METHOD OF MAKING REINFORCED COMPOSITE STRUCTURES

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ABSTRACT

Process for making composite structures formed of reinforcement strands embedded in a metal matrix in which essentially cylindrical continuous filaments having a diameter within the range of 5–200 microns are wound in layers around a form while the matrix metal is substantially simultaneously deposited between successive layers and between adjacent strands in a given layer, the filaments being guided to the form at a rate sufficient to give a clearance between adjacent filaments equal to at least one-half the filament diameter and the amount of matrix metal between layers being sufficient to give a similar clearance between successive layers equal to at least one-half the filament diameter, the aggregate of the volume of the filaments in the composite structure not exceeding about 60% of the total volume thereof. The matrix metal can be deposited in various ways, including electroplating and vapor deposition.

4 Claims, 8 Drawing Figures
METHOD OF MAKING REINFORCED COMPOSITE STRUCTURES

This application is a continuation-in-part of my application Ser. No. 486,078 filed Sept. 9, 1965, and now abandoned.

This invention relates to novel processes for making reinforced-matrix composite structures and also to novel filament-reinforced structures made according to these processes, which structures have particular utility in applications where high-strength and low weight is required, for instance, in outer-space hardware.

The present state of the art teaches processes for making reinforced structures wherein both the processes and the resulting structures suffer from serious defects and/or limitations. Several of these prior art techniques are as follows:

The prior art liquid-infiltration technique involves forming of a metal matrix by raising the temperature of the matrix metal above its melting point to put it into a liquid state. The reinforcement filaments or elements are preformed into an array within a mold into which the liquid matrix metal can be poured to surround and infiltrate this array of elements. One apparent disadvantage of this particular process resides in the difficulty involved in orienting the reinforcements in the array and holding the desired orientation while the molten matrix metal is poured thereinto. Even relatively simple forms such as cylindrical, conical, spherical, or rectangular forms are very difficult to pre-shape, and it is also difficult, after they are shaped, to make the molten metal completely infiltrate the reinforcements. Another very serious limitation of this type of process is that, because of the sustained high temperature required to melt most useful matrix metals, there are relatively few filamentary reinforcements which are not damaged either by melting, by thermal shock, or by chemical interaction when the metal is poured thereonto at an elevated temperature. For instance, it would be impossible to place fiber glass reinforcements within most matrix metals by this process. Another serious limitation resides in the fact that many of the matrix metals which would be useful under severe operating conditions, for instance in motor parts, cannot be melted at convenient temperatures to permit their infiltration into matrix reinforcements.

Another class of prior art technique involves powdered-metallurgy methods which are most frequently used at present to produce metal matrix composites. According to this prior art teaching the matrix metal is mixed in powdered form and consolidated at an elevated temperature and/or pressure, or by sintering. Obviously, the reinforcement filaments or elements must be arranged within the powdered matrix metal before it is consolidated, and this leads to serious difficulties caused by physical damage to the reinforcements as a result of pressing the matrix during consolidation. Accordingly, relatively hard or brittle reinforcing elements cannot be used with this technique. Moreover, it is very difficult to orient the reinforcing agents, or to place them under even slight tension for the purpose of making sure that they are suitably oriented, such that they can properly reinforce the composite structure in predetermined stress directions. Another serious disadvantage resides in the high temperatures necessary for consolidation, which temperatures can cause undesirable chemical interactions between matrix and reinforcing materials, thereby resulting in inferior composite structures. Moreover, it is very difficult to form components having curved or complex contours of types which are best reinforced by continuous filaments.

