

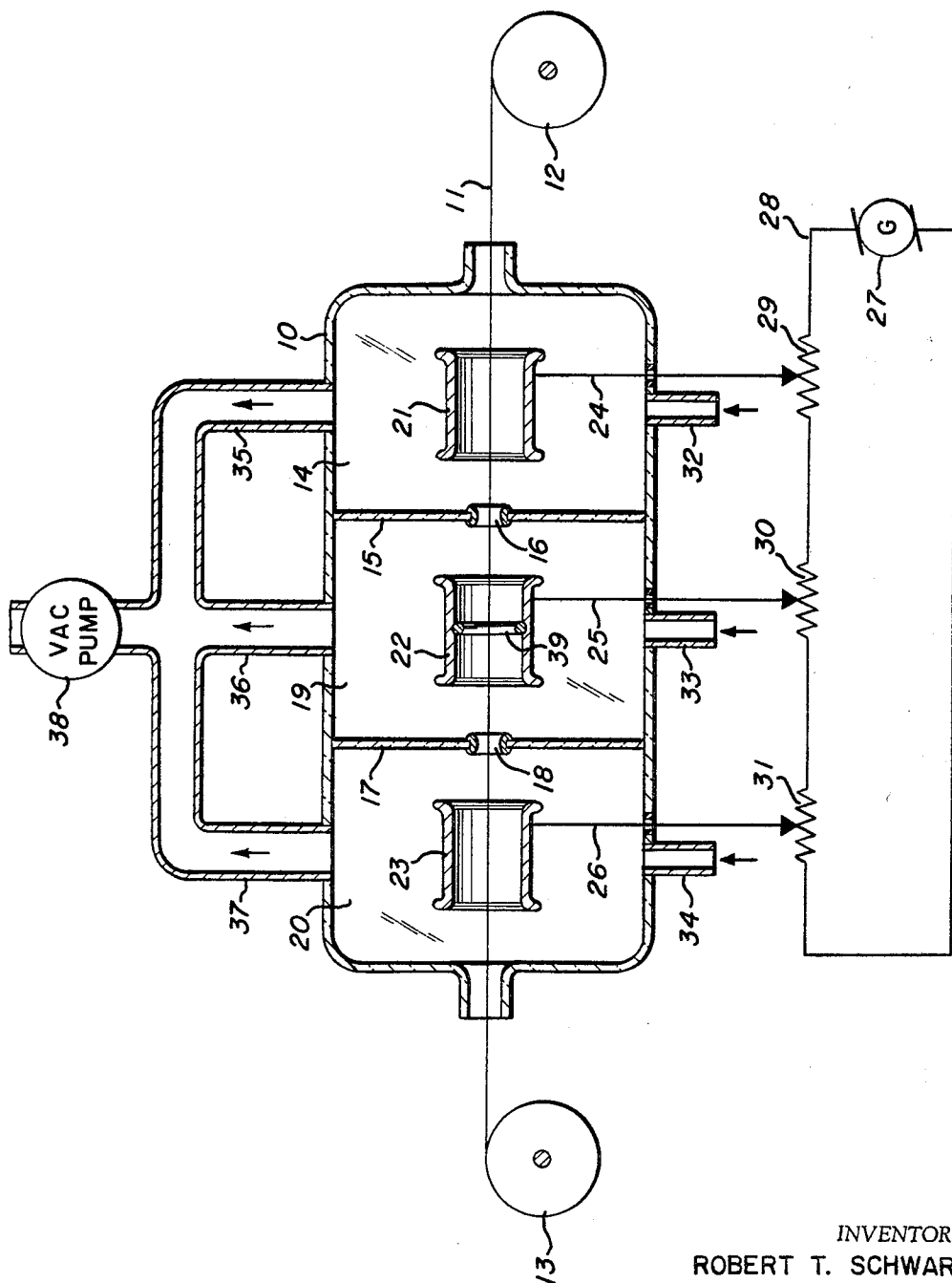
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METHOD OF MAKING METAL OR METALLOID CARBIDE YARN BY DECOMPOSING
THE RESPECTIVE CHLORIDE IN THE PRESENCE OF CARBON YARN
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1

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METHOD OF MAKING METAL OR METALLOID CARBIDE YARN BY DECOMPOSING THE RESPECTIVE CHLORIDE IN THE PRESENCE OF CARBON YARN

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9 Claims

ABSTRACT OF THE DISCLOSURE

Yarn composed of metal carbides or metalloid carbides is made by passing metal carbides or metalloid carbides is made by passing carbon yarn through an atmosphere of a gaseous chloride of the metal or metalloid and simultaneously decomposing the chloride by heat or by an electrical discharge to cause the metal or metalloid to react with the carbon in the yarn.

