior to wrapping it around said innermost layer so that it comprises two back-to-back layers of substrate with piles projecting from both sides thereof. Alternatively, the method comprises the further step of placing two sheets of said material together prior to wrapping it around said innermost layer so that it comprises two back-to-back layers of substrate with piles projecting from both sides thereof. Advantageously, said material having piles projecting from both sides thereof is wrapped around said innermost layer to form a plurality of intermediate layers wherein the pile of one intermediate layer is enmeshed with the pile of another intermediate layer.

Preferably also, the method comprises the additional step of providing a seamless woven tube and using it as an intermediate layer of the structure between intermediate layers formed by said material.

Preferably also, a thermoplastic bonding medium is incorporated into at least one of the sheets of material or is located between layers of said material prior to wrapping of said material around the innermost layer, and the method comprises the additional step of subjecting the structure to a heat treatment to fuse or bond at least regions of the structure together.

Preferably also, the thermoplastic bonding material is incorporated into the substrate or the pile in the form of a thermoplastic yarn. Alternatively or in addition the thermoplastic bonding material is incorporating into the structure in the form of a sheet or net.

Preferably also, the heat treatment comprises the additional step of heating the fibrous structure immediately before or after the tube or band has been located over
the structure. Alternatively, the heat treatment comprises the additional step of heating the fibrous structure once it has been removed from the former.

In another method, the heat treatment is carried out as the material is being wrapped around the former. For example, the heat treatment may be carried out by blowing hot air over the material as it is being wrapped around the former.

Preferably also, the former is mounted on a shaft and the method comprises the additional steps of rotating the shaft as each layer of said material is wound around the former to tension the material so that it conforms to the profile of the underlying layer.

Preferably also, the former is expandable and collapsible to facilitate the location of the tube or band around the former and to facilitate removal of the former from the completed fibrous structure. Advantageously, the former is adapted to be inflatable and deflatable.

According to a third aspect of the present invention there is provided a carbon or carbonizable fibrous structure manufactured in accordance with the method of the second aspect of the present invention.

Other preferred but non-essential features of the various aspects of the present invention are described in the dependent claims appended hereto.

The various aspects of the present invention will now be described by way of example with reference to the accompanying drawings, in which:

Fig. 1 is a perspective view of an embodiment of fibrous structure according to the first aspect of the present invention; and

Figs. 2 to 7 are diagrams showing sequentially steps in the manufacture of the structure shown in Fig. 1 in accordance with the second aspect of the present invention, of which Figs. 2 to 4 are perspective views of steps in the production of a
material used in the manufacture of said structure and Figs. 5 to 7 are perspective views showing steps in the manufacture of the structure itself.

In order to produce a carbon or carbonizable fibrous structure that can be used to produce a preform for the manufacture of friction products or hollow, heat-resistant structures, a structure in accordance with the invention is made of carbon yarn or precursor carbon yarn. To produce a carbon resin structure, the fibrous structure of the invention may be made of carbon yarn in conjunction with yarns made of any or a mixture of polyether ether ketone (PEEK), polyphenylene sulphide (PPS), polyester, nylon 6-6 and nylon 6. Such combinations made be co-mingled, blended, twisted, braided or interwoven together. The yarn may also be used in a braided form. This has two advantages, particularly if pure carbon yarn is used. First, it makes the yarn easier to handle because carbon fibres and precursor carbon fibres are fine, brittle and slipper). Second braiding improves the product because it reduces the shedding of fibres from the fibrous structure during and after manufacture, which improves its wear resistance.

Any of these yarns or others as appropriate for the ultimate use of the structure may be used to make carbon or carbonizable fibrous structures in accordance with the invention. Various embodiments of such structures will now be described. All of them comprise a layered tube made up of a plurality of layers of material, all of which are preferably made from yarns as described above that are suitable for the end purpose for which the structure is to be used. The fibre fraction required for the structure is achieved by a combination of an appropriate choice of the yarns used to make the material used in the structure together with an appropriate method of construction of the material itself as is described in more detail below.