The novel processes according to the present invention involve the making of reinforced matrix composites by depositing the matrix material reinforcement in a form or mandrel to which filamentary reinforcements are applied, for instance by rotating the mandrel and winding the reinforcements thereon while the matrix material is being deposited. The deposition of the matrix material is accomplished at low temperatures for instance by electroplating, vaporizing (sometimes called gas plating), vacuum evaporation, or even plasma or flame spraying techniques which can be used even with reinforcing materials having relatively low melting points. Although the present novel process does not lend itself to the application of reinforcing members in just any direction whatever, the winding of reinforcements onto rotating forms is extremely advantageous, where conveniently done, because it applies the reinforcements as continuous filaments; because it permits the application of reinforcements which are oriented in circumferential directions; and because it provides reinforcements whose density can be programmed to place the filaments closer together in zones of high stress and further apart in zones of low anticipated stress. Moreover, the spacings of the filaments can be controlled very accurately, which is an important aspect of the invention, and the filaments can be tensioned to provide a structure which is prestressed.

It is not necessary that the reinforcements be wound exactly simultaneously with the deposition steps. The same result can be achieved by alternating winding and deposition so as to wind a layer of reinforcement filaments around a suitable form, then deposit matrix material on the surface and between and upon the filament layer and so on.

Another important advantage of the present process is that the filaments can be spaced in a precision manner so as to introduce the clearance with such accuracy therebetween essential to the achievement of a high quality composite structure.

Another important advantage of the present invention is that the winding rate and the winding tension can be separately and independently adjusted in relation to the rate at which matrix material deposition occurs, thereby providing means by which the ratio of reinforcing material to the matrix material can be conveniently controlled so as to not exceed the maximum relationship capable of giving satisfactory products.

Another advantage of the present process is that unusual combinations of reinforcing elements with matrix metals can be accomplished because of the low temperatures at which the process is carried out. In other words, the reinforcing materials are not required to enter into any physical or chemical interaction with the matrix material where the temperature is not elevated. Even where the deposition is accomplished by plasma or flame spraying low-melting-point reinforcement material can be successfully used by confining the spray to a sector of the mandrel or form which is small as compared with its circumference, so that the heating is brief, as distinguished from sustained heating. Typical reinforcement materials include tungsten wire, steel wire, beryllium wire, glass filament, quartz filament,
The present process has produced unexpectedly superior results which in some cases have actually exceeded the "theoretical" values which were predicted on the basis of prior experience and theory. Ordinarily, the properties of a composite cannot be expected to exceed the sum of the properties of each component when weighted according to the percentage of the component which is present. As an example, a composite containing 25 percent of 500,000 psi boron filament and 75 percent of 125,000 psi nickel matrix would not be expected to have a tensile strength higher than 25 percent \( \times 500,000 \) plus 75 percent \( \times 125,000 = 218,000 \) psi. Composites made by powdered metallurgy or liquid infiltration prior art techniques exhibit strength values far less than the values theoretically predicted. However, the composites produced by the present deposition processes exhibit strength values at least as good as theoretically predicted, and in many cases exhibit unexpectedly superior properties. As an example, the boron nickel composite referred to above had a tensile strength of 300,000 psi, rather than 218,000 psi as predicted.

Consequently, the present novel process produces composite structures incorporating continuous filaments which can be oriented and accurately spaced and tensioned during formation of a wide variety of contours; and in which the reinforcements can be conveniently and smoothly varied according to their density; and in which the reinforcements suffer no damage or undesired interaction during fabrication; and in which the composites exhibit theoretically expected, or even higher strength values.

It has been discovered that in the formation of composites structures of the type in question, one of the most serious problems is the existence of voids within the body of the structure due to the failure of the matrix metal to be deposited completely around the reinforcement filaments. This problem is especially troublesome where the filaments are essentially circular in cross-section, as contemplated by this invention, as the crevices underlying the circular sides of the filaments, i.e. the angle included between the circular sides and a horizontal plane extending tangentially at the lower side of the strands, are difficult to fill with the metal. Moreover, if the metal is deposited in these areas, it can grow in a different manner than that deposited above and between the filaments with the result that voids can occur at the junction where the depositions meet. By careful selection of the size of the filaments, regulation of the delivery of the filaments to the form to maintain minimum clearances between adjacent filaments in a layer and between successive layers, and imposition of a maximum on the proportion by volume of filaments in the total composite structure, solid void-free structures uniformly and reproducibly exhibiting the superior properties heretofore noted can be produced.

