

[54] **ZIRCONIUM DIFFUSION BARRIER IN
TITANIUM-SILICON CARBIDE
COMPOSITE MATERIALS**

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[58] Field of Search..... **29/195 A, 191.4, 191.2, 191, 29/194, 198**

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[57] **ABSTRACT**

A composite article, comprising silicon carbide-containing reinforcing filaments in a titanium or titanium alloy matrix, is found to have increased strength when the filaments are initially provided with a thin coating of zirconium. The zirconium acts as a barrier to interdiffusion of titanium and silicon carbide and prevents weakening of the composite structure which would otherwise result from such interdiffusion.

5 Claims, 5 Drawing Figures

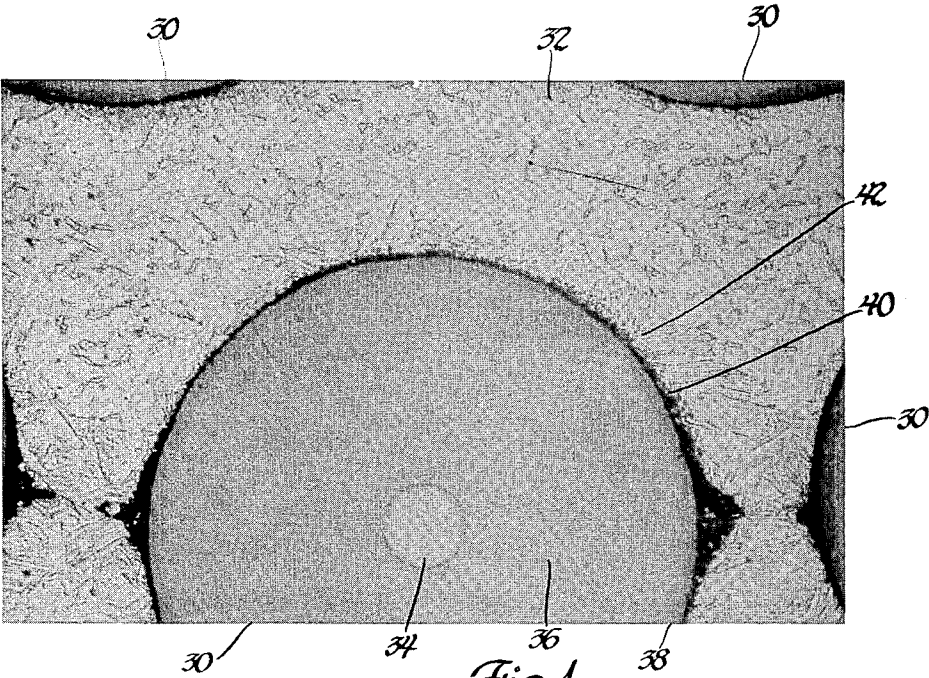


Fig.1

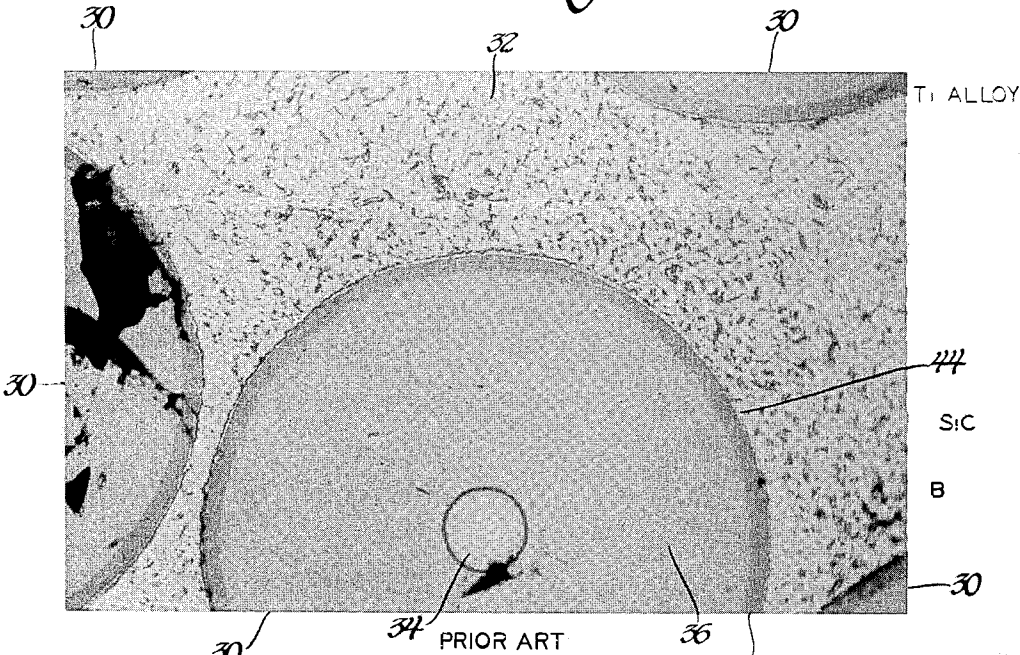
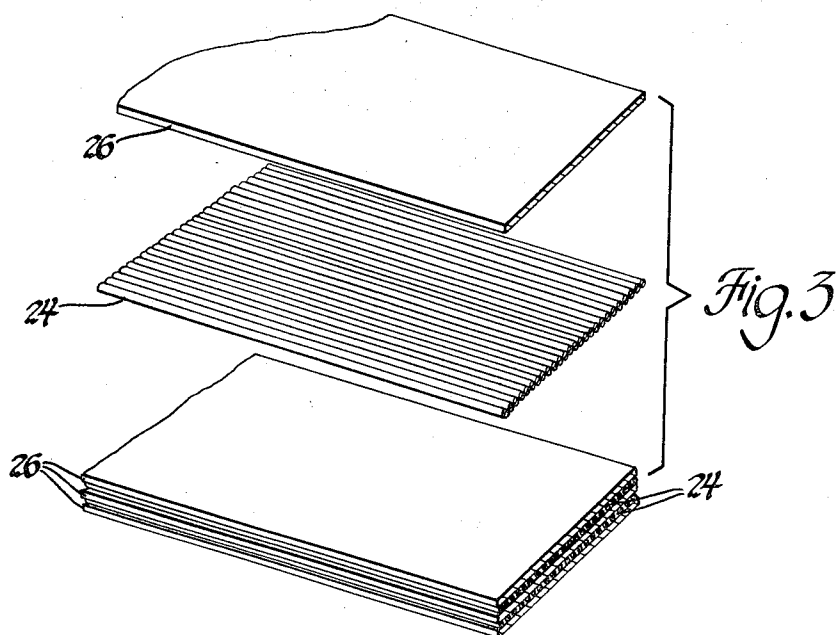
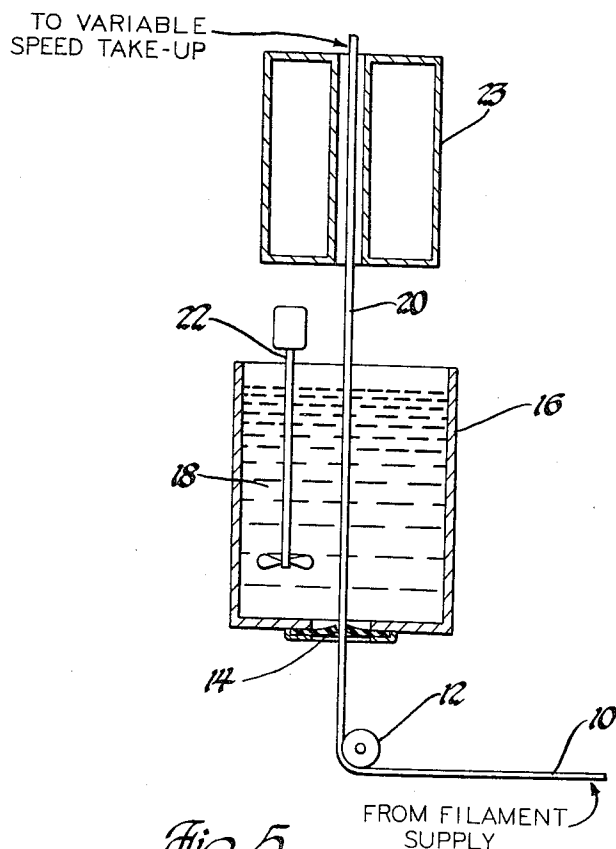
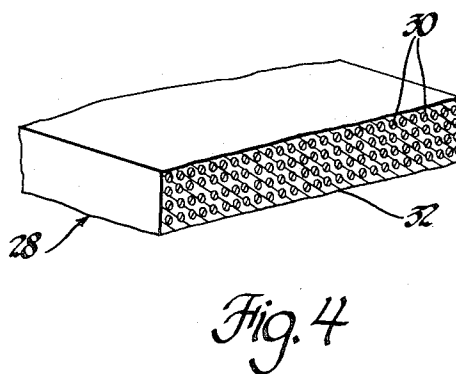


