United States Patent

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[54] **TIN-CARBON FIBER COMPOSITES**
16 Claims, 1 Drawing Fig.

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[50] Field of Search 29/191.4, 180, 183.5, 191, 191.2, 192, 195

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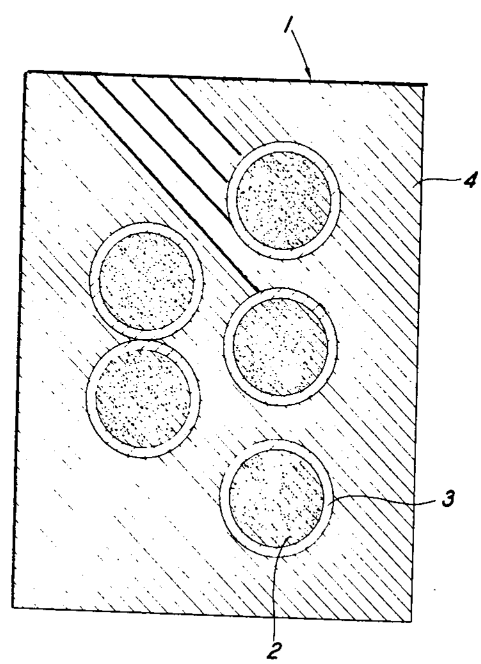
ABSTRACT: Low-density, high-strength tin base composites are provided by coating carbon fibers with a metallic coupling agent and then bonding them together, preferably in a parallel or aligned manner, by means of a tin or tin base alloy matrix. Such composites are characterized by physical properties which are much superior to those evidenced by the matrix material alone and find utility in applications where the chemical properties of tin are desired but its use is prohibited or limited due to its poor physical properties.



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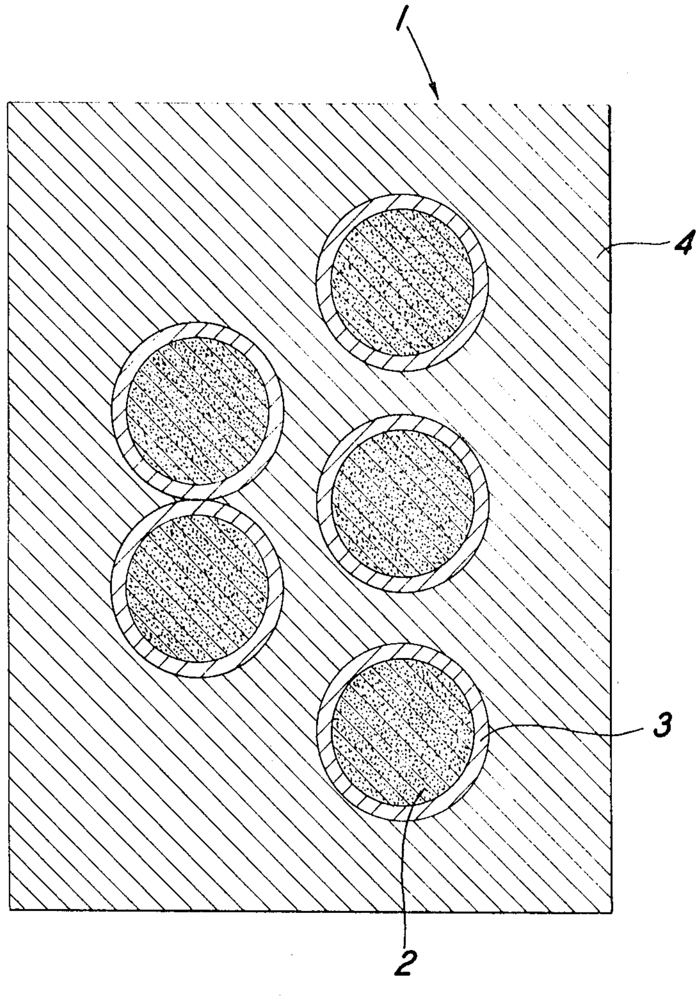

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TIN-CARBON FIBER COMPOSITES

BACKGROUND OF INVENTION

1. Field of the Invention

The present invention relates to carbon fiber-tin composites made up of a plurality of carbon fibers coated with a metallic coupling agent and bonded together, preferably in a side-by-side or parallel manner, by means of a tin base metal matrix.

2. Description of Prior Art

Tin is an element which finds wide useage in industry. One of its most important uses is as a protective coating for stronger materials or substrates. The use of pure tin alone as a material of construction is limited by its inherently poor physical properties, such as low tensile strength and modulus of elasticity. It is presently common practice in industry to increase the tensile strength of tin by alloying it with copper and/or antimony. However, the resultant alloy is still quite weak.