The nature of the present invention will be more fully revealed by the following detailed description and the accompanying drawings wherein:

FIG. 1 is a perspective view of apparatus for winding reinforcement filaments on a mandrel form and electroplating the matrix metal thereon, the plating tank being partly broken away to show its interior.

FIG. 2 is a perspective view of apparatus for either vapor plating or vacuum deposition of a matrix material on a mandrel form and for winding filamentary reinforcements thereon;

FIG. 3 is a partial perspective view of apparatus for producing on a mandrel form a wound-reinforcement composite including means for spraying the matrix material on the mandrel in the vicinity of the winding;

FIG. 4 is a partial perspective view of apparatus for applying filamentary reinforcements to a dome-end vessel within a matrix deposition zone;

FIG. 5 is a partial perspective view of apparatus for cross-winding reinforcements upon a polygonal mandrel form in a deposition zone;

FIG. 6 is a partial cross-sectional view through a composite made by the apparatus shown in FIG. 5;

FIG. 7 is a partial perspective view showing apparatus for winding reinforcements upon a nozzle-shaped mandrel;

FIG. 8 is a cross-sectional view taken through a nozzle made by the apparatus shown in FIG. 7, and wherein the reinforcements are non-uniformly distributed so as to have maximum concentration near the throat constriction of the nozzle.

Referring now to the drawings, FIG. 1 shows apparatus for making a cylindrical reinforced composite, the machine including a supporting frame 1 having a deposition tank 2 mounted thereon opposite a mandrel drive head 3 including an appropriate motor M with a speed control N, and having a gear reducer (not shown). The deposition tank 2 has a seal bushing 4 through which a shaft 5 coupled to the gear reducer extends into the tank 2. This shaft supports a mandrel form 6 whose external shape conforms with the desired shape of the finished product. The deposition tank 2 includes windows 2a and a packing gland 7 which supports and guides a reciprocatory tube 8. Another gland similar to the gland 7 is located at the left side of the deposition tank 2 and passes the other end of the tube 8 to a supporting yoke 9 which is slidably bearable upon the frame 1. The yoke supports a filament-feed spool 10 which stores the filament wire 11 in supply adequate to complete the job, and this filament wire passes from the spool into the tube 8 through a seal 12 within the tube and to a small guide roller 13 which is journaled in the wall of the tube 8. The roller 13 can be moved longitudinally back and forth parallel to the axis of the shaft 5 by reciprocating the tube 8 in the glands 7.

Such reciprocation is accomplished by moving the yoke 9 back and forth along the frame 1 either manually by turning the hand-wheel 13 or automatically by depressing the lever 15 so as to clamp a split nut (not shown) on the lead screw 14 in a manner well-known in the lathe art. The lead screw 14 is rotated by an appropriate gear (not shown) located within the drive housing 3, and means D is provided for adjusting the rate of rotation, and/or the direction of rotation, of the lead screw 14 relative to the shaft 5.

Within the deposition tank 2 there is located an anode 16, and direct current is applied between the cathode-mandrel 6 and the anode 16 through appropriate wiring from a battery 17, the current being controllable in any suitable manner via the variable resistor 18.
The tank 2 is at least partially filled with a suitable electrolyte 19, specific examples thereof being given below. The mandrel 6 has a conductive surface 6a which may be obtained in one of a number of suitable ways, for instance by spraying, or alternatively the mandrel may be precoated or metallized before insertion into the deposition tank 2.

