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[54] APPARATUS FOR FORMING SILICON CARBIDE FILAMENTS

[72] Inventors: **Christian Combe**, St. Maur; **Andre Clouet**, Paris; **Michel Marchal**, Palaiseau; **Michel Villard**, Vitry sur Seine; **Pierre Grenier**, Sceaux, all of France

[73] Assignee: **Thomson-CSF**, Paris, France

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[51] **Int. Cl.** **B01k 3/00**, B01k 1/00, C23b 3/06

[58] **Field of Search** ..... 118/48–49.5; 117/107.1, 106 C; 204/130, 140, 206

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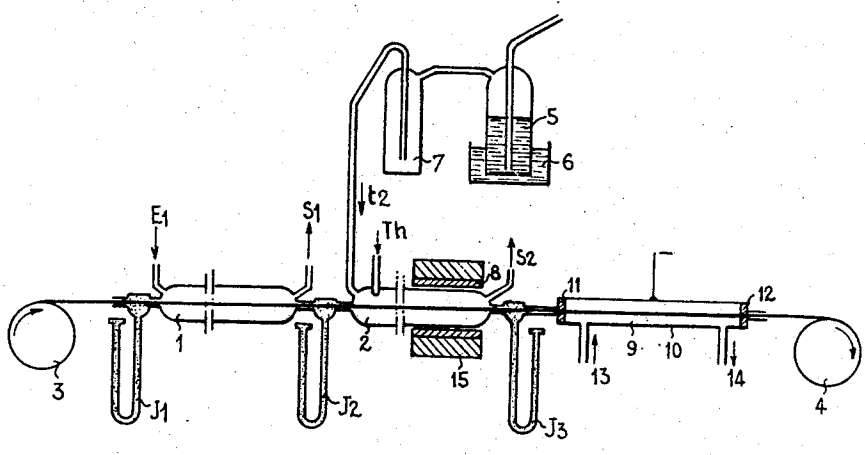
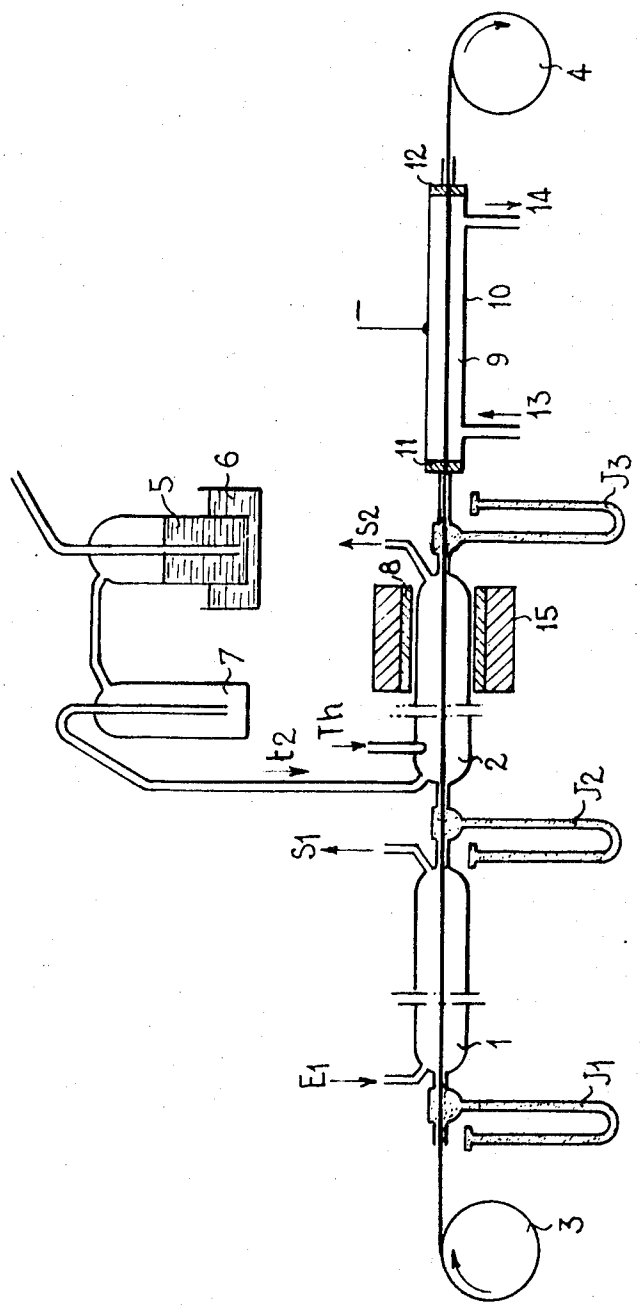
Primary Examiner—John H. Mack
Assistant Examiner—T. Tufariello
Attorney—Flynn and Frishauf