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

The present invention relates to carbide yarns and particularly to a method and apparatus for manufacturing same.

In the art of reinforced structural and ablative plastics and related composite materials, attention has of late been focused upon a variety of filamentous reinforcing components to be embedded in and/or coated with a variety of resinous matrix materials. With the advent of high speed aircraft, aerospace vehicles and rocket engines, a particular emphasis has been placed upon the development of such reinforcements which are characterized by high refractory capabilities. Still more recently, it has been recognized that particular utility may be enjoyed in aerospace and atmospheric exit and re-entry applications where the refractory reinforcement is further endowed with relatively low thermal and/or electrical conductivity.

While certain metal and metalloid carbides have been known to possess the desired refractory potential coupled with low electrical and thermal conductivities, they have for the most part been available in forms which, because they are relatively frangible, being hard and brittle, do not lend themselves to conventional manufacturing and assembling techniques. While vapor deposition techniques have been available for synthesizing carbides upon small diameter wire substrates which provide a certain reinforcement of the composite filament upon flexing, the presence of the wire places a lower limit upon the minimum final diameter of the composite filament and thus results in a sacrifice of flexibility that might otherwise be gained.

It is accordingly an object of this invention to provide a novel method and apparatus for the manufacture of carbide material in the form of a yarn, roving, cable or other strand-like or filamentous configuration.

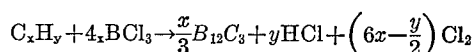
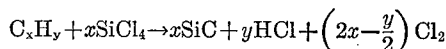
Still another object of the present invention is to provide carbide yarns or filaments which will possess the desired high temperature strength and conductivity of the carbide on the one hand but will retain the flexibility, strength and other structural characteristics of the yarn on the other.

2

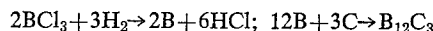
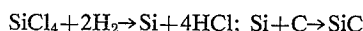
Yet another object of the invention is to provide a filamentous carbide reinforcing material which is compatible with conventional plastics and other refractory substances employed in high speed aircraft, aerospace vehicles and rocket engine components.

Still another object of the invention is to provide a method and apparatus for the manufacture of such carbide filaments which do not require a metallic wire core or substrate.

To achieve these and other objects and advantages which will appear from a reading of the following disclosure, the present invention teaches the conversion of high-carbon-content yarns, strands or related filamentous materials to carbide by the exposure of the precursory filaments to metal or metalloid halides such as silicon tetrachloride or boron trichloride in a variety of reaction environments principally characterized by elevated temperatures, reduced pressures and/or electronic energization. In a particular modification of the invention, the halide in gaseous form is brought into contact with the carbon yarn in a partial vacuum where the yarn and the gas are heated to a temperature within the range of from 1000 degrees to 1800 degrees centigrade which supports a surface-phase reaction between the carbon yarn and the halide wherein the metal or metalloid atoms of the halide displace certain of the hydrogen atoms of the carbon yarn according to the following equations:



In a variation of this procedure, the metalloid halide is reduced to metal by hydrogen and the resultant metal is reacted with the carbon to form the carbide according to the following equations:



In certain refinements of these procedures, improved yields in terms of carbide formation as well as of its density and uniformity are achieved more quickly where iron or iron-supplying constituents are placed in the reaction zone to catalyze the chemical interchange. In yet a further refinement the carbon yarn is exposed to a near or partial vacuum and/or is pre-heated to drive off such volatiles as may be inherent therein and more clearly to develop its porosity immediately prior to its exposure to the halide. In this regard it is to be noted that many of the improvements provided by the within invention such as the improved integration of the carbide coating and the carbide yarn as a substrate and the improved permanency of the ultimate association of the coated yarn with a plastic matrix derive from the fact that the boride-forming metals or metalloids, once plated or similarly deposited upon the yarn surface, diffuse into the yarn, penetrating beneath its surface and there enter into a synthesizing carbide-forming reaction with the strand, not only at its surface but also in the zone beneath and adjoining same.

The boron and silicon atoms have been found to have a sufficiently high mobility that they will readily penetrate the yarn and result in a thicker carbide coating; whereas other carbide-forming elements such as tantalum or tungsten are not so mobile and tend to limit the carbide formation to the surface or the area very near the surface of

the yarn. As a matter of fact, in certain cases it is believed that the carbon atoms in the yarn tend to migrate outwardly to diffuse in the coating to form a carbide sheath which is distinct from the yarn itself.

To achieve the ultimate benefit from the teachings of this invention, it has been found desirable, if not critical, to so correlate the reaction parameters; e.g., the temperature and pressure of the reaction zone and the relative amounts of the halide and hydrocarbon materials being reacted, that there is no plating of the silicon or boron upon the yarn or any bridging of the individual fibers of the yarn by a deposited formation. Rather, the reaction environment is preferably so controlled that only a chemical reaction between the halide and the carbon yarn can occur. At the same time, it is preferred that all of the carbon in the yarn be converted to carbide; and this result may be achieved by the practice of this invention, particularly where the pores of the yarn are evacuated prior to its exposure to the halide gas. The desired uniform formation of a completed carbide yarn has been found to be even more consistently achievable where the exposure of the halide to the carbon is accompanied by an electronic energization of the former at the yarn surface. In one embodiment of the apparatus for practicing the within invention, such electrical energization of a controlled reaction atmosphere is provided by a vacuum tube or similar glow-discharge device through which the carbon yarn is passed and into which the halide gas is introduced to contact the yarn at a point wherein the glow-discharge is focused for maximum electronic excitation.

The carbide yarns thus produced have been characterized by the refractory and conductivity characteristics of the carbide on the one hand but of the strength, flexibility and other physical characteristics of the yarn on the other, with the result that the desired properties of the carbide may be conveniently incorporated, in the form of a reinforcement for example, in a variety of resinous or plastic matrices. Because of the flexibility and yarn-like properties of the strand, the product lends itself to incorporation in reinforced plastic composites by presently known techniques and in presently available apparatuses with little or no modification of either. In this manner, the teachings of the present invention capitalize upon the gains in ease and economy of manufacture that have been heretofore made in the art of textile reinforcement of rubber and plastic items.

The invention thus generally described may be more clearly understood by reference to the following detailed description of certain specific examples and embodiments thereof in connection with some of which reference may be had to the drawing which is a schematic elevational illustration in partial cross section of a preferred apparatus for practicing the method of the invention.

As illustrated in the drawing, the reaction zone for accomplishing the carbide conversion of carbon yarn according to the present invention may be within a vacuum tube or chamber-defining closure 10 through which a carbon yarn 11 is continually moved as by being drawn from a supply spool or reel 12 and taken up upon a suitable sleeve or reel 13. The carbon yarns available for use as the precursory or substrate material in the practice of the invention include the broad variety of presently available carbon yarns which are either carbonized or partially carbonized or other such yarns which are generally formed by the heating of high-carbon-content natural or man-made fibers, particularly the viscous, cellulose and acetate varieties, to carbonization temperatures in a reducing atmosphere over a prolonged period of time during which all of the material within the yarn is converted to carbon or to partially carbonized form. Specific yarns of this variety which have been successfully employed in the present invention include the VYB carbon yarns obtainable by such designation from the Union Carbide Corporation.

As the yarn 11 enters into the vacuum tube or a similar

glow-discharge chamber 10, it passes first through what might be termed an outgasing zone 14 which is defined and separated from the rest of the interior of the chamber 10 by an impervious baffle 15 which might be composed of a suitable refractory material such as quartz and have a small opening 16 therethrough to accommodate the continuing travel of the yarn 11. Adjacent the outgasing chamber 14 on the opposite side of the baffle 15, and further defined by the similar wall or baffle member 17 having an opening 18 to accommodate the movement of the yarn, is the plating or main reaction zone 19. The terminal portion of the chamber 10 as defined by the baffle member 17 is the post-heating or annealing zone 20. Positioned within each of the zones 14, 19 and 20 are the companion electrode units which, in the illustrated embodiment are in the form of electrically conductive hollow cylindrical sleeves 21, 22 and 23 respectively. These sleeve-type electrodes are electrically energized by their association via the respective conductor wires 24, 25 and 26 with a power source such as the direct current generator 27. Their more particular association with the generator may involve the interposition between the generator supply trunk 28 and the individual conductors 24, 25 and 26 of the respective variable resistance units 29, 30 and 31. By manipulation of these variable resistances, the electrical current and the electromotive potential supplied to each of the sleeve-type electrodes 21, 22 and 23 may be selectively varied. Because the strand itself is an electrical conductor and may be given its own electrical charge, e.g., ground potential by virtue of its association with the ground through electrically conductive supports such as the reels 12 and 13, the energization of the electrodes will result in the creation of a non-uniform electrical field around the yarn in the various zones of the vacuum tube which will result in the focusing or concentration of the various gases to provide the most favorable environment to support the particular reaction within such zones to be hereinafter more fully described. Further to preserve the optimum reaction potential of the particular zone, especially insofar as the atmosphere surrounding the strand is concerned, the openings 16 and 18 through the baffle members should be only large enough to permit the free movement of the yarn therethrough. Thus, where a coated strand of on the order of eight microns is to be manufactured, the openings 16 and 18 may be on the order of 0.2 inch in diameter. Because of the close proximity of the heated strand to these openings, it is preferred in many cases that they be composed of a refractory material in the form of a jewel such as of boron nitride which may be simply in the form of a coating approximately 0.1 inch thick around the edges of the openings.

