[11] 3,770,488
[45] Nov. 6, 1973

Pepper et al.

[54] **METAL IMPREGNATED GRAPHITE FIBERS AND METHOD OF MAKING SAME**

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[22] Filed: **Apr. 6, 1971**

[21] Appl. No.: **131,823**

[52] U.S. Cl. ..... **117/47 R**, 23/209.1 F, 57/153, 57/164, 117/71 R, 117/114 G, 117/114 R, 117/160, 117/213, 117/228, 117/DIG. 11

[51] **Int. Cl.** **B44d 1/20**

[58] **Field of Search** ..... 117/47 R, 114 R, 117/228, 213, 71 R, DIG. 11, 114 C, 160; 23/209.1 F; 57/153, 164

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[57] **ABSTRACT**

A technique for effecting the impregnation of graphite yarn with a metal matrix by a process which includes enhancing the wettability of the graphite yarn by initially immersing the yarn in a metal infiltrate composed of either a molten tin-titanium alloy, a molten copper-tin-titanium alloy of molten sodium. After removal from the molten infiltrate, the yarn is then immersed into a molten bath of a metal impregnate composed of either aluminum, aluminum-base alloys, magnesium, or magnesium-base alloys. The metal impregnant leaches out the metal infiltrate from the graphite yarn. This permits the metal impregnant to fill up the interstices of the yarn and coat the graphite filaments of the yarn.

10 Claims, No Drawings

METAL IMPREGNATED GRAPHITE FIBERS AND METHOD OF MAKING SAME

BACKGROUND OF THE INVENTION

This invention relates to a method for producing metal impregnated graphite fibers and to a graphite reinforced metal product produced therefrom. More specifically, this invention concerns itself with a method for producing a metal matrix-graphite fiber composite by impregnating a graphite yarn with either molten aluminum, molten magnesium, molten aluminum-base alloys or molten magnesium-base alloys.

Recent advances in the field of aerospace technology has created a need for structural materials capable of withstanding the severe conditions encountered within an elevated temperature operational environment. Rocket and missile components, such as turbine blades, nose cones, nozzles, vanes, partitions and other like elements, require high temperature construction materials characterized by high strength to density and modulus to density ratios. Graphitic carbon, especially in the form of fibers or filaments, displays many of the characteristics required by structural materials subjected to the stresses and strains of a high temperature environment. It has been found satisfactory from a mechanical stress standpoint and its low density makes it useful where weight is a consideration. Graphite possess a high melting point and its high structural strength at elevated temperatures permits its use in situations where other materials, such as metals, have proved unsatisfactory. It is a good conductor of electricity and is somewhat resistant to high temperature degradation and attack by chemical reagents.

However, at very high temperatures the use of graphits often involves certain drawbacks. For example, graphite errodes and corrodes under the impact of high gas pressures and temperatures. Also, some chemicals react with graphite or are absorbed in an undesirable manner which cannot be easily controlled. Additionally, although currently available graphite filaments exhibit considerable strength in tension, bundles of the filaments need a binder such as a metal matrix to form a material with good properties in compression, binding and shear, as well as tension.

With the present invention, however, there has been found a metal impregnated graphite fibrous material that exhibits a very high degree of strength and elasticity at elevated temperatures. The reinforced material is produced by a novel process that can accomplish the successful impregnation of commercially available graphite yarn with a metal matrix. The metal matrix is formed from either aluminum, magnesium or their base alloys. As is well known, these materials do not normally wet graphite. In this invention, however, the surfaces of the graphite filaments are treated in such a manner that the metal matrix in question readily wets the graphite and completely infiltrates the interstices of the graphite yarn bonding itself to the surfaces of the graphite filaments.

The impregnation by the metal does not cause any significant degradation of the mechanical properties of the graphite fibers. It does, however, provide a metal matrix-graphite fiber material that is characterized by a high strength and modulus to density ratio. These characteristics make the material especially useful as a structural material for high temperature applications. Further, aluminum, magnesium and their base alloys, as well as graphite, are cheap raw materials, the metal impregnated graphite yarn of this invention offers a low cost, high performance composite system, useful in modern aerospace operations.