[57] **ABSTRACT**

Apparatus to form silicon carbide filaments which are essentially uniform throughout their cross-section, which includes a reaction chamber, a thermal screen surrounding the reaction chamber to equalize the temperature therein, a thermal gradient oven concentric with the thermal screen and surrounding the chamber, and a plurality of thermocouples located in the chamber and sensing temperature, and controlling the oven to provide for essentially uniform temperature distribution within the oven, the chamber having inlet means for the admission of organosilane so that conversion of heated tungsten to tungsten carbide is carried out essentially at uniform temperatures throughout the entire chamber; an electrolytic cell follows the chamber in the path of the filament.

2 Claims, 1 Drawing Figure

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APPARATUS FOR FORMING SILICON CARBIDE FILAMENTS

The present invention concerns the production of continuous filaments of silicon carbide having extremely high mechanical resistance evolved from a core of tungsten, graphite or any other material that is conductive or that may be rendered surface-conductive. The invention is also concerned with a method for forming such filaments.

BACKGROUND OF THE INVENTION

Silicon carbide filaments can be used as reinforcement elements, whether in the form of a fiber sunk in a metal or in a resin, or as a threadlike support for a variety of bases, so as to furnish composite materials having remarkable mechanical or surface properties.

Known techniques for obtaining continuous filaments of silicon carbide aim at inducing the deposit of this carbide by decomposition of chemical vapors on contact with an electrically conductive wire heated to a high temperature.

Silicon carbide has been obtained by pyrolytic decomposition on contact with a hot tungsten wire of organo-silane vapors transported by hydrogen or mixed hydrogen-diluent gas current. In the course of this process, the diameter of the tungsten wire increases by reason of the formation of the deposit, and it is necessary to progressively increase power to heat the tungsten wire in such a way as to bring back the surface temperature of the filament to a value for which the speed of increase of the deposit is substantial.

Filaments obtained hitherto by this method have in cross-section a microstructure consisting of concentric stratifications. These stratifications correspond to differences of microstructure depending on deposit conditions and in particular to temperature; each time that it is necessary to adjust the heating power in order to renew an appreciable speed in the increase of the deposit, the formation of a new layer is induced, whose structure is different from that of the immediately preceding layer.

This method leads to the appearance of strains between the different strata which are susceptible of causing cracks in the deposit.

The present invention has as its principal object improvements in this method with a view to manufacturing filaments whose structure is regular. Another object of the present invention is to provide a device for use with this method.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a method for making a silicon carbide filament by pyrolytic reaction of a gaseous organosilane in contact with a heated tungsten wire within a reaction zone as the wire is moved through the zone. The temperature of the wire along its length within the zone as it is moved through the zone is substantially constant, and the temperature of the zone is also maintained substantially constant. It is also advantageous to keep substantially constant the gaseous composition, the discharge temperature, and the velocity of the wire through the zone.

In accordance with the invention, there is also provided a reactor for use with said method. The reactor is characterized by a reaction chamber surrounded in part at least with a thermal screen and a thermal gradient oven concentric with each other and an electrolytic cell secured to and communicating with the discharge end of said chamber.

BRIEF DESCRIPTION OF THE DRAWING

Advantages of the invention will become apparent to those skilled in the art from the following description considered in conjunction with the drawing which is a schematic flow diagram illustrating the preparation of a silicon carbide filament.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

It is preferable that the gaseous mixture should flow parallel to the wire in the reaction chamber.

