# United States Patent [19]

**Pepper et al.**

[11] **3,918,141**

[45] **Nov. 11, 1975**


[54] **METHOD OF PRODUCING A GRAPHITE-FIBER-REINFORCED METAL COMPOSITE**


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[73] Assignee: **Fiber Materials, Inc.,** Biddeford, Maine



[22] Filed: **Apr. 12, 1974**

[21] Appl. No.: **460,563**

[52] **U.S. Cl.** ..... **29/419 R;** 29/191.2; 29/527.3; 29/527.7

[51] **Int. Cl.**[2] ..... **B23P 17/04**

[58] **Field of Search** ..... 29/191.2, 195 C, 419 R, 29/527.5, 527.7, DIG. 47, 527.3; 164/75



[56] **References Cited**

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| 3,441,392 | 4/1969 | Divecha et al. | 29/182.8 |
| 3,442,997 | 5/1969 | Parratt | 264/108 |
| 3,510,275 | 5/1970 | Schwope et al. | 29/419 X |
| 3,550,247 | 12/1970 | Evans et al. | 29/419 |
| 3,553,820 | 1/1971 | Sara | 29/419 |
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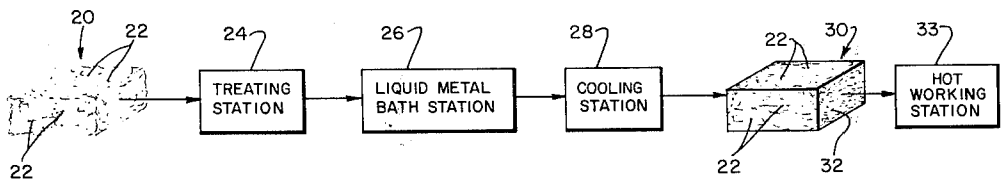
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[57] **ABSTRACT**

Production of a graphite fiber/metal composite material having substantially axially oriented fibers from a substantially random mat of graphite fibers. The mat is coated with a wetting agent and the coated mat is then impregnated with a molten metal such as aluminum, lead, copper or zinc, and cooled to form a solid ingot or billet. The billet is then hot-worked at a temperature slightly below the liquidus temperature to reduce the cross-section of the mat and thereby substantially align the fibers.