Fig.2

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ZIRCONIUM DIFFUSION BARRIER IN TITANIUM-SILICON CARBIDE COMPOSITE MATERIALS

The invention herein described and claimed was made in the course of work under contract or subcontract thereunder with the Department of Defense.

This invention relates to the relatively lightweight, high strength composite articles of the filament-reinforced titanium or titanium alloy type. More particularly, this invention relates to improvements in composite articles formed by hot pressing interposed layers of silicon carbide-containing filaments and titanium metal.

There are many applications in the aircraft and space technology and elsewhere for materials of relatively low density and high strength. For example, compressor blade and certain airfoil surfaces require these materials. In the search for such materials composite structures have been investigated. It is known, for example, that filament-reinforced titanium alloy composites may take advantage of the relatively low density of titanium and provide an increase in the otherwise relatively high strength of titanium and its alloys. There are commercially available reinforcing filaments for this purpose having high moduli of elasticity of the order of 60×10^6 psi or higher. Examples of such filaments are silicon carbide fibers having a tungsten core and silicon carbide coated boron filaments having a tungsten core (known as "Borsic" filaments). In practice high strength reinforcing filaments are initially prepared in the form of sheets of parallel, closely spaced fibers held in place by encapsulation in a suitable plastic or metal binder material. The sheets of filaments are cut into a desired two-dimensional configuration and then interposed between foils of titanium or other suitable metal likewise formed in a suitable pattern. The interposed layers of reinforcing filaments and metal sheets are pressed together at a suitable elevated temperature in a vacuum. The plastic encapsulating material, if present, is decomposed and/or vaporized and the metal is caused to flow around individual parallel filaments thereby forming a composite body wherein the filaments are completely surrounded by a metal matrix.

When composites of titanium or titanium-based alloys and silicon carbide-containing filaments have been formed, it has been found that the strength of the composite is considerably lower than expected. It is believed that the decrease in strength is due to the interdiffusion of the silicon carbide at the surface of the filaments and the titanium in the surrounding matrix. The interdiffusion is believed to result in a chemical species at the interface of the filament and the matrix that weakens the composite structure.

Accordingly, it is an object of the present invention to provide an improved, relatively lightweight, high strength silicon carbide-containing filament-reinforced titanium based article wherein the reinforcing filaments carry a relatively thin coating layer of zirconium which acts as a barrier to the interdiffusion of silicon carbide and titanium. Such a composite has a substantially higher tensile strength than similar composite articles containing no such barrier.

It is another object of the present invention to provide an improvement in the method of preparation of titanium-based composites reinforced with silicon carbide-containing filaments by hot pressing wherein the

filaments are initially provided with a thin coating of zirconium which resists inter-diffusion of the silicon carbide and titanium during subsequent hot pressing or during any other occasion when the composite is in a high temperature environment.