The wire's surface temperature can be between about 1,100° C. and about 1,400° C; preferably, variations do not exceed 30° C. along the length of the wire in the chamber. The most favorable temperature in the case of a gaseous mixture charged with evaporated methyltrichlorosilane (CH_3SiCl_3) is between about 1,200° C. and about 1,300° C. In order to maintain the surface temperature of the wire at its proper value after thermal equilibrium has been established in the reaction chamber, it is particularly advantageous to stabilize the overall temperature of the chamber and that of the wire by controlling the wire's heating current by means of temperature sensors or transducers (e.g., thermocouples) located at different selected points in the reaction chamber.

In accordance with an important characteristic of the present invention, a thermal screen, which can be made of a reflecting metal (e.g., aluminum), is placed around the reaction chamber and along an adjustable length measured from the extremity of the chamber from which the wire issues. The screen has the effect of reducing inequalities of temperature along the wire which, in the absence of the screen, would be colder at the exit end of the chamber because the silicon carbide deposit would necessarily be thicker at this end.

The gaseous mixture can be evacuated at atmospheric pressure and be introduced under conditions closely approximating normal conditions of temperature and pressure. Nevertheless, it is advantageous to provide for thermal regulation of the chamber in which the gaseous mixture is formed.

At the exit from the deposit chamber in which the coating of silicon carbide is achieved, the wire enters a vessel in which the electrolytic treatment is effected. Although this arrangement is preferred, it is also possible to collect the wire on a receptor spool and subsequently subject it to electrolytic treatment.

The method in accordance with the present invention can be executed with the apparatus represented schematically in the drawing. This apparatus includes, with regard to deposit of silicon carbide, two cylindrical chambers **1** and **2** preferably of glass disposed on a more or less horizontal axis and joined to each other by the horizontal branch of a mercury trap J_2; the nonadjacent extremities of chambers **1** and **2** issue into the horizontal branches of two other mercury traps J_1 and J_3. The mercury traps utilized here reflect a special concept, so that the temperature of the mercury can be maintained at a low value, of the order of from about 40° C. to about 60° C. and the well-known Ignitron effect can be totally eliminated here.

The extremities of the horizontal branch of the mercury-containing glass trap J_2 are joined to capillary tubes traversed by the wire. Capillary forces suffice to prevent any escape of mercury by way of the annular space existing between the wire and the inner wall of the capillary tube. As illustrated by the drawing, a tungsten wire issues from a reeling drum **3** and unwinds through the chambers by way of the mercury traps. As will be shown in greater detail below, the wire is transformed into a silicon carbide filament in the course of its transit within deposit chamber **2**, and, issuing from chamber **2** in this new state, it enters chamber **9** where it undergoes electrolytic treatment. Alternatively, the silicon carbide filament can also be stored on a receptor spool (not shown) for subsequent introduction into structure **9**.

The wire in chambers **1** and **2** is heated by Joule effect by means of appropriate sources of electric current (not shown), the source being connected to the wire in chamber **1** by the mercury of traps J_1 and J_2 and to the wire in chamber **2** by the mercury of traps J_2 and J_3. Any type of electrical contact sliding on the wire can also be used to the same effect, but the mercury traps are preferable.

A brake (not shown) can be placed to advantage on discharge spool **3**. A tensioning device can be used to stretch the wire, at high temperature, so as to eliminate any torsion of the wire which could result from the way in which the wire is drawn.

The first chamber **1** is a chamber for cleaning the wire in an atmosphere of hydrogen. It is equipped with inlet line E_1 connected with a hydrogen source (not shown) and exit line S_1

communicating with the atmosphere. The role of the first chamber 1 is to clean the surface of the tungsten wire of all grease or any organic material and to free this surface of any occluded oxygen. In chamber 1, the wire is heated to a temperature of between about 800° C. and about 1,200° C. The cleaning operation is noteworthy in that the wire passes directly into the treatment chamber 2 without returning to the outside air.

A gaseous mixture is charged from vessel 5, which contains a liquid organo-silane, preferably methyltrichloro-silane. The mixture is made up of silane vapors drawn by bubbling a hydrogen current free of water vapor under normal temperature and pressure conditions into vessel 5. The composition of the mixture is carefully controlled and kept constant by insulation of vessel 5 and thermal regulation in a thermostat controlled bath 6. The gaseous mixture is passed through filter 7 before entering deposit chamber 2.