**13 Claims, 4 Drawing Figures**



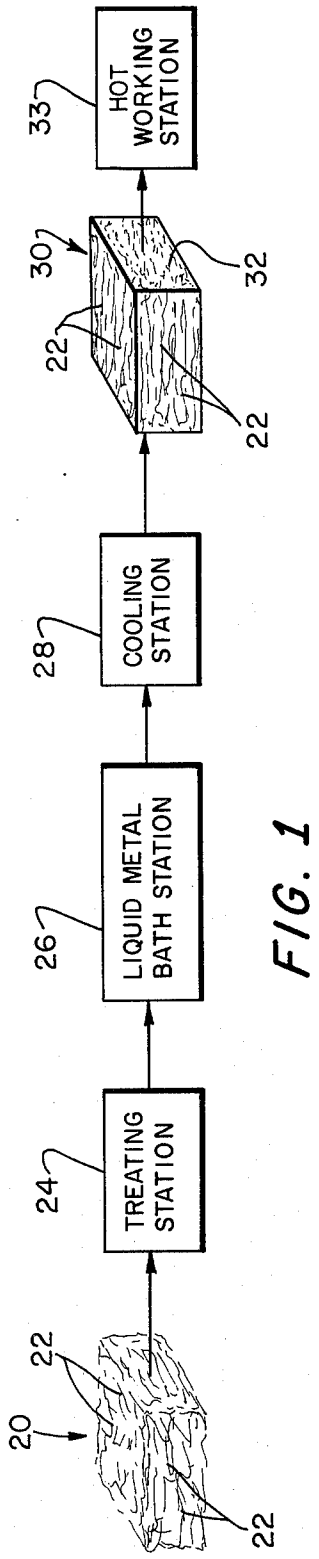

HOT WORKING STATION
33
30
32
22
22
COOLING STATION
28
LIQUID METAL BATH STATION
26
TREATING STATION
24
22
20
22

FIG. 1

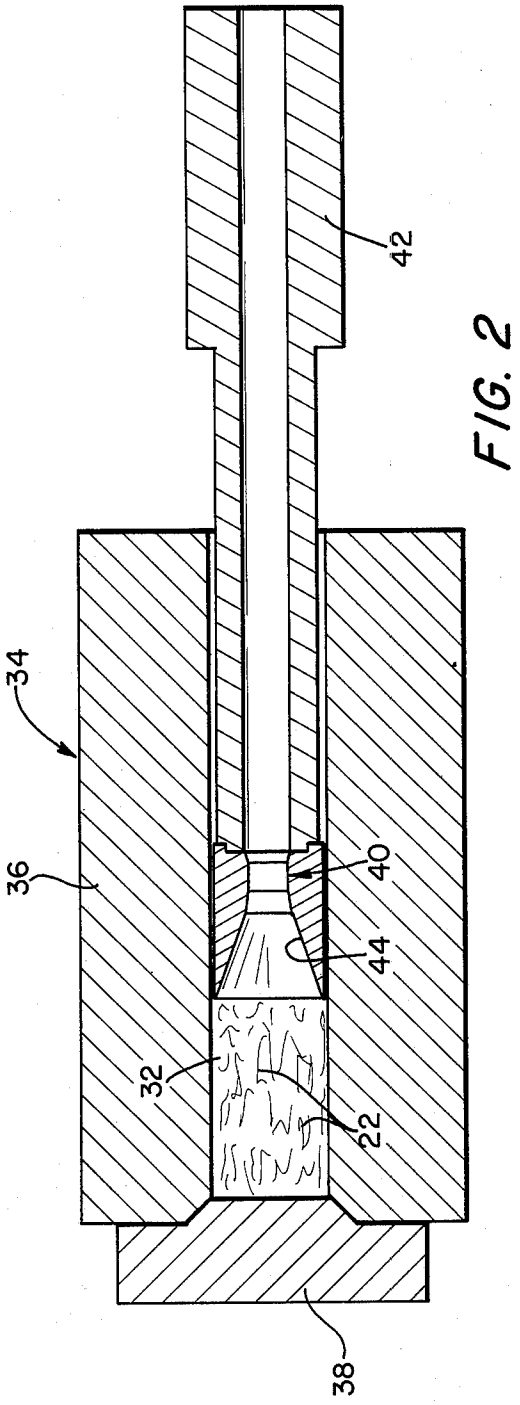

42
34
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40
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32
22
38