As shown in Fig. 1, an embodiment of fibrous structure 1 according to the invention comprises a layered tube with an innermost layer 2 and an outer layer 3. In this embodiment both the innermost layer 2 and the outer layer 3 comprise a sheath in the form of a seamless woven tube. Preferably, these tubes are formed from a multi-ply woven web that by virtue of the weave pattern can be opened out to form a tube. Such weave patterns are known to persons skilled in the art. Between the layers 2 and 3 are intermediate layers 4 that are formed by a single piece of material 5 that is rolled-up
around the layer 2 before being secured in position by location of the outer layer 3 over
the top of it. This material 5 is in the form of a substrate 6 with a pile 7 projecting from
at least one side thereof.

It will be appreciated that such a structure is in accordance with the 'xy2'
principle as the woven layers 2 and 3 and the substrate 6 of the layers 4 comprise yarns
or fibres that lie in the "x-y" planes of the structure while the pile 7 of the layers 4 lies
in the "z" planes. Several methods of producing the material comprising the substrate 6
and the pile 7 will now be described with reference to Figs. 2 to 4.

In one method, the substrate 6 comprises a woven substrate as shown in Fig. 2.
Assuming that in the finished structure 1 one or more lengths of the substrate 6 are
coiled to form the inner layers, then it will be apparent that the warp fibres 8 of the
substrate will extend chordally in the "y" direction and the weft fibres 9 of the substrate
will extend will longitudinally in the "x" direction. However, in other embodiments,
the substrate 6 of the material may comprise a nonwoven material, such as a felt mat,
an airlaid mat, or a knitted material. In all of these cases, the fibres forming the
substrate 6 will still provide fibres that extend in the "x-y" planes of the structure 1.

As indicated above, the yarns or fibres used to produce the substrate 6 will be
made of carbon or precursor carbon. If such yarn is to be used that is either woven or
knitted to produce the substrate 6, then its will preferably be used in a braided or
wrapped form to make it easier to handle. However, in all cases the quantity of yarn or
fibre used to make the substrate 6 is carefully controlled, for example by controlling the
number and spacing of the ends and picks in a woven fabric, so that the required
carbon fibre fraction can be achieved.

Once the substrate 6 has been produced, it is further processed to apply the pile
7 to at least one side as shown in Fig. 3.

It is possible to tuft the substrate 6 to produce the pile 7, for example by
injecting the pile 7 into the substrate 6, or a tufted substrate 6 could be produced in a
single operation by weaving it using a carpet loom. In either case the pile 7 may be cut
or remain uncut. In addition, the yarn forming the pile 7 may be used in an unbraided or unwrapped form to allow the individual fibres to separate and to occupy any cavity within the structure 1 when it has been formed. This allows a more even dispersion of fibres throughout the structure 1 as a whole. Preferably, however, the pile 7 is raised by fracturing the yarns making up the substrate 6. This can be carried out by needling of the substrate 6, carding one or both surfaces of the substrate 6 and/or by abrading one or both surfaces of the substrate 6.

Needling of the substrate 6 is carried out using a needle loom wherein barbed needles penetrate the substrate 6 by passing through it a vertical manner while the substrate 6 is retained horizontal and indexed forward, no horizontal tension being applied during penetration by the needles so as not to distort the substrate 6. The barbed needles break the yarns making up and pull the broken ends out of the plane of the substrate 6 so that they form the pile 7 on the surface.

Alternatively, fracturing or the yarns making up the substrate to raise the pile 7 may be carried out by passing the substrate 6 against a rotating abrasive surface. This abrasive surface material may be formed silicon carbide chippings on a Carborundum \textsuperscript{[M]} wheel or similar. Alternatively, the rotating abrasive surface may comprise card clothing of either a flexible or a fixed metallic profile.

In all cases it will be appreciated that the pile 7 projects outwards from the substrate 6 and provides the fibres that extend radially in the "z" directions of the structure. If tufted, the density of the tufts making up the pile 7 is carefully controlled to ensure a required carbon fibre fraction is achieved in the finished structure 1. Preferably, however, the density of the substrate 7 is reduced by fracturing the yarns making up the substrate 6 to make the pile 7, which also enables a more homogeneous, low density structure 1 to be produced. Normal woven apparel fabrics ate around 35% - 50% fibre with 65% - 50% entrapped air. As indicated above, a homogeneous carbon fibre fraction of between 15% and 35% is required, and a fibre fraction between 15% and 20% is the most preferable for the production of preforms that are used to produce friction products. The fracturing of the yarns making up the substrate 6 to make the pile 7 reduces the density of these yarns and the substrate 6 itself by breaking
down the yarns and increasing the thickness of the resulting piled material 5 to a point where the desired fibre fraction can be achieved.