In accordance with the invention, a substantially uniform deposit of silicon carbide is formed by pyrolytic reaction of the silane-containing gaseous mixture on contact with the hot wire, the surface temperature of this wire being maintained practically constant throughout the length of the wire inside deposit chamber 2 during the entire duration of the process. The temperature, which depends on the silane utilized, is between about 1,000° C. and about 1,400° C. with a minimum variation of 30° C. between any two points of the wire. The most favorable temperature used with methyltrichlorosilane is between about 1,200° C. and about 1,300° C. At the same time, the temperature prevailing in deposit chamber 2 is likewise kept substantially constant, as are the dynamic flow characteristics of the gaseous mixture with regard to any point of the wire within chamber 2; it has already been mentioned above that the composition and the temperature of the gaseous mixture are controlled before their entrance into chamber 2.

By reason of the operating conditions, gas intake and exit lines E_2 and S_2 respectively, of chamber 2 are oriented so as to direct the gases along the length of the wire. This prevents local cooling in the wire and favors a stable temperature of the gaseous mixture as well as its laminar displacement around the filament.

As a modification, notably in function of the heating power of the wire, the gases can be introduced in the same direction as the movement of the wire, as is indicated in the drawing by arrows, or in the opposite direction. Gas flow is best conducted under normal atmospheric pressure. This is why deposit chamber 2 is surrounded, to an adjustable length counted from the wire exit end thereof, by thermal screen 8 which can, for example, be made of a reflecting metal, and by an oven 15 having a thermal gradient. In the area of its extension, screen 8 and oven 15 compensate for heat losses occurring by way of the walls of deposit chamber 2. By regulation of the temperature gradient and position of oven 15 and by observing the surface temperature of the wire, for example by means of a pyrometer (not shown), temperature variations along the wire can be limited so as to maintain this temperature within the limits of plus or minus 15° C. Along the entire length of the wire in chamer 2.

When, within deposit chamber 2, overall thermal equilibrium is established, for which the wire possesses the selected temperature, this equilibrium is controlled by temperature points at various points of the chamber by means of thermocouples, of which one (Th) is represented in the drawing.

A single deposit chamber 2 has been represented, by way of simplifying the figure, but it is preferred to arrange several similar deposit chambers in series. The reactive gaseous mixture can be distributed in each chamber individually, but it is also possible to make the gases pass directly from one chamber to the other. The number of deposit chambers and the length of each of them are directly related, the combination of the two determining the final diameter of the silicon carbide filaments produced.

By way of illustration, a more detailed example is now given of the method whereby the methyltrichlorosilane is decomposed to produce a silicon carbide filament.

A tungsten wire having a diameter of from about 10 to about 20 microns and moving at a linear velocity of from about 0.2 to about 2 meters per minute, is introduced into chambers 1 and 2. Cleaning chamber 1 is charged with pure hydrogen containing less than about 30 parts per million (ppm) of water vapor via line E_1. Deposit chamber or chambers 2 are charged with a reactive gaseous mixture containing about 15 volumes of vaporized methyltrichlorosilane per 100 volumes of hydrogen via line E_2. The reactive gases are passed in the direction of the wire's movement at a velocity of approximately 1 meter per minute; these gases escape thereafter into the outside air through line S_2.

Wire velocity as well as composition and discharge of the gaseous mixture are kept constant.

A heating current is introduced into the wire between mercury traps J_1 and J_2 on the one hand, and J_2 and J_3 on the other. The temperature of the wire in cleaning chamber 1 is maintained at approximately 1,250° C.

The temperature of the wire in deposit chamber 2 is maintained at approximately 1,250° C. As soon as indications given by several thermocouples Th, of which only one is shown, placed at representative points within the deposit chamber 2 show that thermal equilibrium has been achieved within this chamber, oven 15 is adjusted so that temperature variations along the wire will not exceed about 20° C. to about 30° C. The heating current is then regulated so that the average temperature of the wire can be as close as possible to 1,240° C. deposit chamber 2 being in thermal equilibrium.

Thereafter, the thermocouples placed in deposit chamber 2 permit the regulation of the heating current so that the thermal equilibrium temperature of chamber 2 will remain practically unchanged during the entire process.