FIG. 2

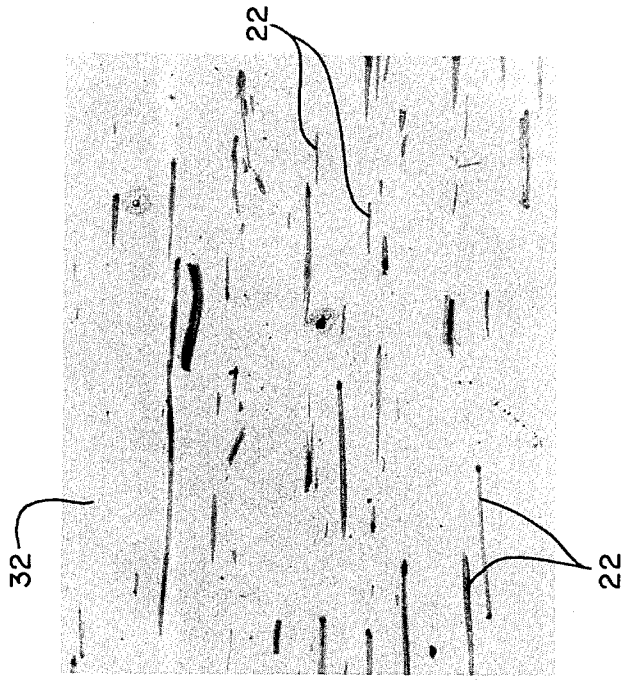



FIG. 4

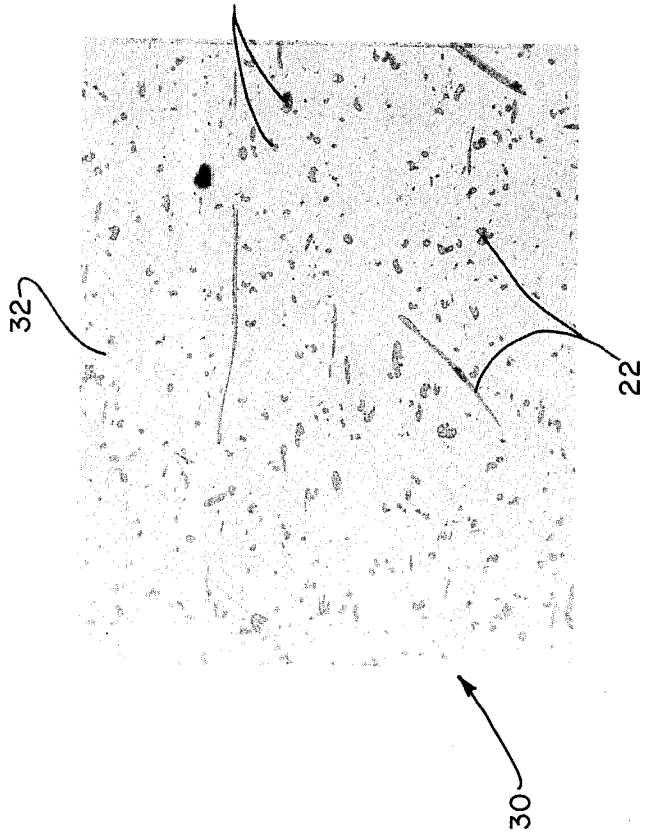



FIG. 3

# METHOD OF PRODUCING A GRAPHITE-FIBER-REINFORCED METAL COMPOSITE

The present invention relates to composite materials and more specifically to methods for making composites of graphite fibers embedded in a metallic matrix.

High strength, low weight structures can be formed of composites of filaments embedded or bound in a matrix. Particularly, carbon fibers have high tensile strength and a high modulus of elasticity, so that composites formed of a metal matrix containing such fibers can be used for components required high strength-to-density and high modulus-to-density ratios over a wide range of temperatures. Metal-graphite composites also combine the lubricating properties of graphite with the toughness of the metal to provide a material with a low coefficient of friction and wear resistance. Composites of graphite with metals such as aluminum exhibit great strength and high electrical conductivity.

It has been recognized in the prior art that if the fibers can be substantially oriented in the direction of maximum expected stress this will impart increased tensile strength and an increased modulus of elasticity to the composite. It is believed that this increased strength is achieved at least in part due to the bond between the fiber and the metal matrix, the discreteness of the fibers and the unidirectional arrangement of the fibers. Existing processes for producing composites with substantially aligned fibers have disadvantages. One prior art method involves first forming a bundle of substantially aligned fibers, which is then impregnated with a chosen metal, as for example in Sara, U.S. Pat. Nos. 3,473,900 and 3,553,820. However prealigning the fibers is somewhat difficult and may add appreciably to production costs.

Parratt U.S. Pat. No. 3,442,997 proposes producing a fiber reinforced composite by dispersing fibers such as glass, silicon nitride or asbestos in a viscous liquid medium, extruding the mixture through an orifice, and treating the extruded mixture to change the liquid into a solid carrier. The carrier is then removed by burning. An obvious disadvantage of this method is that the resulting composite typically will have relatively low density due to voids left from the burned-off carrier. On the other hand Parratt mentions that fibers have also been oriented by extrusion in situ in metal matrixes, but points out that such extrusions can cause severe damage to brittle fibers.

