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Joo et al.

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[54] **PROCESS FOR VAPOR DEPOSITION ON GLASSY-CARBON SUBSTRATE**

[75] Inventors: **Louis A. Joo,** Johnson City; **Thomas W. Martin; John A. McKee,** both of Elizabethton, all of Tenn.

[73] Assignee: **Great Lakes Carbon Corporation,** New York, N.Y.

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[51] **Int. Cl.**..... **C23c 13/04**

[58] **Field of Search**..... 117/106 R, 106 A, 106 C; 423/447; 264/29

[56] **References Cited**

UNITED STATES PATENTS

3,519,472	7/1970	Dyne et al.	117/106 C
3,553,003	1/1971	Carlton et al.	117/106 C
2,131,021	9/1938	Bernis	264/29

Primary Examiner—William D. Martin
Assistant Examiner—Janyce A. Bell
Attorney, Agent, or Firm—D. R. Cassady

[57] **ABSTRACT**

Glassy-carbon monofilament containing additional sulfur in combined form, has "high-temperature creep" properties useful in the deposition of boron, boron carbide, silicon carbide, and pyrolytic graphite thereupon.

2 Claims, No Drawings

PROCESS FOR VAPOR DEPOSITION ON GLASSY-CARBON SUBSTRATE

BACKGROUND OF THE INVENTION

Substitutes for steel and aluminum alloys in the construction industry have been sought for many years. With the recent advent of the aeronautic and space exploration programs, this search has narrowed itself to be concerned with light-weight materials with high specific strength and specific stiffness. Composites of boron filament-reinforced plastic have fulfilled this need.

Monofilmanets of boron have been manufactured by the vapor deposition of boron, formed from the high temperature reaction of boron trichloride and hydrogen, onto a tungsten filament base. The deposition is fraught with many problems of operability and acceptability of the final product. Of particular note are the irregularities of the surface of the boron-on-tungsten filament and the structural effect on the final product of breaks in the tungsten boride base.

The first of these defects is caused by the irregular build-up of boron on the striated surface of drawn tungsten wire. The second is caused by processing irregularities and the brittleness of the base material. The effect of substrate breaks is noted particularly in that the substrate breaks cause extreme variations in the strength of the filament since the structural properties of the final product are the additive properties of separate elements.

Apart from the above-mentioned deficiencies is the high cost of tungsten filament.

More recently, a carbon monofilament has been successfully used as a substrate for boron deposition. Carbon monofilament successfully overcomes many of the difficulties encountered with tungsten. It is considerably less costly; an extemely smooth surfaced filament can be extruded; and since the structural properties of the substrate do not materially add to those of the boron, breaks in the substrate are better tolerated.

When boron is vapor deposited onto tungsten, the first phenomenon is the formation of tungsten boride as the substrate. This reaction is important to the deposition since during deposition the boron elongates linearly as well as in cross-section. This linear expansion is accomodated by the increase bulk of the tungsten boride over tungsten.

When boron is deposited over carbon, no boride is formed; the carbon itself must expand to accomodate to the size of the boron particles. Presently this limits the thickness of the boron that can be deposited on a carbon filament. This property of carbon to expand during deposition at high deposition temperatures is denominated "high temperature creep."

The resistance of the carbon monofilament itself is generally used to provide the heat of reaction and deposition of boron. High resistance and high temperatures increase the rate of deposition of boron. As the boron deposits, the resistance of the filament decreases lowering the temperature and the rate of deposit. If, during deposition, the expansion of the boron deposit exceeds the limit of elasticity of the carbon, the carbon breaks. The break in the carbon causes spot heating due to increased resistance at the break and a bump to occur in the boron due to rapid deposition at that point. This irregularity in the boron structure may even cause a break to occur in the filament while the filament is in the reactor.

Similarities exist in the process of vacuum deposition of certain other elements and compounds on carbon monofilament. Of particular relevance to this invention, and included within its process embodiment, are the deposition of boron carbide, silicon carbide and pyrolytic graphite. Silicon carbide is deposited by the vapor deposition of decomposition products of organosilicon compounds; pyrolytic graphite by the deposition of natural gases or related hydrocarbons; and boron carbide by the addition of natural gases or related hydrocarbons to the previously exemplified boron vapor deposition reactants.

SUMMARY OF THE INVENTION

This invention relates to glassy-carbon fibers possessing unusual and unexpected properties and to their use in the manufacture of inorganic refractory fibers by the vapor-deposition method.

The fibers of this invention are manufactured by the spinning, oxidation, and carbonization of a sulfur-doped carbonaceous pitch from petroleum or coal tar origin. In preparing the fibers, the pitch is (1) purified and the melting range modified if necessary to prepare a spinnable pitch; (2) an effective amount of sulfur is added which will, however, not cause an increase in the melting point of the pitch to above 300°C. or cause formation of second-phase insoluble material when the sulfur is caused to react with the pitch; (3) the sulfur is reacted with the pitch at about the melting point of the pitch until all apparent reaction has ceased and there is substantially no unreacted sulfur in the pitch material; (4) the sulfur-doped pitch is spun, oxidized, and carbonized in a manner exemplified below and well-known to those skilled in the art.

The glassy-carbon fibers of this invention possess more high temperature creep than conventionally produced glassy-carbon fibers when heated to a temperature from about 1,100° to about 1,600°C. For this reason, the fibers are superior to prior art glassy-carbon fiber substrate for the deposition of boron, boron carbide, silicon carbide, and pyrolytic graphite and the like refractory materials thereupon by vapor deposition techniques.