It has been proposed to increase the tensile strength of tin by reinforcing it with an inert fibrous material. One of the most promising materials available today for this purpose is carbon textiles. However, it has been discovered that strong, nonporous carbon fiber-tin composites cannot be simply formed by bonding carbon fibers together by means of a tin matrix. This is believed to be due to the fact that carbon fibers are not adequately wetted by molten tin and that when the so-coated fibers are cooled the tin thereon, at least in part, dewets or separates from the carbon fibers and, accordingly causes voids or weak spots to be present in the resultant composite article.

It was discovered that this problem can be overcome by first coating the carbon fibers with a thin but continuous metallic film or coupling agent which has a melting point greater than tin and is also readily wetted by tin. Carbon fiber-tin composites so-produced not only are essentially nonporous, but they also increase the tensile strength properties of tin to a much greater extent than the most effective alloy additions.

SUMMARY

Broadly stated, the carbon fiber-tin composite of the invention comprises a plurality of carbon fibers each of which is coated with a thin layer of a coupling metal having a melting point greater than tin which are bonded together, preferably in a side-by-side or parallel manner, with a tin base binder or metal matrix. Generally, this composite article may be provided by a process which comprises coating carbon fibers with a thin but continuous film of a suitable metal, shaping an aggregate of the so-coated fibers into the desired form, infiltrating the voids between the individual fibers with molten tin or tin base alloy and cooling the resultant tin infiltrated aggregate to produce a composite article.

A graphite fiber-tin composite, containing approximately 33.5 volume percent fibers, is characterized by a density 20 percent less than tin, a modulus of elasticity twice as great as tin, and a tensile strength approximately 24 times greater than tin. This composite can be formed into any desired shaped by known techniques which will readily suggest themselves to those skilled in the art. Its properties readily suggest its use as a material of construction in apparatus which require strong, corrosion resistant parts or components.

DESCRIPTION OF THE DRAWING

The sole FIGURE shown in the drawing presented herewith is a diagrammatical illustration of a rectangular section of a carbon fiber-metal matrix composite article produced according to the teachings of the instant invention.

Referring now in detail to the drawing, there is shown in cross section a rectangular composite article 1 consisting of aligned graphite fibers 2 having disposed on their surface a continuous 2-micron thick coating of nickel 3. These so-coated fibers are bonded together by a tin matrix 4. The graphite fibers 2 are approximately 1 inch in length and disposed in the tin matrix 4 in a parallel or side-by-side manner. The length dimension of the fibers 2 is perpendicular to the surface of the drawing.

Description of the Preferred Embodiment of the Invention

Carbon textiles in any form can be employed in the practice of the instant invention. However, it is preferred to employ carbon fibers in yarn or monofilament form. Carbon textiles are available commercially and are generally produced by the techniques described in U.S. Pat. Nos. 3,107,152 and 3,116,975, among others.

The coupling metal used can be any metal which has a melting point greater than the metal matrix which adheres to the carbon and is readily wetted by the matrix metal without forming low melting point alloys or brittle intermetallic phases. Metals which are preferred as coupling agents are nickel, titanium and chromium. The selected coupling metal can be deposited on the carbon fibers by a variety of methods. The techniques available for accomplishing this include electrodeposition from a suitable plating bath, thermal decomposition of the appropriate metal halide or sputtering. The exact deposition technique to be employed is dictated by a number of factors. Sputtering can be used on relatively complex shapes and results in a tenacious bond between the coupling metal and the carbon fiber substrate. Such a bond is a highly desirable feature in carbon fiber-metal matrix composites. Thermal decomposition of the appropriate halide requires a heating of the carbon fiber substrate and, accordingly, somewhat limits the type of shapes which can be coated in this manner. Electrodeposition of a metal from a plating solution is an ideal way of coating carbon fibers with a thin metallic film and is the preferred coating technique.

While the preferred binder or matrix metal is tin, it will be readily appreciated by those skilled in the art that tin base alloys of low melting point metals such as lead, antimony, and bismuth may also be employed in the practice of the instant invention.

The following example illustrates in detail the practice of the instant invention.

A single ply of graphite yarn having an average filament diameter of 6.9 microns and consisting of 720 monofilaments per ply was cut into a plurality of 4-inch lengths. These 4 inch sections of graphite yarn were then predipped into acetone to facilitate their subsequent coating with nickel. Nickel was plated on the so-treated graphite yarn by using a nickel anode and an electroplating plating solution prepared by dissolving 200 grams of $NiSO_4 \cdot 6H_2O$ and 22 grams of H_3BO_3 in 500 ml. of distilled water. The plating solution temperature was maintained at approximately 52° C. The plating current varied between about 400 to about 1000 milliamperes. A metallographic examination of the resultant fibers showed that all monofilaments had a coating of nickel thereon and that the average coating thickness ranged from 1 to 3 microns. These nickel clad fibers were then cut in approximately 1-inch lengths and placed in an aligned position (all parallel) in a cylindrical capillary tube measuring approximately 1 inch in length and having an internal diameter of about 0.135 inches which was provided with a top and bottom closure. The surface of the cylinder was provided with 12 randomly placed holes or openings to facilitate the ingress of tin into the cylinder and hence into the voids between the aligned graphite fibers. The cylinder containing the fibers was placed into an airtight chamber which also contained a vessel of tin. The chamber was then evacuated to a pressure of approximately 2×10—mm. of mercury to out gas the graphite fibers. The chamber with the tin therein was heated to a temperature of approximately 300° C. The cylinder containing the aligned fibers was then submerged below the surface of the molten tin. The chamber was subsequently filled with argon gas to a pressure of about 1atmosphere to insure that molten tin filled essentially all the voids between the aligned graphite fibers. After about 30 seconds of pressurizing the specimen, the capsule was withdrawn from the molten tin, cooled, and removed from the chamber.

