United States Patent Office 3,379,555 Patented Apr. 23, 1968

3,379,555

VAPOR DEPOSITION OF PYROLYTIC GRAPHITE ON TUNGSTEN

Ralph L. Hough, Springfield, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force

No Drawing. Filed May 1, 1964, Ser. No. 364,338
1 Claim. (Cl. 117—46)

ABSTRACT OF THE DISCLOSURE

Synthesis of pyrolytic graphite on heated substrate within a chamber of temperature range 1200–3500° C. and containing hydrocarbon gas such as methane series, halides, methylamine, triethylamine, etc., on a tungsten wire of .0002 to .001 inch diameter for increasing the wire tensile strength 50 to 100% to the order of 66,400 pounds per square inch.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without the payment to me of any royalty thereon.

This invention relates to the synthesis of pyrolytic graphite and particularly to the vapor deposition thereof upon heated substrates with and without combining chemically with the substrate. The invention also relates to the formation of pyrolytic graphite fibers of materially improved tensile strength, by process and by product.

For many years prior to this invention, the art has enjoyed the capability of synthesizing reasonably pure carbon in the form of graphite by many so-called carbonizing processes involving heat, such as coking, charring and other thermal decomposition. In all of these methods, however, the yield of the carbon has been disappointingly low and the cost alarmingly high, all with the not surprising effect of seriously limiting the commercial applications to which such methods could be put.

More recently it was learned that higher yields of carbon material in graphite form could be obtained by the pyrolytic deposition of carbon upon a heated substrate within a chamber filled with a vapor laden with carbon atoms such, for example, as would be provided by a hydrocarbon gas. While such pyrolytic vapor deposition is being more and more widely adopted for a variety of experimental and commercial applications, the benefits of improved carbon production efficiency are in most, if not all, cases substantially negated by an attendant loss in the structural continuity of the final carbonaceous product.

The presence of defect structures in the pyrolytically deposited graphite has been particularly damaging in the case of fibers or filaments composed wholly or in part of such material. In these instances, the defects not only interrupt the continuity of the carbon and become points of weakness in the strand but also result in surface irregularities and erratic configurations which deleteriously affect the strength and the ease of handling such materials. These particular disadvantages are becoming more and more critical in view of the fact that the art is daily increasing its demands for fibers and filaments of carbonaceous materials, and especially for continuous strands in the form of graphite-coated finely drawn metallic substrates of great length.

Although the pyrolytic deposition of carbon is a relatively new art, considerable attention has been given of late to research and the development of improved processes particularly those contemplating the use of a vapor deposition chamber laden with a gas of the carbon atoms to be deposited. While various and sundry incidental improvements have resulted from such efforts to date, structural discontinuities, surface irregularities, and the inability to achieve fibers or strands of reasonably high tensile strength have continued to be serious problems.

It is accordingly an object of the present invention to provide an improved method for the synthesis of pyrolytic graphite in the amount of 94% by volume on a tungsten wire that, by diffusion is converted to tungsten carbide in the amount of 6% by volume.

Another object of the invention is to provide a method for the vapor deposition of pyrolytic graphite upon heated substrates.

Still a further object of the present invention is to provide pyrolytic graphite in filamentary form of a tungsten graphite structure having a tensile strength that is from 50 to 100% higher than when made with precursor gases not disclosed herein.

Yet another object of the invention is to provide a method for the vapor deposition of pyrolytic graphite upon heated filamentary substrates to form graphite strands.

Still another object of the invention is to provide such a method wherein the resulting strand will be characterized by the smoothness, general uniformity and freedom from structural discontinuities of the graphite material thereof.

Yet another object of the invention is to provide such a method wherein the resulting strand will be characterized by ultimate tensile strengths substantially higher than those heretofore achievable in such filamentary materials and usable as such.

The nature of and the manner in which these and other objects and advantages will be achieved will appear from the following disclosure.

Nothwithstanding the fact that all previous research has indicated that the source of the carbon atoms in pyrolytic processes has little effect upon the deposition system and the resulting products, this invention achieves the foregoing objects and provides the substantial improvements over the prior art by teaching the employment of specific source gases not heretofore indicated in the vapor deposition process. The particular source gases capable of providing these striking improvements have been found to be of the class of materials which consists of the bromides, iodides, and amines of the methane series or parafinic hydrocarbon gases and especially those having four or less carbon atoms in the molecule; i.e., methane, ethane, propane and butane. Illustrative source gases are methylamine, methyl bromide, methyl iodide, methylene bromide, methylene iodide, ethyl bromide, ethyl iodide, triethylamine, carbon tetrabromide, carbon tetraiodide, bromoform, iodoform, nitroform, and corresponding compounds in the ethyl, propyl and butyl groups.