Still another prior art method for forming a fiber-reinforced composite is disclosed in Schwope et al U.S. Pat. No. 3,510,275. Schwope et al disclose dispersing metallic fibers in a powder matrix of another metal, and orienting the fibers by working methods such as forging, swaging, rolling, extrusion and the like under conditions such that the matrix is hot worked while the fiber material is cold worked. According to Schwope et al this working affects both the fiber and the matrix material, resulting in a compacted material having elongated fibers which are substantially aligned. Schwope et al state that this process is applicable to a wide range of different metal matrixes and fibers; however, the process is illustrated only for molybdenum fibers which are notoriously somewhat ductile and soft, and over a relatively broad working temperature range of about 1450° to 1800°F.

A principal object of the present invention is therefore to provide a relatively simple and inexpensive process for forming a metal fiber composite in which relatively brittle fibers are substantially axially aligned. Another object of the present invention is to provide a method of the type above described where the fibers are graphite and the metal is aluminum, copper, lead or zinc or an alloy in which one of these metals is a major constituent. Yet other objects of the present invention will in part appear obvious and will in part appear hereinafter.



The invention accordingly comprises the process and the several steps and the relation of one or more of such steps with respect to each of the others, which are exemplified in the following detailed disclosure and the scope of the invention all of which will be indicated in the claims.

Generally, to effect the foregoing and other objects the present invention involves treating a mat of substantially randomly oriented graphite fibers with a wetting agent, and impregnating the treated mat with a selected molten metal, and cooling the impregnated mat to form a solid billet. The billet is then hot worked at a temperature slightly below liquidus temperature of the metal to reduce the cross section of the billet and elongate the billet substantially in one direction only. This working causes the graphite fibers to be substantially axially aligned in a direction perpendicular to the direction of reduction, with relatively little fiber breakage.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. **1** is a side elevational view, diagramatically illustrating the process according to the teachings of the present invention;

FIG. **2** is an enlarged side elevational view, in section, showing a die assembly useful in the process according to the teachings of the present invention;

FIG. **3** is a microphotograph of a graphite-fiber metal composite at an intermediate stage in the process of the present invention; and

FIG. **4** is a microphotograph of a graphite-fiber metal composite produced according to the process of the present invention.

Although graphite fibers are preferred in the practice of the instant invention it is intended that the term "carbon fibers" should include both graphite and non-graphitic carbon fibers. The carbon fibers used in the invention may be made from any of a large number of precursors such as pitch, rayon, polyacrylonitrile or the like in the form of yarn, tow, webs which are woven, knitted, felted, and the like. In a preferred form the fibers are graphite, derived from spun pitch and designed in a random layered relationship in a mat. Such fibers have an average diameter of about eight microns, and an average length of from 1–3 inches. Carbon fiber mats of this type are well known and available commercially, being one of the least expensive forms in which graphite fibers are available.

A number of metals may be used as the metallic matrix of the composite of the present invention. Preferred are aluminum, lead, copper and zinc, and various alloys in which at least one of these metals is a major constituent. As is known in the art, molten metals such as aluminum do not readily wet graphite. However, it is known that graphite fibers can be treated with selected agents, which will render them wettable by molten metals, for example, by coating the graphite fibers with a tantalum film by electrodeposition from a fused salt bath, out-

gassing the fibers by pumping them down to a very low pressure and submerging the outgassed fibers into a pressurized molten aluminum bath to fill the interstices of the fibers as taught in U.S. Pat. No. 3,553,820. A similar process is described in U.S. Pat. No. 3,571,901 issued to R. V. Sara in which the carbon fibers are first coated with silver or a silver aluminum alloy by electrodeposition from the plating solution, the fibers are then contacted with aluminum foil, and the combined foil-fiber is heated while under pressure to the solidus temperature of the foil. In both of these systems, it is also suggested that the metal coating can be applied by sputtering or by reduction of salts of the metal.

Preferably however, the graphite fiber mat used in the present invention is pretreated with a coating of titanium boride, titanium carbide or mixtures thereof according to the process of copending patent application Ser. No. 343,650, assigned to the common assignee. According to this latter process, the graphite fibers of the mat are provided with a coating of a substantially uniform layer, preferably in the range between 100 to 10,000 A in thickness, of titanium boride, titanium carbide, or a mixture thereof. While there are many techniques for coating fibers, the preferred method involves a vapor phase deposition whereby the material of the coatings is deposited as a consequence of the simultaneous reduction of a mixture of a gaseous compound of titanium and a gaseous compound of boron. Vapor deposition techniques to form coatings are well known in the art and usually are carried out at temperatures between about 900° to 1400°C. For example, it is known that intermetallic compounds, such as hafnium boride, can be deposited as a coating from a mixture of gaseous hafnium chloride and boron trichloride reduced by hydrogen gas.

The coated fiber mat is then impregnated with a selected molten metal. Typically the mat is drawn through a bath containing the molten metal matrix and because the mat fibers are wetted infiltration of the interstices between the fibers by the molten metal will occur. The impregnation process is preferably carried out under substantially atmospheric pressure, typically in the range of about 4 psig. The metal impregnated/fiber mat is then allowed to cool below the solidus temperature of the metal thereby forming a solid ingot or billet composite. At this point the graphite fibers of the mat are still oriented randomly.

The fibers are substantially axially oriented by hot working the solid billet at a temperature in the range of between a minimum of not greater than about 50°C below the solidus temperature of the metal and a maximum below the liquidus temperature and about the solidus temperature of the metal. For example, for a metal matrix formed from an aluminum/magnesium alloy comprising 95% aluminum, the balance magnesium and minor inpurities, which has a normal melting point of 628°C, working will be at about 615°C.

Working may be by press forging, extrusion, rolling, drawing and the like which results in reduction of the cross section of the billet and elongation of the billet substantially in one direction only.

The billet is worked for a time sufficient to reduce its cross-section not less than 20%, typically to 90%.

Despite the relatively brittle nature of graphite fibers and the fact that the metal is at least partially in the solid state, hot working the billet in the above-described manner is found to result in alignment of the graphite fibers in the billet substantially in a direction perpendicular to the direction of reduction without excessive fiber breakage.

A preferred method for producing graphite fiber/metal composite material according to this invention is shown in the drawings. Referring to FIGS. 1–3 of the drawings a graphite fiber material such as an inexpensive random fiber mat indicated generally at **20** comprising a plurality of fibers **22** is provided with a continuous coating of a wetting agent at a treating station **24,** such as a vapor deposition station. However, it will be understood that the graphite fibers may be coated by other means, such as by immersion of the fibers in a liquid bath of selected treating agent. The coated fiber mat is then immersed in a bath of liquid metal indicated generally at station **26.** The liquid metal infiltrates and impregnates the mat. The impregnated mat is then removed from the liquid metal bath and the impregnated mat is cooled at a cooling station **28** to below the solidus temperature of the metal, to form a billet or ingot **30.** At this stage, it should be noted that the fibers **22** are oriented at random in the metal matrix **32.**

An important feature of the present invention is the ability to align relatively brittle graphite fibers without excessive fiber damage or breakage. This is accomplished by hot working the formed billet at a station **33,** in a manner which minimizes shear on the fibers while substantially aligning the fibers within the solid metal matrix.