A metallographic examination of the resultant nickel coated graphite fiber-tin composite showed that the nickel coating was well bonded to the graphite fiber substrate; that the tin matrix material had uniformly and completely wetted the so-coated fibers without disturbing the continuity of the nickel coating; and that no undesireable reaction zone was formed at the nickel-tin interface.

The physical properties of a nickel clad graphite fiber-tin composite are listed below. For comparison, similar property data is also listed for pure tin.

Physical Properties of Tin and A Nickel Clad Graphite Fiber-Tin Composite Containing 33.5r/o Fibers

Material	Density	Modulus of Elasticity	Tensile Strength
	g./cm.^{3}	$\times 10^6$ lb./in.^{2}	lb./in.^{2}
Tin	7.05	7.8	2000
Ni clad graphite fiber-tin composite	5.56	16.2	47,400

From the foregoing data, it is observed that a composite of the invention, containing approximately 33.5 volume percent graphite fibers, is characterized by a density 20 percent less than tin, a modulus of elasticity twice as great as tin, and a tensile strength approximately 24 times greater than tin metal.

A composite so-produced, in addition to its utility as a chemical corrosion resistant material of construction, is extremely useful as a low density material of construction for subsonic and supersonic aircraft, space system components, and various nuclear devices.

While the foregoing example concerns a composite where the fibers are positioned in a side-by-side relationship, it is readily apparent to those skilled in the art that the graphite fibers may be randomly orientated in the tin matrix if more isotropic physical properties are desired without losing the benefits of the instant invention. In addition, it is obvious that the thickness of the metal coupling agent can be varied as desired. For example, a thickness of only 0.1 microns has been found to be effective. Likewise, it will be appreciated by those versed in the art that although graphite fibers and fabrics are preferred in the practice of the instant invention, nongraphitic carbon fibers and fabrics may also be employed. Also, other methods of infiltrating the metal clad carbon fibers with tin and tin base alloys will readily suggest themselves to the skilled artisan.

As used herein and in the appended claims the term carbon is meant to include both the nongraphitic and graphitic forms of carbon.

The foregoing example is presented for illustrative purposes only and is not intended to unduly limit the reasonable scope of the instant invention. The limitations of the invention are defined by the following claims.

What is claimed is:

1. A corrosion resistant composite article comprising a plurality of carbon fibers bonded together by a tin base metal matrix, said carbon fibers having a substantially continuous coating of a coupling metal having a higher melting point than said tin base metal matrix on their outer surface.

2. The corrosion resistant article of claim 1 wherein said tin base metal matrix is essentially tin.

3. The corrosion resistant composite article of claim 1 wherein said fibers are graphite.

4. The corrosion resistant composite article of claim 1 wherein said carbon fibers are in yarn form.

5. The corrosion resistant composite article of claim 1 wherein said carbon fibers are arranged in a side-by-side, parallel relationship.

6. The corrosion resistant composite article of claim 1 wherein said coupling metal is selected from the group consisting of nickel, titanium and chromium.

7. The corrosion resistant composite article of claim 1 wherein said coupling metal is nickel.

8. The corrosion resistant composite article of claim 7 wherein said coupling metal is from 1 to 3 microns thick.

9. The corrosion resistant composite article of claim 3 wherein said graphite fibers are in yarn form.

10. The corrosion resistant composite article of claim 3 wherein said graphite fibers are arranged in a side-by-side, parallel relationship.

11. The corrosion resistant composite article of claim 3 wherein said coupling metal is selected from the group consisting of nickel, titanium and chromium.

12. The corrosion resistant composite article of claim 3 wherein said coupling metal is nickel.

13. The corrosion resistant composite article of claim 12 wherein said coupling metal is from 1 to 3 microns thick.

14. The corrosion resistant composite article of claim 2 wherein said fibers are graphite.

15. The corrosion resistant composite article of claim 14 wherein said coupling metal is nickel.

16. The corrosion resistant composite article of claim 15 wherein the thickness of said nickel coupling metal is from 1 to 3 microns.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,622,283 Issue Date November 23,1971

Inventor(s) Raymond V. Sara

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 29, insert a comma (,) after "accordingly".
Column 2, line 66, change "10-mm." to read "10^{-6}mm."
Column 3, line 12, change "33.5 r/o" to read "33.5 v/o".

Signed and sealed this 20th day of March 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents