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3,495,940

PRODUCTION OF HIGH TEMPERATURE RESISTANT CONTINUOUS FILAMENTS

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U.S. Cl. 23—209.3 13 Claims

ABSTRACT OF THE DISCLOSURE

The continuous production of continuous filament high temperature resistant carbonaceous fibers by means of forming a thin film of a sensitizing metal on an organic fibrous precursor, electrolessly plating a thin layer of copper on the sensitized surface, and electrodepositing additional copper on top of this thin copper layer. Thereafter an electric current is passed across the plated fiber to pyrolyze the organic fibrous precursor.

The search for industrial high performance materials is turning increasingly toward reinforced composites. Theoretically, highly carbonaceous fibers such as carbon (amorphous) and graphite fibers have among the best properties for high strength reinforcement. Among these desirable properties are high corrosion and temperature resistance, low density, high tensile strength and high modulus. Graphite is one of the very few known materials whose tensile strength increases with temperature. Uses for such high temperature resistant fibers include filament windings for aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles.

Two major factors retarding the large-scale use of these high temperature resistant carbonaceous fibers are (1) their high cost of production and (2) their general unavailability in the form of continuous filaments. Continuous filaments are necessary for winding composites in a practical, large scale manner.

Production of fibrous carbon by pyrolysis of hydrocarbon gases or by discharge between carbon electrodes has been reported. These methods, however, are obviously not suitable for the production of a uniform continuous filament. Carbonization of organic fibrous precursors appears to be the only practical industrial route to such carbonaceous fibers.

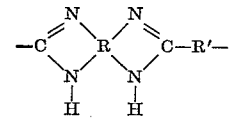
The prior art methods for such pyrolyses generally involve long processing periods, high power requirements, and expensive and bulky heating apparatus such as closed furnaces. The processing and equipment costs tend to dwarf the fiber raw material cost. Conventional pyrolysis processes are slow ranging in the order of 15 to 100 hours (see, for example, French Patent No. 1,430,803 and Belgian Patent No. 678,679). In general, known processes for producing carbonaceous fibers require long preoxidative stabilizing treatments before the fiber can be safely pyrolyzed. These treatments often involve many hours (e.g. 16 hours) and elevated temperatures (e.g. 300° C.).

It is an object of this invention to prepare uniform, high temperature resistant, continuous filament carbonaceous fibers from a fibrous precursor. It is a specific object that a lengthy high temperature preoxidation step be avoided. It is a further object that the pyrolysis be rapid and continuous.

These objects have now been realized by the process of this invention which broadly comprises forming a thin film of a sensitizing metal on the surface of the precursor fiber and then passing this sensitized fiber through certain copper solutions to autocatalytically and electrolessly plate a thin layer of copper on this sensitized surface. Thereafter additional copper is electrodeposited on top of this electroless plating. An electric current is then passed across the plated fiber to effect temperatures of about 1000° C. If amorphous carbon fiber is desired, the plating is then removed. If graphitic fiber is desired, the electric heating can be continued to effect temperatures over 2000° C. and the metal plating will evaporate. One can also treat the carbon fiber produced by the method of this invention in other known ways to produce graphite fibers.

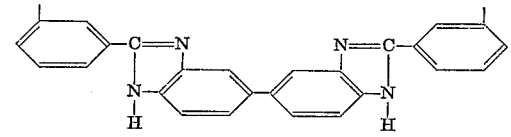
A wide variety of fibrous precursors can be employed in the process of this invention. Such suitable fibers include acrylics, polybenzimidazoles, nylons, and carbon fibers. A wide variety of acrylic fibers are known to the art, i.e. fibers formed from at least 85% by weight acrylonitrile and up to 15% of monomers copolymerizable therewith. Preferred fibers of this class in the process of this invention are acrylonitrile homopolymers and that formed from 93–94% by weight acrylonitrile and 6–7% by weight methyl acrylate.

A preferred subclass of polybenzimidazole precursors for use in this invention consists of recurring units of the formula:



wherein R is an aromatic nucleus having each of the two depicted pairs of nitrogen atoms substituted upon adjacent carbon atoms of the said aromatic nucleus and R' is a carbocyclic ring.

The most important and preferred polybenzimidazole is poly-2,2'-m-phenylene-5,5'-bibenzimidazole which consists of recurring units of the formula:



This species, commonly referred to as simply PBI, can be prepared as described, for example, in Example II of Patent No. 3,174,947.