In the preferred embodiment illustrated, each of the reaction zones 14, 19 and 20 is provided with a gas inlet fitting or conduit 32, 33 and 34 respectively, through which a controlled gaseous atmosphere may be introduced as will be hereinafter explained. To promote the flow of the gas introduced via these conduits and to insure its uniform distribution throughout the tube 10, each of the zones 14, 19 and 20 may, via the respective exhaust or withdrawal conduits 35, 36 and 37, be associated with a vacuum pump 38. In a preferred adaptation of this invention as illustrated, the individual discharge conduits are interconnected in a manifold arrangement to insure uniform pressure as between each of the zones 14, 19 and 20 and thereby further to reduce the likelihood that the atmosphere in one chamber will flow through the openings 16 and 18 into adjoining chambers.

In the practice of this invention, as the yarn is taken from the supply spool 12 and enters the glow-discharge tube 10, it is first brought into the outgasing pre-treatment chamber 14 where, in response to the glow-discharge or ionization effect of the electrically energized sleeve electrode 21 and the electrically conductive strand 11, the latter is heated to the point at which the volatile matter therein will be evaporated, ionized or driven off.

To stimulate the purging of such volatile matter, the outgasing chamber 14 may be provided during such heating with a flow of a reducing gas such as hydrogen introduced via the conduit 32 and withdrawn by the passage 35. It has been found that, by proper adjustment of the variable resistor 29, the electrical energization of the electrode 21 may be adjusted to the point at which the yarn may be economically and quickly heated to temperatures of on the order of 2000 degrees centigrade which are more than adequate to accomplish the outgasing and purging which, in many cases are important to the preparation of the yarn for undergoing the plating reaction.

Once the yarn has been preheated, it passes through the opening 16 in the baffle member 15 into the plating or primary reaction zone 19 wherein the sleeve-type electrode 22, like the electrode 21 in the chamber 14, is electrically energized by manipulation of the variable resistance 30 to create a non-uniform electric field, the effect of which is to concentrate the reagent gas in the vicinity of that portion of the yarn 11 within the electrode 22 at the place where the surface reaction is to take place and simultaneously to heat the yarn to temperatures within the range of from 800 degrees to 1600 degrees centigrade to stimulate such plating reaction. Particularly where the outgasing pre-treatment operation has been performed prior to the introduction of the yarn into the plating zone, the effect of the concentration of the reagent gas at the yarn's surface is to cause the gas to penetrate the yarn, filling the interstices defined by the fibers at least at the surface thereof and then, while within such interstices, to undergo a gas-phase plating reaction upon the yarn. As previously explained, this plating occurs when a metal or a metalloidal halide such as silicon tetrachloride, boron trichloride, titanium tetrachloride, tungsten hexachloride or tantalum pentachloride is introduced into the chamber 19 via the inlet passage 33. In certain cases, it may be desired to admix the reagent gas with a suitable carrier gas such as hydrogen or an inert gas such as helium or argon. To maintain the desired concentration of such gas within the plating chamber, and to promote a flow of the gas through the chamber to remove the soot and other impurities formed during the plating reaction, the gas may be withdrawn via the discharge conduit 36. The relative flow rates of the gas entering and leaving the chambers may be controlled, e.g., by manipulation of the vacuum pump 38, to provide a vacuum within at least the plating chamber 19 or the outgasing chamber 14 within the range of from 0.1 to 20 millimeters of mercury which has been found to improve the quality and association with the yarn of the carbide. Depending upon the particular reaction conditions provided by proper manipulation of the electrical energization and gas flows as hereinabove described, the metal or metalloid within the reagent gas will either combine with the carbon of the yarn to form the metal or metalloidal carbide or will be reduced to a metal which will plate out upon the carbon and within the interstices of the surface fibers thereof. This plated metal, in turn and in response to the continued heating of the yarn by the influence of the electrode 22, will then combine with the carbon of the yarn to form the desired carbide. As previously indicated, where the metal or metalloidal atoms are of a high mobility such as is the case with boron or silicon, the plated metal will permeate more deeply into the yarn as a result of which the carbide coating thereon will be present at a greater depth below the finished yarn surface and will be more intimately associated with the yarn substrate. On the other hand, where a less mobile metal or metalloidal atom is plated upon the yarn, the carbon atoms of the yarn itself may penetrate outwardly into the deposited coating thereby resulting in the formation of a carbide sheath which surrounds but does not penetrate the yarn and, in some cases, might even be considered as separate and distinct from the yarn core. Such sheath formation has been found to occur where a tantalum or tungsten halide is employed as the reacting gas.