One or more of the source gases of this class are placed within a suitable chamber such as the interior of an elongated hollow tubular body in which is positioned or through which may pass a heated substrate or baffle upon which the graphite will become deposited or "plate out." Where strand or filament formation is desired, a finely drawn metallic filamentary substrate such as a tungsten wire with a diameter on the order of from .0002 to .001 inch may be positioned within or moved through such a gas-filled elongated tubular chamber. Where the temperature of such substrate while it is within the chamber is elevated (usually by ohmic heating upon the passage of electricity through the substrate) to from 1,200 to 3,500 degrees centigrade, a relatively pure, high density, uniform and smooth graphite coating free from soot and other harmful impurities on the then tungsten carbide wire, irregularities and coating discontinuities will be deposited upon the filamentary substrate to provide the strand which, because of its complete coating by the graphite, is referred to herein as a graphite strand.

When the source gases of the type disclosed by this invention are employed in the vapor deposition process, it is theorized that the nitrogen, iodine or bromine atoms carry the carbon atoms (actually in the form of hydrocarbon radicals) into the pyrolytic process as part of a complete and electro-chemically neutral molecular structure rather than as ionized or electrically charged atomic particles. One possibility is that relatively heavy brominated, iodinated or amine intermediates are formed in concentric layers about the heated filament and act to protect the hot surface upon which the pyrolytic deposition is taking place from soot particles which tend to form in the relatively cooler regions more remote from the heated surface. In addition to this protective activity of the layers of intermediates thus formed, it is conceivable that the intermediates actually repel or react with the soot to keep it from deleterious contact with the filamentary substrate as it is being coated. The lack of appreciable quantities of soot on the newly forming surface results in a paucity of nucleation sites upon or from which undesirable grain growths might develop to the detriment of the strength, density, smoothness and uniformity of the graphitic coating.

Another possibility contributing particularly to the high strength of the coating is that the relatively heavy iodinated, brominated, or amine intermediates act as third bodies which provide multiple collision sites and actually guide the pyrolytic graphite precursors on to the hot filament surface. Thus, even in the absence of surface roughness and accompanying multiple high-energy topographical sites, new layers of the graphite may be rapidly formed by the high incidence angle relative to the filament surface resulting from the collisions with the intermediates, while existing layers continue to build up with carbon atoms responding to low incidence angle collisions with the intermediates. The speed, reliability, and over-all predictability of the operation may be thus substantially enhanced and aided by the guiding influence of the heavier molecular intermediates.

To demonstrate the improvements provided by the teachings hereof in the face of all prior research indicating the non-criticality of the choice of the source gas for the carbon atoms and in the face of still more precise experimentation which demonstrated that no such improvements are obtainable where chlorinated and fluorinated hydrocarbon gases are so employed, tests of the type outlined below were conducted. A tungsten filament 25 microns in diameter and heated to a temperature of 1,900 degrees centigrade was passed through an elongated hollow chamber 4 feet in length at a speed of 1.26 inches per second. The chamber was filled with a 15 volume percent mixture of the hydrocarbon source gas and argon which is the remaining gas or carrier gas for the hydrocarbon source gas which is selected from that class of preferred source gases taught by this invention according to the following example.

Ethyl iodide (C_2H_5I) employed as the hydrocarbon graphite source gas produces a graphite coated tungsten carbide filament that is 100 microns in diameter. The resultant graphite coated filament exhibits an ultimate tensile strength of 66,400 pounds per square inch. The percentage by volume of pyrolytic graphite deposited on the tungsten carbide filament is 94, with the tungsten carbide making up the other 6 percent by volume.

The source gas which is present in the amount of at least 0.5 volume percent, preferably is a bromide, an iodide or an amine of one of the paraffinic hydrocarbon gases, and more particularly a gas selected from the lower-boiling-point methane series gases such as methane, ethane, propane and butane. Greatly improved filaments were noticeable in all instances where the substrate was heated to at least 1,200 degrees centigrade in an atmosphere comprising at least 0.5 volume percent of the paraffinic gaseous compound selected from the class taught by this invention.

While the present invention has been described in considerable detail in connection with certain specific embodiments, tests, and examples thereof, it is to be understood that the foregoing particularization and detail have been for the purpose of illustration only and are not to be interpreted as limiting the invention which is defined in the subjoined claim.

I claim:

1. The method of producing a graphite coated tungsten strand of high tensile strength on the order of 66,400 pounds per square inch comprising the steps of (a) heating at a temperature from 1200 to 3500° C. a tungsten filament which has a diameter on the order of 25 to 100 microns, and (b) contacting said filament with a gas mixture of argon and a source gas, said gas mixture constituted of at least .5 to 15 volume percent of said source gas selected from the group consisting of the amines of methane, ethane, propane and butane at a rate and for a period of time such that the resulting strand consists of a tungsten core covered by a coating consisting of 6% volume of tungsten carbide and 94% volume of graphite.

References Cited

UNITED STATES PATENTS

2,091,554	8/1937	Mendenhall.	
2,946,668	7/1960	Richelsen.	
2,652,621	9/1953	Nelson.	
2,671,735	3/1954	Grisdale et al.	
3,130,073	4/1964	Van der Linden et al.	
3,167,449	1/1965	Spacil.	
3,172,774	3/1965	Diefendorf.	
3,206,331	9/1965	Diefendorf	117—226

ALFRED L. LEAVITT, *Primary Examiner.*

A. G. GOLIAN, *Assistant Examiner.*