After formation of a piled substrate 6 as shown in Fig. 3, this material 5 can be used directly to produce the structure 1, as will be described below. Preferably, however, it is further processed to provide a pile 10 on the other side of the substrate 6, as shown in Fig. 4. This doubled-sided piled material may be produced in several ways. First, it could be produced by treating the other side of the substrate 6 in exactly the same way as the pile 7 was produced. Alternatively, two lengths of tufted substrate 6 may be joined together having been kid back-to-back so that their piles 7 project outwards on both sides. The substrates 6 may be joined together by tacking, stitching or by being bonded together, for example by sandwiching between them a thermoplastic bonding material, for example a polyester, preferably in the form of a sheet or net, and subjecting the resulting “sandwich” to a heat treatment to melt the bonding material and to fuse the two substrate layers 6 together. In another alternative, the tufted substrate 6 may be simply folded over itself, preferably in half along the warp direction, so that the pile 7 is outermost and projects outwards on both sides of the folded substrate 6. Again, the folded back-to-back substrate 6 may be secured by tacking, stitching or be use of a suitable adhesive such as a thermoplastic bonding medium.

Once a doubled-sided piled material 5 has been formed, as shown in Fig. 4, then it can be used to form the fibrous structure 1 as shown in Fig. 1. A method of accomplishing this will now be described. However, preferably, in the finished structure 1, at least regions of the structure 1 are bonded or fused together to make it semi-rigid so that it will hold its shape. To this end, preferably a thermoplastic bonding medium is incorporated into the material 5 or between layers of the material so that on heat treatment the bonding medium will melt to fuse parts of the structure 1 together.

As already described above, a thermoplastic bonding material may be incorporated between back-to-back layers of the substrate 6. However, in addition, thermoplastic yarn may be incorporated into the weave of the substrate 6 by using it for
some of the warp and/or weft yarns. Alternatively or in addition, some of the pile 7, 10 may comprise a thermoplastic yarn. Such yarns may comprise polyester yarns.

As shown in Fig. 5, manufacture of the structure 1 commences with the location over a former 11 of the innermost layer 2. Typically, the former 11 will be cylindrical with a circular cross-sectional profile but it should be appreciated that it could be made with any cross-sectional profile that may vary along its length and that may taper long its length. If the profile is complex, then it is likely all the layers of structure 1 will be made thin enough to enable them to closely follow the profile as they are built up on the former 11.

In order to facilitate the location of the innermost layer 2 over the former 11, the latter may be mounted on a rotatable shaft 12 and made expandable and collapsible, for example by being inflatable and deflatable. In its deflated state it is possible to locate the innermost layer 2 around the former 11 with ease and without damage. Inflation of the former 11 to a predetermined cross-sectional size in conformity with the inner diameter of the tubular layer 2 then holds this layer rigid. The intermediate layers 4 made of the double-sided tufted material 6 as shown in Fig. 4 are then formed by winding the material 6 around the innermost layer 2 and then around itself as shown in Fig. 6. Any number of intermediate layers 4 can be built up. As these layers 4 are being wound, the outwardly projecting pile 7 on the already-wrapped material 5 and the inwardly projecting pile 10 on the material 5 being wrapped become enmeshed, which increases the stability of the structure and the integration of the various layers 4 with one another and ensures that the structure 1 remains self-supporting once it has been removed from the former 11.

If the material 5 incorporates thermoplastic yarns, the stability of the structure 1 can also be improved by subjecting the structure 1 to a heat treatment to melt these yarns and fuse regions of the structure 1 together. This heat treatment may be carried out as the structure 1 is being formed. For example as the material 5 is being wound around the former 11 it could be subjected to a blast of blown hot air from a hot air "knife" of a temperature typically around 200°C, which is sufficient to soften and melt the thermoplastic yarns so that the layers 4 of material 5 are bonded together as they
are being wrapped. Alternatively, a heat treatment may be carried out towards the end of the manufacturing process, as described below.