SUMMARY OF THE INVENTION

In accordance with this invention, metal matrix-graphite yarn composites are fabricated by a method which involves impregnating commercially available graphite yarn with either aluminum, magnesium, aluminum-base alloys, or magnesium-base alloys. These materials do not readily wet graphite fibers and, as a consequence, previous attempts at fabricating metal reinforced graphite fiber composites have not proved successful. However, the wettability of graphite fibers is successfully achieved by the process of this invention by treating the surfaces of the graphite filaments in such a way that aluminum, magnesium or their base alloys wet the graphite fibers and completely impregnate the interstices of the graphite yarn. The process involves the steps of initially infiltrating a graphite yarn with a molten metallic material followed by the step of leaching out the metallic material from the graphite yarn with either molten aluminum, magnesium or their base alloys. The resultant product is a graphite yarn impregnated with a metal matrix of either aluminum, magnesium or one of their base alloys. The initial metallic infiltrate which has been found suitable for enhancing the wettability of the graphite filaments is a molten material selected from the group consisting of a tin-titanium alloys, a copper tin-titanium alloys and sodium.

In the first step of the process, the graphite yarn is immersed into a molten bath of the metallic infiltrate. The processing parameters for the initial infiltration step, such as the temperature of the molten infiltrate, the immersion atmosphere and the length of time the yarn is immersed in the infiltrate, can be varied to control the degree of wettability of the graphite fibers. After immersion in the metal infiltrate, the graphite yarn is removed from the molten infiltrate bath and then passed through a molten bath of the metal which is to be impregnated into the graphite yarn. The resultant product, because of its high strength to density and modulus to density ratio, makes an excellent raw material for the production of metal matrix-graphite yarn composites. These composites are made by melting or diffusion bonding together lengths of the impregnated yarn. The composites can be used as structural components for high temperature aerospace applications such as the fabrication of vanes, nose cones, nozzles, partitions, blades and similar elements.

Accordingly, the primary object of this invention is to overcome the problems encountered during previous attempts at fabricating metal reinforced graphite yarns.

Another object of this invention is to provide a metal impregnated graphite yarn capable of being fabricated into metal matrix-graphite fiber composites for use as structural materials in aerospace applications.

Still another object of this invention is to provide a method for impregnating graphite yarn with either aluminum metal, aluminum metal alloys, magnesium metal or magnesium metal alloys.

A further object of this invention is to provide a metal impregnated graphite yarn that is characterized by high strength to density and modulus to density ra-

tios and an ability to retain these desirable ratios at elevated temperatures.

The above and still other objects and advantages of the present invention will become more readily apparent upon consideration of the following detailed description thereof.

DESCRIPTION OF PREFERRED EMBODIMENTS

Pursuant to the above objects, the present invention contemplates the fabrication of a metal impregnated graphite yarn. Aluminum, magnesium or their base alloys have been found suitable for use as the metal impregnant. It is characterized by a combination of high strength to density and modulus to density to ratios, and is especially useful as a structural material for high temperature operations.

The impregnated yarn is prepared by a technique which involves the step of initially infiltrating commercially available graphite yarn with a molten infiltrate followed by the step of impregnating the infiltrated yarn with a metal impregnate. The infiltrate enhances the wettability of the graphite filaments in the yarn thereby permitting the impregnation of the yarn with the desired metal impregnant. Tin-titanium alloys, copper tin-titanium alloys, and sodium have been found suitable as the infiltrate.

In order to accomplish a successful impregnation of graphite yarn, the interstices of the yarn must be completely filled and impregnated with the desired metal matrix. Before infiltration of the yarn by the matrix can occur, the matrix must wet the graphite filaments. The condition of the wetting is defined as a state where the contact angle between a drop of the matrix and a flat graphite surface is less than 90°. Molten aluminum, magnesium and their base alloys do not readily wet graphite at temperatures up to approximately 800°C. and at temperatures in excess of 800°C rapidly react with graphite to form aluminum or magnesium carbide. This leads to degradation of the mechanical properties of the graphite yarn.

Prior to this invention, the successful impregnation of graphite yarn with molten aluminum, magnesium or their base alloys has not proved feasible. With this invention, however, the fabrication of a metal reinforced graphite yarn has been successfully accomplished by a method which comprises the steps of initially infiltrating a graphite yarn with a molten metal infiltrate followed by the step of leaching out the metal infiltrate from the graphite yarn with a molten metal impregnate. The resultant product comprises a graphite yarn impregnated with a desired metal matrix. Tin-titanium alloys, copper-tin-titanium alloys and sodium have been found to be uniquely suitable as the metal infiltrate for use in the first step of the process of this invention. These materials enhance the wettability of the graphite filaments thereby enabling the successful impregnation and bonding of the graphite filaments by the metal matrix.

The role of the chemically active element titanium in the wetting of graphite yarn by the tin and copper alloys referred to above is to react chemically with the surfaces of the graphite filaments lowering the interfacial tension between the metal alloys and the graphite filaments. This causes complete wetting and infiltration of the graphite yarn by the metal matrix. Microprobe analyses have shown the presence of a surface layer of titanium carbide on the graphite filaments in metal impreganted infiltrated graphite yarn specimens.