DETAILED DESCRIPTION OF THE INVENTION

Filaments, yarns, rovings, and tows, generally called "fibers" of carbonaceous material have been well-known as substrate for deposition of metals, metalloids, and the carbides thereof. In a typical deposition reaction, the fiber is heated, as for example by resistant heating, induction heating, high frequency heating, or the like in an atmosphere containing the appropriate elements or compounds of the elements to be deposited upon the fiber. The available heat from the fiber serves to cause the reaction necessary to form the desired deposit and to cause deposition to occur.

We have found that when the carbonaceous precursor used in the above deposition reaction has been prepared from a precursor material containing added sulfur, the resulting fiber upon deposition at above 1,300°C. will be substantially free from stress and substrate breaks due to the demand upon the substrate to elongate beyond its elastic limit during the deposition process.

The addition of sulfur to rubber, asphalt, petroleum and coal tars, and the like, to permit stabilization by the cross-linking of the existant chain link molecules of carbonaceous material is well known. Eggloff, in U.S. Pat. No. 1,896,277, disclosed and claimed a cracked hydrocarbon product comprising from 5 to 10 parts of sulfur. The product was useful as thermosetting plastic similar to "Bakelite." Gamson, in U.S. Pat. No. 2,447,004, disclosed and claimed a new composition of matter consisting of a liquifiable hydrocarbon and from about 6 to about 25 percent sulfur in combined form or from about 25 to about 50 percent total combined sulfur content. Gamson's product was a solid, dense, hard, infusible, amorphous substance.

The fibers of this invention can be manufactured by the method of Otani, (Otani and co-workers, U.S. Pat. No. 3,392,216; *Carbon*, Vol. 3, pp. 31–38; *Carbon*, Vol. 4, pp. 425–432) or by the procedure of Joò et al., Ser. No. 734,257, filed June 4, 1968, and incorporated herewithin by reference. According to Otani, a pitch material is heat treated to raise the melting point to a spinnable temperature, melt spun, oxidized in air or ozone to achieve stabilization, then carbonized at up to 1,000°C.

By the Joò et al method, coal tar pitch is (1) filtered, (2) heated within the range of 280°–305°C. for 10–100 hours while volatile materials are being removed therefrom, (3) spun at a temperature from above the melting point to about 300°C., (4) oxidized by contacting with air at about 100°C. to about 10°C. below the softening point, (5) heated within the range of 100°–500°C. at a rate equal to or slower than 5°C./hour in a nitrogen atmosphere, and (6) heated within the range 500°–1,100°C. at a rate equal to or slower than 10°C./hour in a nitrogen atmosphere.

In a preferred embodiment, steps (1) and (2) above are replaced with a two-step extraction process wherein the pitch is extracted by contacting the raw pitch starting material with a suitable solvent, as for example benzene, to remove the low-boiling components therefrom; the residue is then extracted by dissolution into a second suitable solvent, as for example quinoline, separating therefrom the insoluble, undesirable second-phase coke-like material contained therein by filtration, centrifugation, or like means; and evaporation of the added solvents from the spinnable pitch.

In any of the above embodiments, prior to the spinning step, (3), an effective amount of sulfur is added to the pitch and caused to react therewith. The amount of sulfur should be such that the melting point of the pitch is not raised to above 300°C. nor is any significant amount of second-phase insoluble material formed during the sulfur-pitch reaction. Sulfur is preferably added in a mutually pitch-solubilizing and sulfur-solubilizing solvent, as for example quinoline or the like.

In a preferred embodiment, from about 3 to about 7 weight percent of sulfur is added to the pitch and dissolved therein.

The sulfur-pitch mixture is heated to above the melting point of the pitch and allowed to react thereat until the reaction proceeds to completion, as evidenced by the cessation of ebullition, and until the sulfur content of the pitch has attained a uniform level, being now in combined form. The resultant pitch is spun, oxidized, and carbonized as described above.

After carbonization the resulting carbon fiber is suitable for use as substrate in the above defined vapor deposition reactions. For example, boron filament is prepared by passing a mixture of hydrogen and boron trichloride over the carbon fiber heated by internal electrical resistance to a temperature of about 1,500°C. in a closed deposition chamber. The mixture of hydrogen and boron trichloride can be prepared conventionally by mixing streams of hydrogen and boron trichloride gases to produce the desired concentration of boron trichloride in hydrogen (2:3 v/v) inside the chamber. The mixture thus obtained and the heated carbon fiber are concurrently passed through the deposition chamber at a rate effective to maintain a high rate of deposition of boron consistent with maintaining substantial uniformity of conditions of the boron on the substrate.

What is claimed is:

1. In a process for the manufacture of boron, boron carbide, silicon carbide, and pyrolitic graphite fibers by vapor deposition on a glassy-carbon substrate wherein the fiber used as substrate material has been manufactured from a pitch precursor in which the pitch is melt-spun, oxidized, and carbonized, the improvement which comprises improving the high temperature creep properties of said fiber by adding an effective amount of sulfur to the pitch and causing the sulfur to react with the pitch until substantially no unreacted sulfur remains in the pitch.

2. A method of claim **1** in which from about 3 to about 7 weight percent of sulfur is added to the pitch.

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