United States Patent [19]

Lachman et al.

[11] **3,894,863**

[45] **July 15, 1975**

[54] **GRAPHITE COMPOSITE**

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[22] Filed: **Oct. 3, 1974**

[21] Appl. No.: **511,794**

Related U.S. Application Data

[62] Division of Ser. No. 343,650, March 22, 1973, Pat. No. 3,860,443.

[52] **U.S. Cl.** ..... **75/.5 R**; 75/138; 75/153; 75/166 R; 75/168 R; 75/178 R; 428/366; 428/367

[51] **Int. Cl.** **C23c 11/08**; C23c 1/00

[58] **Field of Search** ..... 117/71 R, 106 C, 106 R, 117/228

[56] **References Cited**

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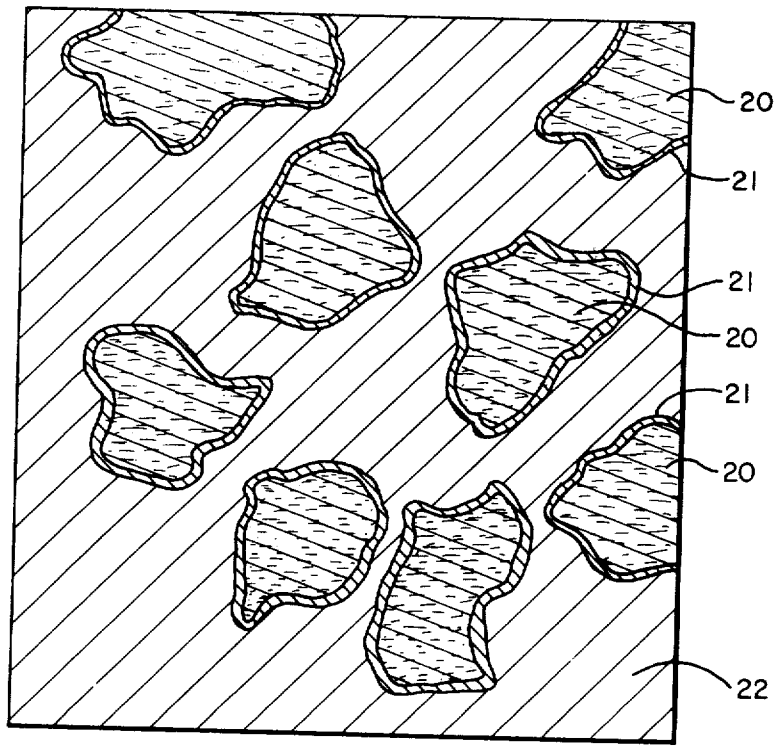
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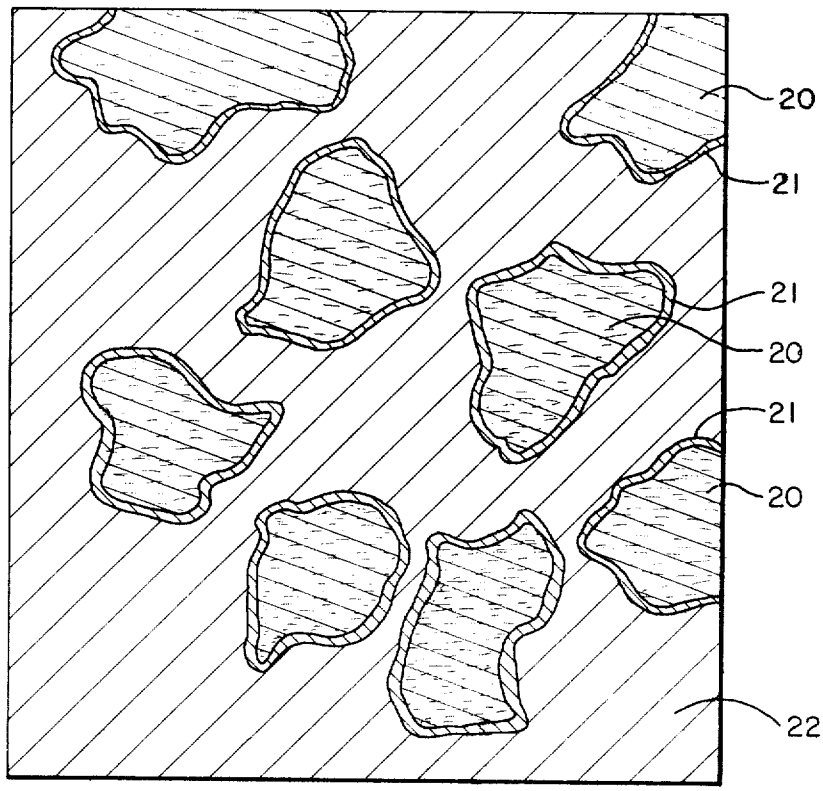
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[57] **ABSTRACT**

A novel graphite fiber/metal composite material, the graphite fibers having a coat of titanium boride which may be mixed with titanium carbide. The coat, which promotes wetting by metals such as aluminum, copper and lead, is formed by an intermediate temperature vapor deposition technique involving the reduction with zinc vapor of a mixture of gaseous titanium and boron halides.