The parameters of the infiltration process, such as temperature and time, can be adjusted so that the coating of titanium carbide on the graphite filaments can be between one or two atom layers to approximately three microns in thickness. The yarn, which has been first infiltrated by immersion in a molten bath of the infiltrate materials, is then passed through a bath containing the desired metal matrix which leaches the infiltrates out of the yarn, leaving the yarn impregnated with the desired metal matrix. Complete wetting occurs between the titanium carbide coated graphite filaments and metal matrix.

The initial step of wetting the graphite yarn can also be accomplished by immersing the yarn in liquid sodium. In this embodiment, the first step is essentially one of removing the adsorbed moisture and oxygen from the graphite fiber surface and cleaning the fiber surface. The use of sodium as the infiltrate instead of the tin-alloy or the copper alloy results in substantially lower processing temperatures and further decreases the possibility of chemical or thermal damage occurring to the graphite fibers during processing.

In order to further illustrate the invention, the following examples are presented which show in detail various embodiments of the invention. The examples are presented for the purpose of illustration, however, and should not be considered as limiting the scope of the invention in anyway.

Example 1

A commercially available graphite yarn, Thornel 50 in this particular example, was immersed for about 10 minutes into a molten bath of metal alloy composed of 5 weight percent titanium with the balance tin. The molten alloy was maintained at a temperature of 900°C within an inert argon atmosphere. After expiration of the 10 minute period, the infiltrated yarn was removed from the alloy bath and then immersed again for 10 minutes into a molten bath of a metal alloy composed of 13 weight percent silicon with the balance aluminum. This bath was maintained at a temperature of 700°C in a vacuum atmosphere of 10^{-3}mm. The resultant product comprised a metal impregnated graphite yarn composed of 72 volume percent of the aluminum-silicon alloy and 28 volume percent of graphite fibers with a resultant tensile strength of 40 thousand psi and a modulus of 15 million psi.

Example 2

A Thornel 50 graphite yarn was infiltrated using the same procedure as disclosed in Example 1. The yarn was immersed for 15 minutes in an alloy infiltrate bath composed of 2 weight percent titanium, 5 weight percent tin with the balance copper. The infiltrate bath was maintained at 850°C in an atmosphere of helium. The infiltrate was then leached out of the graphite yarn by immersing the yarn for 10 minutes into a molten bath of aluminum maintained at a temperature of 670°C in an inert atmosphere. The resultant product contained 70 volume percent aluminum and 30 volume percent graphite fibers.

Example 3

A Thornel 50 graphite yarn was infiltrated in the same manner as example 1 by immersion for 15 min-

utes in a molten bath of liquid sodium maintained at a temperature of 560°C in an atmosphere of argon. After removal from the sodium, the yarn was then immersed for 10 minutes into a molten bath of an alloy composed of 13 weight percent silicon with the balance aluminum. The aluminum alloy bath was maintained at a temperature of 600°C within a vacuum of 10^{-3}mm. The resultant product contained 72 volume percent aluminum alloy and 28 volume percent graphite fibers with a final tensile strength of 106,000 psi and a specific modulus of 20 million psi.

Tin alloys ranging from about 0.25 to about 10 weight percent titanium with the balance tin and copper alloys ranging from about 0.25 to 10 weight percent titanium, 2 to 30 weight percent tin with the balance copper have been found useful as the infiltration material. Immersion temperatures and times for the infiltration step range from about 850° to 1,000°C and from about 10 to 20 minutes. Either argon or helium can be used for the inert atmosphere. In the case of the liquid sodium infiltrate, the processing parameters range from 500° to 700°C in temperature with immersion times of from about 10 to 20 minutes.

Silicon, as well as other elements which form stable carbides, such as beryllium, boron, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenium, tungsten, thorium, iron, manganese, rhenium, and cerium can be used to replace the titanium alloying element in the tin or copper alloy infiltrate.