In accordance with a preferred embodiment of our invention these and other objects and advantages are obtained by initially providing a thin coating of zirconium on the surfaces of the silicon carbide filaments, silicon carbide-coated boron filaments or suitable silicon carbide-containing filaments which are selected for use in the manufacture of a particular titanium metal based composite. Preferably, the zirconium coating is formed by the electrophoretic deposition of zirconium powder onto a filament. In general, this is accomplished by passing a long filament through a suspension of fine zirconium particles in a suitable liquid electrolyte and applying an electrical potential between the filament and the container of the electrolyte. A thin, porous zirconium coating is thus deposited on the filament. The filament is then wound in a single layer on a rotating drum while maintaining a desired close spacing between the turns of the filament. Typically, the filaments are then embedded in a continuous film of plastic by spraying with a solution of polystyrene or in a film of titanium by plasma spraying. The filament sheet is removed from the drum and sectioned into filament mat layers of suitable configuration. Composite panels are produced by stacking filament mat layers alternately with titanium alloy foils to obtain a suitable unbonded assembly. The assembled structure is then consolidated by hot pressing into a high strength, filament-reinforced titanium article. The article is characterized by a titanium matrix reinforced by a large number of silicon carbide-containing filaments insulated from the matrix by a relatively thin layer of zirconium.

Other objects and advantages of our invention will become more apparent from a detailed description thereof which follows. Reference will be made to the drawings in which:

FIG. 1 is a photomicrograph at 1000X of sections of zirconium coated Borsic filaments in a titanium alloy matrix;

FIG. 2 is a photomicrograph at 1000X of sections of uncoated Borsic filaments in a titanium alloy matrix depicting prior art zirconium free composite structures;

FIG. 3 is a partially exploded, perspective view showing alternate layers of fiber sheets and titanium alloy foil from which the composite is ultimately formed;

FIG. 4 is a sectional view in perspective of a portion of a completed composite article showing the planes of Borsic fibers embedded in a titanium alloy matrix; and

FIG. 5 is a schematic view of the apparatus and process by which silicon carbide-containing filaments are electrophoretically coated with zirconium.

A detailed description of a specific example of the practice of our method in the formation of a filament-reinforced titanium composite will further assist in the understanding of our invention.

Borsic filaments are high strength materials comprising a tungsten core, a boron body portion and a silicon carbide coating on the generally cylindrical surface of the boron body portion. The filaments are formed by depositing pure boron onto a one-half mil diameter tungsten wire core until a composite filament having an

overall diameter of about 3 to 4 mils is obtained. Silicon carbide is then deposited on the boron surface until a coating of about 0.1 to 0.2 mil is obtained. The resulting filaments have an average tensile strength of about 370,000 psi and a modulus of elasticity of about 60×10^6 psi. These materials are commercially available and have been employed in the practice of our invention. It is to be understood that the invention is likewise applicable to filaments of substantially pure silicon carbide deposited on a tungsten wire core or other suitable high strength reinforcing filaments containing silicon carbide in the outer portion thereof.

Referring to FIG. 5, Borsic filament 10 from a spool thereof, not shown, was passed over a negatively charged roller 12 adapted to function as a cathode and upwardly through a suitable rubber diaphragm seal 14 in the bottom of a can-like container 16 containing a suspension 18 of zirconium particles. Container 16 was positively charged and functioned as an anode for the electrophoretic deposition. Stirrer 22 was employed to maintain a uniform suspension of the zirconium particles. The composition of the suspension used in the electrophoretic deposition was as follows:

Isopropyl alcohol	180 ml
Nitromethane	120 ml
Cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	0.03 g
Zein	0.6 g
Zirconium powder (1-5 μ)	5 g

Zein is a protein material derived from corn and was employed primarily as a binder to impart green strength to the initial zirconium deposit.

The electrical potential between the filament 10 and the anodic container 16 was 80 volts. The uncoated filament 10 was drawn up through the bath by means of a variable speed takeup spool, not shown, at a rate of eight feet per minute. These coating parameters and the suspension composition provided a porous coating of zirconium on the original filament 10 of a thickness of 0.1 to 0.2 mil. The deposition parameters are not deemed critical, and by increasing the voltage coatings could be applied at significantly higher rates. The coated filament 20 emerging from the bath was passed through a drying oven, schematically represented at 23, which was maintained at 250° F. After drying, the zirconium coatings were found to have excellent green strength and surprisingly good abrasion resistance. They were able to withstand the handling required for further composite fabrication without difficulty.