In a preferred embodiment, the plating is carried out by continuously passing the precursor fiber through a stannous chloride solution and then through a solution containing a salt of a noble metal to form a thin film of the noble metal thereon. Thereafter the sensitized fiber is passed through a basic aqueous formaldehyde solution containing chelated cupric ions to form a thin copper coating. This copper-coated fiber is then electroplated by placing a voltage drop across the fiber and passing the fiber through a suitable copper solution to produce a fine grained plating of sufficient conductivity for further processing.

Wetting of the fiber can be facilitated in the stannous chloride or stannous sulfate solution by the addition of a small amount of detergent. The preferred noble metal salt is a water-soluble silver salt such as silver nitrate. Salts of gold, platinum, rhodium and palladium can also be employed. The basic formaldehyde solution should have a pH in the range of 10 to 14. Suitable basic reagents are metallic and quaternary ammonium hydroxides such as sodium, potassium, calcium and tetramethylammonium hydroxide and the like. Suitable copper chelating agents include tartrates, salicylates, ethylenaminoacetic acids, alkanol aminoacetic acids and alkanolamines. Many such chelating agents are described in greater detail in U.S. Patents Nos. 2,874,072; 2,996,408 and 3,075,855.

Only a very thin film of noble metal salt is necessary because as soon as it is replaced in the formaldehyde solution by a thin film of copper, the process becomes autocatalytic. That is, as long as the thin copper-coated fiber is in contact with the solution, additional copper will plate out until the copper ion is exhausted from the solution.

The copper sheaths resulting from this electroless deposition cannot be directly employed as an electrically conductive medium. They tend to flake and upon pyrolysis form hot spots and burn off. Furthermore, a residence time on the order of one hour would be required to produce a plating having sufficient conductivity to effect a temperature of even 900° C.

I have discovered that if copper is electrodeposited in the conventional manner on top of the electroless plating, fine grained platings can be produced in about two minutes which exhibit sufficient conductivity to reach the necessary pyrolysis temperatures. These fine grained platings do not have a tendency to flake and to produce hot spots. The copper sheath cannot however be successfully electroplated directly on the fibrous precursor and thus the preliminary electroless plating is critical.

The electrodeposition can be conveniently carried out by passing the electrolessly plated fiber over a graphite roll into a solution containing soluble cupric salts such as copper sulfate. A copper bar is immersed in the bath and a voltage drop is maintained between the graphite roll and the bar. The residence time in the bath should be on the order of 2 minutes. The amount of copper electrodeposited should be sufficient to conduct enough current to effect a temperature of at least 900° C. and preferably 1000° C. This generally requires an amount of copper of between 10 to 50%, and preferably 30 to 50%, by weight, of the weight of the organic fibrous precursor.

The plated yarn is then pyrolyzed by placing a voltage drop across it. By adjusting this voltage drop, any desirable temperature profile may be obtained. In a convenient embodiment the plated yarn is passed between two graphite rolls which in addition to guiding and transporting the yarn, form the two rotating terminals for the input of electrical power. As a variation of this embodiment, the heating of the yarn may be conducted in "N" stages between "$N+1$" rolls. By adjusting the voltage inputs between neighboring rolls, any desired temperature profile along the fiber may be attained.

If amorphous carbon fibers are desired, the voltage is regulated to effect a temperature of about 1000° C. and then the copper plating is removed. This removal can be effected simply by washing in a bath of nitric acid from which the copper can later be recovered. If graphite fibers are desired, the plating yarn is simply heated up in the same manner to within the range of 2000 to 3000° C. The copper plating will evaporate and can be suitably condensed on a cold surface, dissolved in acid and reused. The plateless carbon yarn is itself capable of conducting current and thus can be directly heated to form graphite yarn. It is preferable, however, not to remove the metal sheath since the metal sheath provides reinforcing action upon the still weak carbonaceous substrate. On subsequent heating to higher temperatures, the carbonaceous substrate is converted to fibrous graphite of considerably increased strength.

Due to the oxygen sensitive nature of carbon at temperatures above 600° C., the pyrolysis reaction is carried in inert environment, preferably nitrogen.

The following example illustrates a preferred embodiment of the process of my invention.