In many applications, it is desired that, after the yarn has been reacted with the plating and carbide-forming gas, it be passed through an annealing zone such as provided by the chamber 20 wherein again the sleeve-type electrode 23 is so energized by manipulation of the variable resistance 31 that the glow-discharge reaction will heat the carbide-coated or carbide-surfaced yarn to a temperature of on the order of from 1300 to 1600 degrees centigrade. Such post-heating not only results in the further reaction of such metal as may be deposited upon the surface or within the interstices of the yarn with the carbon thereof to form a carbide but also anneals the yarn, further to improve its purity, uniformity and flexibility. In certain instances it has been found desirable to introduce a reducing gas such as hydrogen or an inert gas such as argon into the annealing chamber via the conduit 34 to be withdrawn via the passage 37.

In one refinement of the present invention, the reaction between the halide gas and the carbon yarn may be enhanced by the provision of iron as a catalyst at some point in the reaction zone. In the illustrated embodiment, such a catalyst may be conveniently provided in the form of the iron ring 39 positioned within or against the inner periphery of the sleeve-type electrode 22. In lieu of this, an iron-containing gas such as $\text{Fe}_3(\text{CO})_9$ may be introduced into the reaction chamber either by a separate nozzle or along with the plating gas entering the plating zone via the conduit 33.

While the within invention has been described in some detail in connection with certain specific embodiments thereof, it is to be understood that the foregoing disclosure is for the purpose of illustration only and does not limit the scope of the invention as it is defined in the subjoined claims.

We claim:

1. A method for the manufacture of carbide yarns comprising exposing a carbon yarn to a halide gas of that class thereof which consists of metal chloride gases and metalloidal chloride gases while simultaneously heating said yarn to a temperature within the range of from about 800 degrees centigrade.

2. A method according to claim 1 wherein said halide gas is one of that class thereof which consists of silicon tetrachloride and boron trichloride.

3. A method according to claim 1 wherein said yarn is exposed to said gas in a reaction zone wherein the pressure is a substantial vacuum of within the range of from 0.1 to 20 millimeters of mercury.

4. A method according to claim 1 wherein, prior to its exposure to said gas, said yarn is exposed to a substantial vacuum within the range of from 0.1 to 20 millimeters of mercury.

5. A method according to claim 4 wherein said yarn, at the time it is exposed to said substantial vacuum, is heated to a temperature of within the range of from 800 degrees centigrade to 1200 degrees centigrade.

6. A method according to claim 1 wherein said yarn, after it has been exposed to said gas, is heated to a temperature within the range of from 1300 degrees centigrade to 1600 degrees centigrade.

7. A method according to claim 1 wherein, at the time of the exposure of said yarn to said gas, said gas is electrically energized and concentrated at the surface and within the interstices of the fibers of said yarn.

8. A method according to claim 7 wherein said electrical energization is effected in a glow-discharge tube.

9. A method according to claim 8 wherein said electrical energization is accomplished by electrically energizing an electrode of relatively large surface area near said yarn and electrically energizing said yarn so that an electromotive potential difference exists between said electrode and said yarn whereby a non-uniform electrical field is established between the electrode and the yarn.

References Cited

UNITED STATES PATENTS

679,803	8/1901	Voelker	23—208
821,017	5/1906	Clark	23—208
2,072,788	3/1937	Andrews	23—208
2,138,672	11/1938	White	23—208
2,141,617	12/1938	Ridgeway	23—208
2,978,358	4/1961	Campbell	23—208

3,113,893	12/1963	Sloan	23—208
3,129,188	4/1964	Sowman et al.	23—208

FOREIGN PATENTS

929,927	6/1963	Great Britain.
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