In a preferred embodiment of the invention the billet is hot worked by back-extrusion through a specially shaped die assembly indicated generally at **34.** Die assembly **34** includes a die body **36,** end cap **38,** die forming member **40** and ram **42.** An important requirement is the shape of the die forming member **40** which should have a tapered entrance, e.g. at **44.** By virtue of this tapered shape, shear on the extrusion billet is substantially reduced, whereby fiber damage or breakage is minimized notwithstanding that the working can be at a temperature below the solidus temperature of the metal matrix. Other working methods which reduce the cross-section of the billet such as press forging, rolling, drawing and the like may also be used with some success provided care is taken to prevent excessive shear occuring in the billet. For example, if working is by rolling or drawing, reduction of the billet cross-section should be made gradually by a series of small reductions which may tend to minimize shear. An advantage of using a tapered die assembly **34** is that the total reduction may be in one step without substantial damage to the fibers resulting.

The fibers **22** in the finished composite, i.e. after hot working, are substantially unidirectionally oriented. Of course in actual practice the fibers are not completely and perfectly reoriented but the proportion and degree of unidirectional orientation is quite high, as is shown in FIG. **4.**

The following examples illustrate more clearly the manner in which graphite fiber/metal composites are produced according to the invention. The invention however should not be construed as being limited to the particular embodiments set fourth in the examples.

## EXAMPLE 1

A graphite fiber/aluminum alloy composite material is produced as follows: The graphite material is graphite mat avialable from Union Carbide Corporation under the tradename THORNEL MAT VM-0032. The

manufacturer describes this material as a fiber mat composed of high strength, high modulus graphite filaments (8 average diameter) in a random layered orientation, having a filament tensile strength of 200,000 psi, and modulus of $30 \times 10^6$ psi. The mat itself is reported to have a density of 0.04 lb/ft$^2$, and tensile strength (longitudinal) of about 1.1 lb/in.

A continuous $0.5 \times 0.1$ inch strip of $30 \times 10^6$ modulus graphite mat above described is exposed to a vapor reaction mixture formed of 0.38% $TiCl_4$, 0.21% $BCl_3$, and 0.80% Zn, the balance argon (all percentages by weight). The gas mixture is maintained at a temperature of 650°C and the residence time of the graphite mat in the coating chamber is 6 minutes. A coating of about 200 A, believed to be substantially $TiB_2$ forms on the graphite fibers. The coated fiber mat is transferred under argon to a molten bath containing an aluminum alloy comprising 5.0 wt% magnesium, the balance aluminum (melting point 628°C), and is vacuum impregnated at one atmosphere pressure with the molten metal at 650°C for 3 minutes. A metal-impregnated fiber mat strip results which is removed from the bath and then allowed to cool below the solidus temperature of the metal. Strips of aluminum impregnated graphite fiber mat are placed in a graphite die, heated under flowing argon to 630°C and pressed together. Solid metal-fiber bundles result after cooling below the solidus temperature of the metal. A microphotograph of a bundle appears substantially as shown in FIG. 3 of the drawings. The bundles are machined to billets $0.75 \times 2.5$ inches in diameter, and then hot worked by back extruding under argon through a die as shown in FIG. 2, at 600°C. An extrusion ratio of 9:1 is used. High strength metal graphite composites are obtained which have a density of 0.095 lb/in$^3$, tensile strength of 60,000 lb/in$^2$, and modulus of elasticity of $15 \times 10^6$ lb/in$^2$. A microphotograph of a section of the resulting composite taken along the axis of the direction of elongation of an extruded composite appears substantially as shown in FIG. 4 of the drawings.

## EXAMPLE II

A graphite mat similar to that used in Example I is exposed to a similar gas mixture in which however the composition is as follows: 0.30 wt% $TiCl_4$, 0.14 wt% BCl and 0.80 wt% Zn, the balance argon. The mat is exposed to such gas mixture at 695°C for 30 minutes. The mat is then transferred under argon to a molten bath containing an aluminum alloy comprising 1 wt% magnesium, 0.6 wt% silicon, 0.25 wt % copper, the balance aluminum, and impregnated with the molten metal at 695°C for 3 minutes. A metal-impregnated fiber bundle is prepared by pressing strips of impregnated mat together at 640°C and allowing it to cool below the solidus temperature of the metal alloy. The bundle is then machined and worked at 580°C as in Example I. A high strength metal/graphite fiber composite is obtained.