In accordance with what is now a known practice in the art, the filament was wound on a drum mandrel, not shown. The filament was fed such that the 4 mil diameter filament was wound on 5.4 mil centers to provide roughly a 1.4 mil spacing between the filaments. When the drum had been covered with a single layer of filament winding, further winding was stopped and the filament trimmed. The winding was embedded in a continuous film of plastic by spraying with polystyrene dissolved in toluene. The resulting fiber-polystyrene sheet was then removed from the drum and sectioned into rectangular filament mat layers 1 inch by 3 inches in cross-section. A section of a filament mat layer is depicted at 24 in FIG. 3. An alloy consisting essentially by weight of 3 percent aluminum, 2½ percent vanadium and the balance titanium was obtained in the form of a

foil approximately 2.8 mils in thickness. The foil was cut into rectangular sheets 26, FIG. 3, of the same size and shape as the filament mat layers 24. The foil 26 and fiber mats 24 were then interposed in alternate layers until nine foil layers and eight fiber mat layers had been accumulated, all one inch by three inches in cross-section. A number of like assemblies were prepared and were hot pressed in vacuum at temperatures of 1,400° F., 1,500° F. and 1,600° F. for periods of one-half hour and one hour, respectively, to form a number of tensile test specimens 1/32 inch to 1/16 inch in thickness. A portion of the composite material was removed from each of the long sides of the articles to form the familiar bow tie-shaped tensile specimens. In a like manner a number of filament mats were prepared as described above except that the Borsic filaments were not precoated with zirconium. These mats were also interposed between foils of the titanium base aluminum-vanadium alloy and vacuum hot pressed into tensile test specimens.

After the tensile test specimens had been vacuum hot pressed, representative samples of those articles having zirconium coated filaments and those having uncoated filaments were taken and sectioned. FIG. 4 is a macroscopic, schematic view of the section of a portion of a tensile specimen 28. It is seen that the reinforcing filaments 30, whether coated with zirconium or not, are aligned in planes, each filament being completely surrounded by the titanium alloy matrix 32. The planar arrangement of the filaments is, of course, a natural consequence of the laying up of the filament mats and the titanium foils.

Photomicrographs at 1,000 fold magnification were prepared from sections of the different hot pressed composites. FIG. 1 is a photomicrograph of a section of a reinforced titanium composite wherein a zirconium layer was applied to the Borsic filament prior to vacuum hot pressing at 1,500° F. for one hour at 12,000 psi. Portions of a number of Borsic filaments 30 are seen in the photograph, each completely surrounded by the titanium alloy matrix 32. The tungsten core is seen at 34, the surrounding boron body is seen at 36 and the silicon carbide layer on the boron body is seen at 38. The thin layer of zirconium is seen in FIG. 1 at 40. Some apparent interdiffusion of titanium and zirconium may be seen at 42, but there is no apparent chemical interaction between silicon carbide and the titanium alloy matrix.

FIG. 2 is a photomicrograph of a section of a titanium-Borsic composite in which no zirconium was applied to the Borsic filaments prior to vacuum hot pressing. Otherwise the composite was prepared the same as the composite whose section is depicted in FIG. 1. As in FIG. 1, the tungsten core is seen at 34, the boron body at 36 and the silicon carbide layer at 38. However, in FIG. 2 is also seen a titanium-silicon carbide reaction zone at 44. This reaction zone 44 lies between the silicon carbide 38 and the titanium alloy matrix 32.