If the mandrel is not to be removed from the finished composite product, then it is only necessary that the mandrel have the desired shape and a suitable surface on which deposition can be accomplished. However, if it is desirable to make a hollow composite structure on the present apparatus, then the mandrel must be removable from within the finished product. For example, the mandrel can be made of wax and can have a powdered graphite surface applied thereto in order to render it conductive. With this type of structure, when the composite matrix product has been completely in-plating, the mandrel can easily be removed from the interior thereof by melting the wax. There are also a number of other plastics whose surfaces can be made conductive by the pre-application of metal. Metal mandrels have also been used to advantage, and have been made of aluminum or steel, or of low-melting lead, tin, or other eutectic alloy. These mandrels are preshaped to the desired configuration, and after the composite product has been formed thereon, in some cases the mandrels are removed by mechanical separation, by chemical dissolution, or by melting. Sometimes the outer surface of a component itself forms the mandrel onto which a reinforced matrix is further applied which is not to be removed therefrom subsequently. See, for example, the disclosure of the reinforced vessel as deposited in FIG. 4.

FIG. 2 shows a deposition chamber 20 having several access openings, which are sealed by appropriate covers 20a, 20b, 20c, etc. A vacuum pump located within the housing labeled P is attached to the lower opening of the housing 20 in order to maintain the latter substantially evacuated. Within the deposition chamber 20 is located a mandrel 21 supported on a drive arm 22 containing suitable mechanism for rotating the mandrel, the mechanism not being illustrated in the present drawing. The filamentary reinforcements 23 are taken from a storage spool 24 located within the chamber, and these reinforcements are guided onto the mandrel 21 by a guide roller 25 moved axially of the mandrel 21 by mechanism (not shown). If the vacuum evaporation process is to supply the matrix metal to the mandrel 21, a metal vapor source 26 is placed within the chamber 20 and heated by suitable heater means 26a. On the other hand, the illustrated apparatus can supply the matrix metal by a vapor plating process, then the gas including the appropriate vapor can be supplied from a source S through the cover 20c via a pipe 27 having an internal extension and nozzle 27a for directing the gas toward the winding area on the surface of the mandrel. Various mechanical mechanisms can be used to supply the spool to the guide 25, and for the nozzle 27 during the deposition process, the specific mechanical shaft means having no patentable significance in the present invention.

FIG. 3 shows metal spray apparatus for building up matrix metal upon a mandrel 30 which can be located within a suitable deposition zone. Means (not shown) are provided to rotate the shaft 31 which supports the mandrel opposite a spray nozzle 32 and opposite a translating block 33 including guide roller means 34 over which one or more filaments 35 can pass. The nozzle can be supported on an arm 36 which is fixed to the block 33 so that the spray nozzle 32 applies the spray to the general area where winding of the reinforcements is being accomplished on the mandrel 30. The traverse block 33 can be supported on a rod 37 and upon a lead screw 38 which is also rotated by suitable drive means (not shown). The spraying of the matrix material against the wound filaments of course heats them, but only briefly in a localized zone which quickly passes away from the spray nozzle 32 and therefore can cool rapidly, and before the filaments 35 are damaged by the heat from the spray nozzle.

FIG. 4 shows a more complex filament winding mechanism intended to be located within a deposition zone. This mechanism includes a motor M' support on a stationary frame 40 and driving a shaft 41 to which a large cam 42 is attached. Means (not shown) transmits drive from the motor M' through an arm 41a below the cam 42 to rotate a shaft 43 which supports a mandrel 44, the mandrel in this example comprising a substantially closed vessel which rotates opposite the guide roller 45 which serves to guide reinforcement filaments 46 onto the mandrel surface. The mandrel 44 is rotated about the vertical shaft 41, and also about the inclined shaft 43 so that the filamentary reinforcements are evenly spaced as they are wound on the outer surface of the vessel 44. The guide roller 45 is supported upon a frame 47 which can reciprocate on a rod 48, such reciprocation being accomplished by contact of the cam follower 47a with the periphery of the cam 42. If desired, an additional freedom of motion of the support 47 can be provided by movement of the frame 47 along the rod 49 in response to the other drive means (not shown).

FIG. 5 shows still another winding mechanism for use in a vapor deposition zone, illustrating a polygonal mandrel 50 supported upon a shaft 51 which is rotated by a suitable drive mechanism (not shown). A guide block 52 is supported upon a rod 53 and a lead screw 54 which is also rotated by suitable drive mechanism (not shown). Filamentary reinforcement 55 is delivered from a supply spool over a guide roller 56, and in this case the translating guide block 52 is caused to traverse alternately in opposite directions parallel to the axis of the drive shaft 51 so as to wind successive layers of cross reinforcements 55 upon the mandrel 50 while the deposition of the matrix material (not shown) is being accomplished.