The number of intermediate layers 4 equating to the number of turns of the material 5 in the structure 1 together with the thickness of the material comprising the layers 4 determines the diameter of the finished structure 1 and the latter is chosen according to the structure's end purpose. Typically, the inner diameter of the tubular structure 1 is expected to be of the order of 10 to 15 mm, its outer diameter to be of the order of 45 mm and its length to be of the order of 50-55 mm. This means that if the material 5 is made by folding over the substrate 6, then the width of the substrate is a tape of the order of 100 to 110 mm wide. With such dimensions, it will be appreciated that the material 6 used for the layers 4 is relatively narrow and may be described as a tape even if it is woven and folded in half to produce the material being. However, it will be appreciated that the structure 1 can be made in any dimensions using appropriately sized material 5. The depth of the pile 7, 10, the thickness of the substrate 6 and the tension of the winding around the former 11 may also be controlled to produce the required carbon fibre fraction.

Finally, once the desired number of intermediate layers 4 has been built up, the outer layer 3 is applied to the former 11 over the top of the layers 4, as shown in Fig. 7. This layer 3 may be in the form of a tube or a band and to facilitate its location over the intermediate layers 4 the former 11 may be deflated slightly. Once the layer 3 is in position, the former 11 is inflated back to its previous state to tension all the layers 2, 3 and 4. The structure 1 may then be subjected to a heat treatment or to a further heat treatment if heat has already been applied during winding of the material 4. This will again soften and melt any thermoplastic yarns used in the structure 1 so that the layers 2, 3, and 4 bonded together. Alternatively, a heat treatment could be carried out after the structure 1 has been removed from the former 11. The latter operation is carried out by deflating the former 11 so that it can be readily withdrawn from the finished structure 1.

In a modification, the innermost layer 2 is not made from a seamless woven tube but from a single piece of material that is rolled so that two opposite edges butt up
to one another. The material is then secured in this position by a tie, for example a length of the same yarn as is being used to weave the layer 2, or a peg or staple made from a material such as wood that will burn away or carbonize when the structure 1 itself is carbonized.

In another modification, the structure 1 may be consolidated by the inclusion of a seamless woven tube as one of the intermediate layers 4. In such an embodiment, several layers 4 made of doubled-sided piled material 6 are wound around the innermost layer 2 before a seamless woven tube is applied over them. Several further layers 4 are then applied made of double-sided piled material 6 before the outer layer 3 is applied as described above. The intermediate seamless woven tube may be applied in the same way as the outer layer 3, the former 11 being deflated slightly to facilitate its location over the underlying layers 4.

It will be appreciated that the layers 4 applied to the former may be wound so that the diameter of the structure 1 varies along its length. In addition, it is possible to weave material that is thicker at one side than the other and this can be used to produce seamless tubes that vary significantly in thickness from end to end to the other. The use of these tubes as one or more of the innermost, outermost or one of the intermediate layers enable structures 1 to be produced that have more complex shapes than simple cylinders. Similarly, it is possible to weave tubes that taper from one end to the other so that they fit over a tapering former. This is useful in the production of conical shapes such as may be required to produce a preform for a nose-cone or similar.

Fibrous structures 1 according to the present invention have several advantages, as follows.

1. Their production is simple and minimises waste of yarn and material, which is important as the yarn may be expensive to produce.

2. They are well-defined structures so that there is little or no waste in the production of a preform as very little, if any, material has to be machined away from the preform structure after carbonization.
3. The use of braided yarn for the material for the structure reduces the likelihood of fibre damage during weaving or knitting of the material.

4. The use of woven, non-woven or knitted materials to produce the structure assists in the achievement of the fibre fraction required in the preform.

5. The fracturing of the yarns of the substrate of the material to produce the pile enables a precise fibre fraction to be achieved.
Claims

1. A carbon or carbonizable fibrous structure comprising a layered tube including an innermost layer, an outer layer and at least one intermediate layer, said intermediate layer being formed from a material comprising carbon yarn or precursor carbon yarn in the form of a substrate with a pile projecting from at least one side thereof.

2. A structure as claimed in Claim 1, wherein the substrate comprises a woven, nonwoven or knitted layer.

3. A structure as claimed in Claim 1 or Claim 2, wherein the pile has been raised from the substrate by fracturing the yarns making up the substrate.

4. A structure as claimed in Claim 3, wherein the fracturing has been carried out by needling the substrate or by carding or abrading the surface of the substrate.

5. A structure as claimed in any of Claims 1 to 4, wherein the material comprises a substrate with piles projecting from both sides thereof.

6. A structure as claimed in any of Claims 1 to 45, wherein the material comprises two back-to-back layers of a substrate with piles projecting from one side thereof such that the material has piles projecting from both sides thereof.

7. A structure as claimed in Claim 6, wherein the back-to-back layers of the substrate are bonded together.

8. A structure as claimed in Claim 7, wherein the back-to-back layers of the substrate are bonded together by a thermoplastic bonding material applied to at least one of said layers in the form of a sheet or a net.
9. A structure as claimed in any of Claims 6 to 8, wherein the back-to-back layers of the substrate are formed by a single layer of the substrate diat is folded over itself.

10. A structure as claimed in any of Claims 1 to 9, wherein the innermost layer comprises a seamless woven tube.

11. A structure as claimed in any of Claims 1 to 10, comprising an intermediate layer that comprises a seamless woven tube.

12. A structure as claimed in any of Claims 1 to 11, wherein the outer layer comprises a sheath or band in the form of a seamless woven tube.

13. A structure as claimed in any of Claims 1 to 12, comprising at least two intermediate layers formed by a substrate with a pile projecting from at least one side thereof, the projecting pile of one of these layers intermeshing with the pile of at least one other of these layers.

14. A structure as claimed in any of Claims 1 to 13, wherein at least regions of the structure are bonded or fused together by incorporation of a thermoplastic bonding medium into the material or between layers of the material prior to a heat treatment during manufacture of the structure.

15. A structure as claimed in Claim 14, wherein the thermoplastic bonding material is incorporated into the substrate or the pile in the form of a thermoplastic yarn.

16. A structure as claimed in any of Claims 1 to 15, wherein the substrate comprises braided carbon yarn and/or braided precursor carbon yarn.

17. A structure as claimed in any of Claims 1 to 16, wherein the pile comprises carbon yarn or precursor carbon yarn in conjunction with yarns made of any or
a mixture of polyether ether ketone (PEEK), polyphenylene sulphide (PPS), polyester, nylon 6-6 and nylon 6.

18. A method of manufacturing a carbon or carbonizable fibrous structure comprising the steps of
   providing a former;
   locating a first web around the former to form an innermost layer of the structure;
   providing one or more sheets of material comprising carbon yarn or precursor carbon yarn in the form of a substrate with a pile projecting from at least one side thereof;
   wrapping said material around the innermost layer to form at least one intermediate layer of the structure;
   providing a tube or band with an inner diameter comparable to the outer diameter of the structure on the former;
   locating the tube or band over the structure on the former; and
   removing the former to leave a free-standing fibrous structure.

19. A method as claimed in Claim 18, comprising the additional initial steps of
   producing said one or more sheets of material by providing one or more sheets of a substrate and raising a pile on at least one surface of the sheet or sheets of substrate by fracturing the yarns making up the substrate.

20. A method as claimed in Claim 19, wherein the fracturing of the yarns making up the substrate is carried out by at least one of needling of the substrate, carding one or both surfaces of the substrate and abrading one or both surfaces of the substrate.

21. A method as claimed in any of Claims 18 to 20, comprising the additional step of folding said sheet or sheets of material over itself prior to wrapping it around said innermost layer so that it comprises two back-to-back layers of substrate with piles projecting from both sides thereof.
A method as claimed in any of Claims 18 to 20, comprising the additional step of placing two sheets of said material together prior to wrapping it around said innermost layer so that it comprises two back-to-back layers of substrate with piles projecting from both sides thereof.

A method as claimed in any of Claims 18 to 22, wherein said material has piles projecting from both sides thereof and wherein said material is wrapped around the innermost layer to form a plurality of intermediate layers wherein the pile of one intermediate layer is enmeshed with the pile of another intermediate layer.

A method as claimed in any of Claims 18 to 23, comprising the further step of providing a seamless woven tube and using it as an intermediate layer of the structure between intermediate layers formed by said material.

A method as claimed in any of Claims 18 to 24, wherein a thermoplastic bonding medium is incorporated into at least one of the sheets of material and/or is located between layers of said material prior to wrapping of said material around the innermost layer, and wherein the method comprises the additional step of subjecting the structure to a heat treatment to fuse or bond at least regions of the structure together.

A method as claimed in Claim 25, wherein the thermoplastic bonding material is incorporated into the substrate or the pile in the form of a thermoplastic yarn.

A method as claimed in Claim 25, wherein the thermoplastic bonding material is incorporated into said material in the form of a sheet or net.

A method as claimed in any of Claims 25 to 27, wherein the heat treatment comprises the additional step of heating the fibrous structure immediately before or after the tube or band has been located over the structure.
29. A method as claimed in any of Claims 25 to 27, wherein the heat treatment comprises the additional step of heating the fibrous structure once it has been removed from the former.

30. A method as claimed in any of Claims 25 to 27, wherein the heat treatment is carried out as said material is being wrapped around the former.

31. A method as claimed in Claim 30, wherein the heat treatment is carried out by blowing hot air over said material as it is being wrapped around the former.

32. A method as claimed in any of Claims 18 to 31, wherein the former is mounted on a shaft and the method comprises the additional step of rotating the shaft as each layer of said material is wound around the former to tension the material so that it conforms to the profile of the underlying layer.

33. A method as claimed in Claim 32, wherein the former is expandable and collapsible to facilitate the location of the tube or band around the former and to facilitate removal of the former from the completed fibrous structure.

34. A method as claimed in Claim 33, wherein the former is adapted to be inflatable and deflatable.

35. A carbon or carbonizable fibrous structure manufactured in accordance with the method as claimed in any of Claims 18 to 34.
# INTERNATIONAL SEARCH REPORT

**PCT/GB2012/000155**

## A. CLASSIFICATION OF SUBJECT MATTER

- INV. B32B1/08
- B32B5/26
- B32B5/02
- ADD. 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)
  - B32B

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)

- EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>GB 1 215 589 A (CARBORUNDUM CO) 9 December 1970 (1970-12-09) page 1, line 11 - line 45 page 1, line 78 - page 2, line 41</td>
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</tr>
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<td>A</td>
<td>GB 2 099 365 A (LOLLAINE CARBONE) 8 December 1982 (1982-12-08) page 1, line 5 - line 100 page 1, line 115 - page 2, line 21</td>
<td>1, 2, 5, 13-17, 3-4, 6-12, 18-35</td>
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### Further documents are listed in the continuation of Box C.

**X** See patent family annex.

* Special categories of cited documents:
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  - "E" earlier application or patent but published on or after the international filing date
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**Date of the actual completion of the international search**

- 2 May 2012

**Date of mailing of the international search report**

- 08/05/2012

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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Li chau, Holger
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<th>Publication date</th>
<th>Patent family member(s)</th>
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<tr>
<td>GB 1215589</td>
<td>09-12-1970</td>
<td>AT 288320 B</td>
<td>25-02-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE 728642 A</td>
<td>19-08-1969</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 1646454 Al</td>
<td>01-07-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 1215589 A</td>
<td>09-12-1970</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 335959 B</td>
<td>14-06-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 3657061 A</td>
<td>18-04-1972</td>
</tr>
<tr>
<td>GB 2099365</td>
<td>08-12-1982</td>
<td>CA 1198268 Al</td>
<td>24-12-1985</td>
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<tr>
<td></td>
<td></td>
<td>DE 3220306 Al</td>
<td>09-12-1982</td>
</tr>
<tr>
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<td></td>
<td>FR 2506672 Al</td>
<td>03-12-1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2099365 A</td>
<td>08-12-1982</td>
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<tr>
<td></td>
<td></td>
<td>IT 1151237 B</td>
<td>17-12-1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 58000643 A</td>
<td>05-01-1983</td>
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<tr>
<td></td>
<td></td>
<td>NL 8202003 A</td>
<td>03-01-1983</td>
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