TABLE I

Examples	Metal Matrix	Volume % of metal matrix	Time (min)	Temp.°C
4	Mg	60	10	670
5	Mg-10 pct Al	65	10	650
6	Al-13 pct Si	69	10	600
7	Al-13 pct Si	66	10	600
8	Al-13 pct Si	72	10	600
9	Al-10 pct Mg	60	10	630
10	Al-6 pct Ai-3.5 pct Cu	65	10	660
11	Al-33 pct Cu	60	10	580
12	Al-4.5 pct Cu-1.5 pct Mg-0.6 pct Mn	60	10	700
13	Al-5 pct Cu	65	10	650
14	Al-5 pct Si	65	10	650
15	Al-9 pct Si	60	10	650
16	Al-11 pct Si	60	10	600
17	Al-7 pct Mg	65	10	650
18	Al-7 pct Zn	65	10	650

The processing parameters for the metal impregnation step may vary from a temperature of about 500° to 850°C with immersion times of from about 10 to 20 minutes. Impregnated yarns composed of from 50 to 75 volume percent metal posses the desirable strength and modulus characteristic needed for high temperature applications.

Table II discloses additional test results on metal impregnated graphite yarns fabricated in accordance with this invention. Typical values of the room temperature tensile properties of the infiltrated yarn and some data from tests of as-received yarn. The results show that no significant degradation of the graphite fibers has occurred on infiltration with the aluminum-silicon alloy. The average uniaxial stress at fracture for the as-received yarn was 193,000 psi. Compare this with the values of 165 and 153,000 psi for the aluminum-silicon alloy infiltrated yarn. Calculations, based on the law of mixtures, taking the strength of the as-received fibers to be 193,000 psi and the strength of the aluminum-silicon matrix to be 20,000 psi, show the aluminum-silicon alloy infiltrated yarn to be between 80 and 90 of theoretical strength.

TABLE II

	tensile strength (psi)	volume percent fibers	Percentage of theoretical strength	uniaxial stress on fibers at fracture epsi)
Aluminum-silicon alloy infiltrated Thornel 50 graphite yarn of example 7	68,800	34	88	165,000
Aluminum-silicon alloy infiltrated Thornel 50 graphite yarn of example 6	61,400	31	83	153,000
As-received Thornel 50 yarn-epoxy matrix	41,400	16		205,000
As-received Thornel 50 yarn-epoxy matrix	39,500	16		193,000

Any of the commercially available graphite yarns may be employed with this invention. The Thornel graphite yarn used in the examples illustrating this invention is 0.015 inches diameter and consists of two plies with each ply constructed of approximately 700 graphite filaments. Each filament is about 7 microns diameter.

From a consideration of the foregoing it can be seen that the present invention provides a process for producing metal impregnated graphite yarns which can be easily fabricated into graphite composites. These materials are especially useful as structural elements for high temperature applications. The invention has been described with particularity with reference to specific embodiments, thereof, however, it is to be clearly understood that the disclosure of the invention is for the purpose of illustration only and is not intended to limit the invention in any way, the scope of which is defined by the appended claims.

What is claimed is:

1. A process for impregnating a graphite filament yarn with a metal impregnant comprising the steps of:

immersing said graphite yarn into a molten metal infiltrate selected from the group consisting of tin-titanium alloys, copper-tin-titanium alloys, and sodium for a period of from about 10 to 20 minutes at a temperature of from about 500° to 1,000°C to enhance the wettability of the graphite filaments of said yarn,

removing said yarn from said molten infiltrate,

immersing said infiltrated yarn into a molten bath of a metal impregnant selected from the group consisting of aluminum, aluminum-base alloys, magnesium and magnesium-base alloys for a period of time sufficient to leach out the molten infiltrate from said yarn and coat the surfaces of said filaments and fill the interstices of said yarn with the metal impregnant.

2. A process in accordance with claim **1** wherein said tin alloy is composed of from about 0.25 to about 10 weight percent titanium with the balance substantially all tin.

3. A process in accordance with claim **2** wherein said tin alloy is composed of about 5 weight percent titanium with the balance substantially all tin.

4. A process in accordance with claim 1 wherein said copper alloy is composed from about 0.25 to about 10 weight percent titanium, about 2 to about 30 weight percent tin with the balance substantially all copper.

5. A process in accordance with claim 4 wherein said copper alloy is composed of about 5 weight percent tin, about 2 weight percent titanium and the balance substantially all copper.

6. A process in accordance with claim 1 wherein said infiltrate is liquid sodium.

7. A process in accordance with claim 1 wherein said graphite yarn is immersed into said molten metal infiltrate within an inert atmosphere.

8. A process in accordance with claim 2 wherein said graphite yarn is immersed in said metal infiltrate at a temperature of from about 850° to about 1,000°C within an inert atmosphere.

9. A process in accordance with claim 4 wherein said graphite yarn is immersed in said metal infiltrate at a temperature of from about 850° to about 1,000°C within an inert atmosphere.

10. A process in accordance with claim 6 wherein said graphite yarn is immersed in said metal infiltrate at a temperature of from about 500° to about 700°C within an inert atmosphere.

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