FIG. 5 shows a cross-sectional view taken through a resulting composite structure, and showing the matrix material 60 with crossed reinforcements embedded therein, the reinforcements in one direction being labeled 61, and the reinforcements running in the normal direction being labeled 62. This apparatus forms a particularly well reinforced composite in which the reinforcements are creased on an arm 36 at right angles or at acute angles if desired, and depending upon the directions and rates of rotation of the shafts 51 and 54 with respect to each other, the spacings between layers of reinforcements being determined by the rate of deposition of the matrix material 60 as compared with the rates of rotation of the shafts 51 and 54.

FIG. 7 shows still another winding means including a shaft 70 driven by suitable driving means (not shown) and supporting a nozzle-shaped mandrel 71 having a
necked-down central portion. The matrix material is deposited on the surface of the mandrel 71, by deposition means (not shown) and filamentary reinforcements 72 are wound thereon from a supply reel 74, the distribution of the reinforcements 72 being controlled by a guide roller 73 which may be either manually or automatically translated in a direction parallel with the shaft 70, but at a non-uniform rate to provide unequal distribution of the reinforcements within the deposition zone of the machine.

FIG. 8 shows a resulting structure including matrix material 80 and reinforcements 81 distributed therewith, and having the greatest concentration of reinforcement in the vicinity of the restricted neck of the nozzle-shaped composite. This drawing is intended to illustrate the manner in which distribution of the reinforcements can be selectively accomplished during manufacture of composite structures.

As mentioned briefly earlier, the reinforcement filaments contemplated by this invention are generally circular in cross-section. Filaments of this configuration are readily available in a variety of materials and a wide range of sizes and can be obtained at minimum cost. Moreover, their symmetry and uniformity confer particularly desirable load-bearing properties in the present composite structures since stress imposed upon them is uniformly distributed, avoiding points of uneven stress which can lead to failure in use. In any event, the operating conditions envisioned herein have been established in conjunction with filaments of this configuration in order to overcome difficulties peculiarly presented by the use of such filaments for composite formation.

Although large filaments might normally be expected to give the best results here due to their greater strength and reinforcement value, such has not been found to be the case. Rather the size of the filaments have been found to be an important factor in the achievement of solid, high quality composites with very small filaments being a virtual requirement for such products. If the filament diameter very much exceeds about 200 microns, the "depth" of the "included spaces" lying under the minimum projections of each filament exceeds the lateral penetrating capacity of practical deposition techniques. Below this limit, as a general rule the smaller the filament the better the results that are obtained subject to the practical qualification that the filament size be consistent with acceptable feeding requirements. At diameters of less than about 5 microns, filaments of the type in question are extremely difficult to handle for purposes of feeding, guiding and other manipulative operations and any further improvement in deposition quality is more than offset by such difficulties. Preferably, the lower limit of diameter is 0.5 mil or about 12 microns.

If very small filaments are to be employed, they are better used in loose bundles or tows which must be essentially twist-free in order to spread out in a substantially single thickness layer which applied under tension to the mandrel form. In this condition, such bundles function as aggregates of single strands as far as this process is concerned except that they are much more readily handled.

It is crucial to the present invention that the helical windings constituting the layers of reinforcement not be laid down in extremely close, tight or contacting relation as penetration of the matrix metal between adjacent windings to form the desired solid embedments is impossible under such circumstances. The superior results characteristic of this invention are dependent upon the maintenance between adjacent filaments within each layer of an average clearance substantially equal to at least one-half the diameter of the particular filament being wounded. This spacing in relation to the selected range of filament size and the extent of the undercut beneath the filament sides applicable to filaments within that range provides an access opening sufficient for the matrix metal to be deposited solidly around and beneath the filaments using the practical deposition procedures herein described.