6 Claims, 1 Drawing Figure




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GRAPHITE COMPOSITE

This is a division of U.S. Pat. application Ser. No. 343,650 filed Mar. 22, 1973 now U.S. Pat. No. 3,860,443.

The present invention relates to composite materials, and more specifically to composites of carbon fibers embedded in a metallic matrix, and the method of making same.

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 aligned in the direction of maximum expected stress can be readily used for components requiring 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 materials such as aluminum and copper, exhibit great strength and high electrical conductivity.

A number of metals in molten form, such as aluminum and the like, do not readily wet graphite. It has been suggested that the graphite can be wetted by molten aluminum if a layer of aluminum carbide is first provided at the interface between the metal and fiber, but that such aluminum carbide phase cannot be tolerated due to its thermochemical and mechanical instability. In U.S. Pat. No. 3,553,820 issued to R. V. Sara, it is taught that aluminum graphite fiber composites can be formed by first coating the fibers with a tantalum film by electrodeposition from a fused salt bath, outgassing 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. 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, then the fibers are 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. Whether using silver or tantalum, it is difficult to obtain uniform thin coatings on the fibers, and in any event, the resulting composites contain substantial amounts of expensive, heavy material such as silver and tantalum.

Electrodeposition and chemical deposition techniques have also been used to deposit the matrix material directly around graphite fibers, the coated fibers being subsequently hot-pressed to form composites. The major disadvantage of forming composites with such deposition techniques is that for the most part, the matrix material is usually limited to a rather pure metal, which for many purposes has markedly inferior properties compared to alloys.

A principal object of the present invention is therefore to provide a simple, unique process for forming metal/graphite fiber composites without resort to high pressures or temperatures. Another object of the present invention is to provide a unique metal/graphite composite in which the composition of the matrix material may be varied over a wide margin. 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, and the products and compositions possessing the features, properties and relation of elements 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 a thin, substantially uniform coating of a wetting agent on carbon fibers, the wetting agent being titanium boride, titanium carbide or a mixture of both, the interstices between the coated fibers being filled with a metal infiltrated initially as a liquid under ambient pressure. Because it is not considered possible to account for the formulae generally of borides in terms of ordinary conceptions of valency, the term "boride" as used herein is not to be considered limited to any particular stoichiometric relation unless specifically indicated.

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 drawing wherein there is shown a diagramatic illustration, in cross-section, of a carbon-fiber metal composite produced according to the teachings of the invention.

Although graphite fibers are preferred in the practice of the instant invention it is intended that the term "carbon fibers" should include both graphitic 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 rayon in uniaxial yarn form, of seven micron average fiber diameter, containing approximately 11,000 fibers in the yarn. Such carbon fibers and textiles are well known and available commerically, and the method of producing same is well known in the art.

The composite of the invention comprises, as shown in the drawing, a plurality of graphite fibers **20** each having a substantially continuous surface coating **21** of a wetting agent which is titanium boride, titanium carbide or a mixture of both. Typically, the fiber diameter is about 7 microns and the coating thickness is as thin as 100 A, so that for the sake of clarity the relative thickness of the coating in the drawing has been exagerated. The fibers are embedded in a solid metallic matrix **22** which may be aluminum, magnesium, copper, lead, zinc, tin and various alloys of these metals such as aluminum/silicon and the like.

In order for infiltration or investment of a bundle of fibers to occur on immersion in a liquid, the liquid must wet the fiber surfaces. As previously noted, molten metals such as aluminum and copper do not readily wet graphite. Consequently, the present invention provides on the surfaces of the graphite fibers a coating of a wetting agent. This coating is 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 in the present in-

vention 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.

In the process of the present invention, the preferred vapor deposition process involves a comparatively low temperature reduction of a mixture of titanium tetrachloride and boron trichloride with zinc metal vapor as the reducing agent. It is postulated that the use of the zinc metal which serves as a "slow" reducing agent permits a wide variety of reactions to occur whereby better control will be obtained over the process.

For example, if the relative weight ratio of boron trichloride to titanium tetrachloride of the mixture thereof is low (i.e. less than about one-third the coating on the fiber will constitute a mixture of titanium carbide and a boride which has an approximate composition expressed substantially as TiB. At higher weight ratios the composition of the deposited coat approaches TiB_2.

The foregoing can be explained on the basis of the following series of postulated reactions that are believed to occur in the gas phase and at the graphite fiber surfaces during the deposition process. It is believed that the first two equations express the reduction processes which are occurring.