The weakening effect upon the composite of the titanium-silicon carbide interaction material 44 may be seen by comparing the tensile strengths of specimens which are prepared in exactly the same manner with the exception of the zirconium coating. For example, three titanium-Borsic composite tensile specimens con-

taining no zirconium coating on the filaments were prepared by vacuum hot pressing interposed layers of filament mats and titanium alloy foils at 1,400° F. for one hour under 12,000 psi pressure. The filaments constituted about 45 percent by volume of the cross-section of the composite. The average ultimate tensile strength of these specimens was found to be 105,000 psi. Three like tensile specimens were prepared under identical hot pressing conditions except that the Borsic filaments each were coated with a zirconium layer about 0.1 to 0.2 mil in thickness. The average ultimate tensile strength of these three zirconium-containing titanium-Borsic composites was 169,000 psi. Therefore, composites differing only in the presence of a zirconium coating are seen to have an approximate 60 percent increase in ultimate tensile strength after hot pressing at 1,400° F. for one hour.

The following table summarizes the hot pressing conditions and the physical properties of other sets of titanium-Borsic composites and titanium-zirconium coated Borsic composites.

Results of Tensile Tests Conducted on Ti 3A1-2.5V — Borsic Composites Both With and Without Zirconium Coated Filament

Filament, v/o	Coating	Coating Thickness, mils	Hot Pressing Parameters		Ave. Ultimate Tensile Str. psi
			temp. °F	time hrs. ksi	
48	None	—	1,500	1.0 12	108,000
45	Zr	0.1-0.2	1,500	1.0 12	160,000
40	Zr	0.1-0.2	1,500	1.0 12	172,000
45	None	—	1,600	0.5 10	115,000
47	Zr	0.1-0.2	1,600	0.5 10	147,000
47	Zr	0.1-0.2	1,600	0.5 10	128,000

It is seen that under all conventional hot pressing conditions a substantial increase in the ultimate tensile strength of the composite is obtained when the silicon carbide-containing filaments are provided with a thin coating of zirconium before being contacted with a titanium alloy at elevated temperatures.

We prefer to apply the zirconium coating on silicon carbide-containing filaments by electrophoretic deposition as described above, because a coating of uniform thickness is obtained and little, if any, zirconium is wasted. However, we have successfully prepared titanium-silicon carbide composites wherein the filaments were shielded from the matrix with zirconium applied in different ways. For example, we have sand-

wiched each filament layer between two zirconium foils before placing the filament layers between titanium foils. We have also embedded the silicon carbide-containing filaments in zirconium powder by spraying the powder onto the filaments in a vehicle consisting of polystyrene dissolved in toluene. In this way the zirconium was applied to the silicon carbide-containing fibers at the same time that the polystyrene coating was applied in the preparation of the filament mat. Composites prepared by either of these techniques had higher strengths than any previously tested in which no zirconium was applied to the filaments before hot pressing.

While our invention has been described in terms of a few preferred embodiments thereof, it will be recognized that other forms could readily be adapted by those skilled in the art. Accordingly, the scope of our invention is intended to be limited only by the following claims.

What is claimed is:

1. A filament-reinforced titanium article comprising reinforcing filaments containing silicon carbide on at least the surface thereof in a titanium or titanium alloy matrix, said filaments having a coating layer of zirconium as a diffusion barrier between said silicon carbide and said titanium matrix.

2. A filament-reinforced composite article comprising many generally parallel silicon carbide-containing filaments in a titanium or titanium alloy matrix, and a diffusion barrier layer of zirconium between said filaments and said titanium matrix.

3. A filament-reinforced composite article comprising many generally parallel fibers distributed in a matrix of titanium alloy, said fibers comprising a boron body portion, a silicon carbide coating on said body and a coextensive coating of zirconium on said silicon carbide.

4. A filament-reinforced composite article comprising many aligned tungsten wire core, silicon carbide-coated boron filaments distributed in a matrix of titanium base alloy, and a thin coating layer of zirconium on said filaments of the order of 0.0001 to 0.0002 inch in thickness.

5. A filament-reinforced composite article comprising many generally parallel tungsten wire core, silicon carbide filaments distributed in a matrix of titanium base metal, and a thin coating layer of zirconium on said filaments of the order of 0.0001 to 0.0002 inch in thickness.

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