The final diameter of the silicon carbide filaments depends on the length of time the wire stays in the deposit chamber or chambers 2. It is usually agreed that a final diameter of the order of from about 100 to about 200 microns is a satisfactory compromise between the volume of the tungsten, the overall volume of the wire, the mechanical behavior of the silicon carbide filament and its utilization as a reinforcement element.

The linear speed at which the wire moves through the system can vary widely, as from a few centimeters to tens of meters per minute. Adjustment ranges and conditions for the temperature and gas discharge in the chambers are increasingly narrow in proportion to the increase in velocity with which the filament moves through the system.

The layer of silicon carbide is deposited in concentric fashion, resulting in a fairly circular cross-section in the product obtained. The tungsten filament is embedded in the central portion and is more often than not decomposed into fragile carburization products. The polycrystalline state of the silicon carbide deposit in forms alpha and beta—and beta—is highly pronounced, since the diameter of elementary crystallite attains values of the order of 0.025 micron. The mechanical resistance of the filaments obtained depends essentially on the conditions for depositing the silicon carbide and the uniformity of the surface state. At this stage of the process, the breaking strength attains commonly average values of from about 220 to about 240 kg./mm.^{2}, values due to the excellence of the surface state. However, despite this excellent surface state whose irregularities have a depth generally not exceeding 0.02 micron, it has been found to be advantageous to provide a super-fine finish to the filament's surface by electrolytic treatment. A suitable technique comprises mounting in series after chambers 1 and 2, electrolysis cell 9 made up of a metallic tube 10, preferably of stainless steel, provided with two plugs 11 and 12 each of which is traversed by a capillary tube through which the wire is passed.

An electrolyte is charged to tube 10 through line 13; the electrolyte leaves tube 10 by line 14 nd is recycled to the tube by a pump (not shown). Tube 10 is carried, with regard to the

wire, to a negative potential by means of a feed mechanism (not shown). At the exit of cell **9**, the wire is rolled onto a receptor spool **4** actuated by a motor (not shown). For a tube **10** of stainless steel whose diameter is approximately 20 mm. and length 400 mm., advantageous results have been obtained under the following conditions:

Electrolyte: 5% KOH solution

Temperature: 20° C. to 25° C.

Duration of contact between wire and elecrolyte: 2 minutes

Difference of potential between wire and tube: 12 volts.

Before subjecting the wire to this electrolytic treatment, breaking strengths ranging in average value between about 220 and about 240 kg./mm.^{2} are commonly observed, the breaking test being effected on samples whose length is of the order of 100 mm.

Following the wire's electrolytic treatment, breaking strength commonly increases to from about 20 to about 30 percent, and average values ranging between about 260 and about 320 kg./mm.^{2} are attained, the modulus of elasticity remaining equal on the average of 45,000 kg./mm^2.

These mechanical properties explain the excellent rigidity and elasticity of the silicon carbide filament as well as ability to accept bending with very small curvature.

While methyltrichlorosilane is preferred organosilane, related silanes can also be employed such as: dimethydichlorosilane and trimethylchlorosilane.

The preceding description is given as a nonlimiting example and the present invention encompasses such variations or modifications as defined by the language of the appended claims.

What is claimed is:

1. Apparatus for the treatment of a tungsten filament to form a silicon carbide filament comprising

an elongated reaction chamber (**2**) having inlet and outlet means for passing a filament of tungsten therethrough, and removing the treated filament from said chamber;

a thermal screen (**8**) surrounding the chamber to equalize the temperature within the chamber;

a thermal gradient oven (**15**) concentric with the thermal screen surrounding said chamber;

a plurality of thermocouples (Th) located within the chamber and sensing the temperature at selected locations therein, the thermocouples being connected to the thermal gradient oven to regulate the heat gradient of the oven and thus the average temperature within the oven;

means (J_3) connected to the outlet means of the chamber to isolate the atmosphere within the chamber;

means introducing and removing gases to, and from the chamber;

and an electrolytic cell (**9**) located to follow, in the path of the filament, said isolating means.

2. Apparatus according to claim **1**, including means (**5**, **6**) supplying a gaseous silane mixture to the chamber, said means comprising

an insulated vessel (**5**) and a thermostatically controlled bath (**6**) surrounding said insulated vessel and maintaining the temperature of said vessel constant.

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