1. $TiCl_4 + Zn \rightarrow TiCl_2 + ZnCl_2$
2. $2BCl_3 + 3Zn \rightarrow 2B + 3ZnCl_2$

It is believed then that the boron thus produced and the carbon of the fibers react with the titanium dichloride somewhat as follows:

3. $2TiCl_2 + XB \rightarrow TiB_X + TiCl_4$
4. $2TiCl_2 + C \rightarrow TiC + TiCl_4$

From equation (3), it appears that if there is enough of the boron halide to provide a relative excess of boron so that X in equation (3) is around the value of 2, the form of titanium boride formed will closely approximate TiB_2.

This latter consideration can be important because to achieve a satisfactory composite, it is not only desirable that the fiber coat promote wetting by the matrix metal, but that it also provides a chemically stable interface between the fiber and the metal of the matrix. For example, if the metal of the matrix is copper, a coating which is a mixture of TiC and TiB is satisfactory. On the other hand, if the metal of the matrix is aluminum or an alloy with a high percentage of aluminum, it has been found that the coating composition should be substantially TiB_2.

Fibers with the requisite coat are then drawn through a bath containing the molten metal matrix and because the fibers are wetted, infiltration of the interstices between the fibers will occur. The entire infiltration process can be carried out at ambient pressure preferably under an inert atmosphere such as argon or the like. The metal-fiber mass is then allowed to cool below the solidus temperature of the metal, thereby forming a solid composite. The composites, which can be originally made in the form of wires, rods, tapes or sheets, can be pressed together at a temperature above the melting point of the matrix to give bulk composites of various shapes such as bars, angle sections and panels. If desired, during the pressing of such shapes, any excess metal may be expressed from the composite in order to increase the volume percentage of the fibers.

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

EXAMPLE I

Graphite yarn containing approximately 11,000 individual fibers of 50×10^6 modulus was exposed to a vapor reaction mixture formed of 0.38 percent $TiCl_4$, 0.21% BCl_3, and 0.80% Zn, the balance being argon (all percentages being by weight). The gas mixture was maintained at a temperature of 650°C for 30 minutes to provide a coating of about 200°A, believed to be substantially TiB_2 on the yarn fibers. The coated fibers were transferred under argon to a molten bath containing 13 percent by weight of silicon-aluminum alloy and kept immersed in the bath at 650°C for 2 minutes. The resulting metal-fiber composite was removed from the bath and then allowed to cool below the solidus temperature of the alloy. A section taken across the long axis of the fibers through the composite appears substantially as shown in the drawing.

A number of sections of the composite described in this Example I were hot pressed in a graphite die under vacuum at 600°C for 5 minutes to form a composite plate 6 inches long by 0.5 inches wide by 0.05 inches thick.

EXAMPLE II

The graphite yarn similar to that used in Example I was exposed to a similar gas mixture in which however the composition was as follows: 0.38 wt.% $TiCl_4$, 0.14 wt.% BCl_3 and 0.80 wt.% Zn, the balance being argon. The fibers were exposed to that gas mixture at 650°C for 30 minutes and transferred under argon to a molten bath containing a bronze alloy of about 90 wt.% Cu and 10 wt.% Sn at about 980°C for one minute. The composite was removed from the bath and allowed to cool to form a solid article.

EXAMPLE III

Coated graphite fibers were prepared as in Example I, and tansferred under argon to a molten bath containing a lead alloy (0.4% Ca, 99.6% Pb) held at about 550° C. The fibers were kept in the bath for 10 minutes, and the composite was then removed and allowed to cool below the solidus temperature of the alloy. The resulting composite could be hot pressed to form bearings.

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

What is claimed is:

1. A composite product comprising a plurality of carbon fibers each have a coating of a material selected from the group consisting of titanium boride, and a mixture of titanium boride and titanium carbide said fibers being disposed in a substantially solid matrix of metal selected from the group consisting of magne-

sium, lead, zinc, copper, aluminum, tin and alloys of said metals.

2. A composite as defined in claim **1** wherein said fibers are substantially graphite.

3. A composite as defined in claim **1** wherein the thickness of said coating is in the range of between about **100** to **10000** Angstroms.

4. A composite as defined in claim **2** wherein said metal comprises aluminum.

5. A composite as defined in claim **2** wherein said metal comprises copper.

6. A composite as defined in claim **2** wherein said metal comprises lead.

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Disclaimer

3,894,863.—*Walter L. Lachman*, Concord, Mass., *Robert A. Penty*, Kennebunk, Maine, and *Paul F. Jahn*, Chelmsford, Mass. GRAPHITE COMPOSITE. Patent dated July 15, 1975. Disclaimer filed Aug. 18, 1977, by the assignee, *Fiber Materials, Inc.*

Hereby enters this disclaimer to all claims of said patent.

[*Official Gazette October 25, 1977.*]