A microphotograph taken along the axis of the direction of elongation the extruded billet appears substantially as shown in FIG. 4 of the drawings.

## EXAMPLES III TO V

Graphite fiber/metal alloy composite materials are produced as in Example I, in which, however the metal alloy and process condition parameters are changed to the following:

| | Example III | Example IV | Example V |
|---|---|---|---|
| Alloy | lead −0.25 wt.% magnesium (m.p. 325°C) | zinc −5 wt.% aluminum (m.p. 382°C) | pure copper (m.p. 1083°C) |
| Gas Temperature | 650°C | 650°C | 650°C |
| Bath Temperature | 620°C | 600°C | 1100°C |
| Pressing Temperature | 330°C | 400°C | 1000°C |
| Hot Working Temperature | 300°C | 380°C | 1000°C |
| Extrusion Ratio | 9:1 | 9:1 | 9:1 |

High strength metal-graphite fiber composites are obtained. Microphotographs taken across the direction of elongation of the extruded billets appear substantially as shown in FIG. 4.

Since certain changes may be made in the above process without departing from the scope of the invention hereinvolved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted in an illustrative and not in a limiting sense.

We claim:

1. Method of forming a composite of metal with a mat of initially randomly arranged carbon fibers, comprising the steps of:
   - coating the surfaces of said mat of substantially random carbon fibers so that said carbon fibers can be wetted by a molten metal;
   - impregnating the coated mat with a molten metal;
   - cooling the metal impregnated mat to a temperature below the solidus temperature of said metal; and
   - working the cooled impregnated mat at a temperature in the range between a minimum of not more than about 50°C below said solidus temperature and a maximum just below the liquidus temperature of the metal, to reduce the cross-section of the impregnated mat in one direction and thereby substantially align said carbon fibers in a direction perpendicular to the direction of reduction.

2. Method as defined in claim 1 wherein said fibers are graphite.

3. Method as defined in claim 1 wherein the step of coating includes reduction of a gaseous compound of titanium in the presence of said fibers.

4. Method as defined in claim 3 wherein said fibers are coated with a titanium compound selected from the group consisting of titanium boride, titanium carbide and mixtures thereof.

5. Method as defined in claim 3 wherein said step of coating is effected for a time sufficient to deposit on each of said fibers a layer having a thickness in the range between about 100 to 10,000 A.

6. Method as defined in claim 1 wherein said step of impregnation includes immersing said coated fibers in a body of molten metal.

7. Method as defined in claim 6 wherein said step of immersing is carried out under substantially ambient atmospheric pressure.

8. Method as defined in claim 1 wherein a major proportion of said metal is aluminum.

9. Method as defined in claim 1 wherein said metal is selected from the group consisting of aluminum, lead,

zinc, copper and alloys in which at least one of said metals is a major constituent.

**10.** Method as defined in claim **1** wherein said step of working comprises extruding the cooled impregnated mat.

**11.** Method as defined in claim **10** wherein said impregnated mat is back extruded through a die having a tapered entrance.

**12.** Method as defined in claim **1** wherein said step of working reduces the cross-section of said impregnated mat not less than 20%.

**13.** Method of aligning reinforcing carbon fibers in a precursor formed of a mat of substantially randomly oriented carbon fibers impregnated with a metal,

comprising working said precursor at a temperature in the range between a minimum of not more than about 50°C below the solidus temperature and a maximum just below the liquidus temperature of the metal, to reduce the cross-section of the mat in one direction and thereby substantially align the carbon fibers in a direction perpendicular to the direction of reduction.

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