A further condition found necessary for superior results is the creation during the winding and depositing sequence of an average clearance between successive layers of filaments such that the filaments in such layers are spaced apart at their closest points a distance substantially equal to at least one-half the filament diameter. This is done by regulating the quantity of matrix metal deposited on and around a given layer before the next layer is applied to the form. By this means, a solid base is laid down for the next layer and aggravation of the problem of getting the metal into the "included spaces" beneath the filament sides is avoided.

Related to the just-described clearances maintained between the filaments in all directions within the composite is an overall limitation on the proportion of the total volume of the composite that can be constituted by the reinforcement filaments. Thus, for purposes of this invention the volume ration of the filaments to the over-all composite cannot exceed about 0.6/1 and specific spacings for specific filaments are to be chosen so as to meet this criterion.

While it is preferred for best results that the layers of filaments be so wound that the filaments in each layer are arranged in alternating or staggered relation to the filaments in adjacent layers, this arrangement is not critical, and the filaments could be in general alignment in the radial or transverse direction.

The composite structures produced by the invention are useful for many purposes in the condition as formed and further treatments such as molding or consolidation by heat and/or pressure, while not excluded if desired for particular circumstances, are not essential to a useful product.

Mention has already been made of the availability of several different deposition procedures for the production of the present composites. Examples of various techniques with respect to four different matrix materials are provided as follows for illustrative purposes:

Electroplated Nickel:
1. 40 oz/gal nickel sulfamate
2. 4 oz/gal nickel chloride
3. 4 oz/gal boric acid

pH 3
Temp.: 100°–140° F.
Cathode current density: 10–300 amps/ft²

4. 40 oz/gal nickel sulfate
5. 10 oz/gal nickel chloride
6. 5 oz/gal boric acid

pH 1–5
Temp.: 100°–150° C.
Cathode current density: 10–300 amps/ft²
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40 oz/gal nickel fluoborate
4 oz/gal boric acid
pH 1–3
Temp.: 100°–170° C.
Cathode current density: 100–500 amps/ft²
Vapor-Plated Nickel:
Nickel carbonyl passed over substrate mandrel at 40° to 200° C.
Electroplated Cobalt-Tungsten:
40–70 g/l sodium tungstate
4–12 g/l cobalt sulfate
7–150 g/l citric acid
50 g/l ammonium chloride
pH 7–8.5
Cathode current density: 50–200 amps/ft²
Electroplated Aluminum:
3 molar aluminum chloride
1 molar lithium aluminum hydride
diethyl solvent
Cathode current density: 5–100 amps/ft²
Vapor-Plated Aluminum:
An aluminum alkyl (triisobutylaluminum) passed over a heated substrate at 250° C.
Vacuum-Evaporation of Aluminum:
Heating in a crucible.
Spraying Aluminum:
1. Plasma spraying, or
2. Gas-torch metal spraying
Titanium Deposition:
1. Vacuum evaporation, or

2. Vapor deposition from a cyclopentadienyl.
What is claimed is:
1. The process of making composite structures comprising a metallic matrix having reinforcing filaments embedded therein, including the steps of:
a. winding a reinforcement filament having a diameter generally within the range of about 5–200 microns onto a form in successive layers in which the adjacent filaments in each layer are spaced apart an average distance substantially equal to one-half of the filament diameter, and
b. either concurrently with the formation of each layer or in alternation therewith depositing the matrix metal in situ around the filaments in said layer in sufficient quantity that the filaments in adjacent layers are spaced apart at their closest points an average distance substantially equal to about one-half of the filament diameter, the total amount of matrix metal deposited being such that the ratio of the volume of filaments to the total volume of the composite structure does not exceed about 0.6/1.
2. The process of claim 1 wherein said filaments are conductive and the matrix metal is deposited by electroplating.
3. The process of claim 1 wherein said form is rotated to wind the filament thereon and the filament is maintained under tension during the winding.
4. The process of claim 1 wherein said filament has a diameter of at least about 1 mil.

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