EXAMPLE

PBI yarn having the properties indicated below is pressed through a bath containing 10 grams of stannous chloride dihydride per liter, 20 mls. of concentrated hydrochloric acid per liter, and 1 ml. per liter of Aquet (non-ionic detergent-Monostat Corporation) in deionized water. The residence time is one minute. The yarn is then passed through a second bath containing 10 grams of silver nitrate per liter for a residence time of 1 minute and a thin film of silver forms. This yarn is then passed through a third bath containing 25 grams of copper sulfate pentahydrate per liter, 25 grams of triethanolamine per liter, 25 grams of formaldehyde (37%) per liter and 25 grams of sodium hydroxide. The bath has a pH of 12. The residence time in this bath is 3 minutes. The copper plated yarn is then passed over a graphite roll and through a fourth bath containing a copper bar, 100 grams of copper sulfate pentahydrate per liter, 30 grams of sulfuric acid per liter and 10 grams of phenol per liter. 1.5 volt D.C. potential is maintained across the graphite roll and the copper bar. After a residence time in this bath of 2 minutes, a fine grained copper-plated yarn is achieved.

The plated yarn is passed over two motor driven graphite rolls separated from each other by about 4 inches. The electrical power is supplied from a 110 volt/15 amp alternating current source and carried to the rolls via spring loaded graphite brushes. The voltage, and consequently the temperature, is regulated with a Variac located between the source and brushes. The voltage is adjusted to achieve a temperature of 1000° C. A yarn sample "A" is removed at this point and the plating is removed by washing in concentrated nitric acid. The remainder of the plated yarn (Sample "B") is heated by means of the same graphite roll system to 2800° C. The plating evaporates and need not be chemically removed. The properties of the yarns are as follows:

Yarn	Density (g./cm.^{3})	Tenacity (g./d.)	Initial Modulus (g./d.)
Unplated starting material	1.30	4.0	146
Sample "A" (heated to 1,000° C.)	1.38	1.2-3	85
Sample "B" (heated to 2,800° C.)	1.58	3.2-5	330-500

As a variant of the process described hereinabove, hollow metal fibers may be produced. For this purpose, the organic precursor fiber should be one that completely depolymerizes on heating, for example, poly (methyl methacrylate) and polyacetals. The metal sheath is produced and heated in the manner described above to produce hollow metal fibers which are of textile grade denier. Light weight metal suits, useful in space applications for example, can be fabricated from this fiber.

Numerous other variations of the above-described process will be apparent to one skilled in the art within the spirit of the present invention.

What is claimed is:

1. A process for the production of high temperature resistant carbonaceous yarns comprising the steps of (1) forming thin films of sensitizing and activating metals on the surface of an organic fiber, (2) electrolessly plating a thin layer of copper on the activated surface, (3) electrodepositing additional copper on top of said copper layer and (4) passing an electric current across said plated fiber to effect temperatures of at least 900° C.

2. A process according to claim 1 wherein said copper layer is of sufficient thickness and said electric current is of sufficient amperage to effect a temperature of at least 2000° C.

3. A process according to claim 1 wherein the amount of said additional copper electrodeposited is equivalent to between 10 to 50% by weight of the weight of said organic fiber.

4. A process according to claim 1 wherein the activating metal is a noble metal.

5. A process according to claim 2 wherein said activating metal is silver.

6. A process according to claim 1 wherein said organic fiber is a polybenzimidazole.

7. A process according to claim 1 wherein said fiber is an acrylic polymer.

8. A process according to claim 1 wherein a temperature of about 1000° C. is effected and then the electric current is terminated and the plated fiber is dissolved in acid to remove the metal plating.

9. A process according to claim 1 wherein said electroless plating is effected by passage through a solution of chelated copper.

10. A process according to claim 9 wherein said solution contains formaldehyde.

11. A process according to claim 10 wherein the pH of said solution is from about 10 to 14.

12. A process according to claim 11 wherein said organic fiber is initially passed through a solution of stannous chloride.

13. A process according to claim 11 wherein the amount of said additional copper electrodeposited is equivalent to between 30 to 50% by weight of the said organic fiber.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,495,940 Dated 3/5/70

Inventor(s) Dagobert E. Stuetz

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

In Column 3, line 72 delete "pressed" insert --- passed ---.

Signed and sealed this 14th day of July 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents