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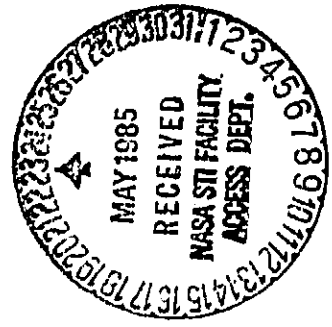
HIGH-RESISTANCE AND RAISED MODULUS CARBON FIBERS

A. E. Standage and R. Prescott

Translation of "Fibres Carboniferes a Haute Resistance et a Module Elevé", Belgian Patent No. 690072, May 2, 1967, Brussels, Belgium, pages 1-17.



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16. Abstract

A Belgian patent for high strength, high modulus carbon fibers has been issued to Rolls Royce Ltd. Great Britain. The manufacturing process, test procedures and application of the fibers are described in the Patent document.

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KINGDOM OF BELGIUM

Ministry of Economic Affairs

INVENTION PATENT NO. 690.072

The Ministry of Economic Affairs announces that, */1

In view of the law of May 24, 1854 concerning patents of invention;

In view of the Convention of Unity for the protection of industrial property;

In view of the report drawn up on November 23, 1966 at 3:00 PM in the Department of Industrial Property;

Article 1. - The company entitled Rolls-Royce Limited, of Nightingale Road, Derby, Derbyshire (Great Britain), represented by Mr. P. Hanseens in Brussels is issued an invention patent for: carbon fibers with high strength and modulus (invented by Mr. A. E. Standage and Mr. R. Prescott) for which the company claims to have already filed a patent in Great Britain on November 24, 1965, under no. 49850/65.

Article 2. - This patent is delivered without prior examination,

* Numbers in the margin indicate foreign pagination

at the applicant's own risk, without any guarantee either of the authenticity, uniqueness, or merits of the invention, or of the accuracy of the description, and without prejudice to the rights of third parties.

A copy of the invention specification shall remain attached to the present document (specification and possible drawings), signed by the person concerned and submitted in support of the patent application.

Brussels, January 31, 1967

By special delegation:

The General Director

Signed: J. Hamels

INVENTION PATENT

Company name: Rolls-Royce Limited

Invented by Arthur Edward Standage

and Roger Prescott

"Carbon fibers with high strength and modulus"

Int. Conv. Priority of claim to a patent application filed in Great Britain on November 24, 1965 under number 49850/65.

The present invention concerns carbon fibers with high strength and modulus.

In their quest for lighter materials capable of withstanding heavy loads, engineers have resorted more and more to composite materials, especially those comprising a relatively weak matrix in which high strength fibers are molded; in this way the fibers absorb most of the applied load while the matrix absorbs relatively little. Various substances have been suggested for use as the basic material in these composite materials. A well known example is that of plastics reinforced with glass: thin fibers of glass are set in the plastic to provide the plastic with mechanical strength.

One of the most recent materials that has been found to have a high resistance in the fibrous form is carbon, particularly in the form of graphite. Any method of producing carbon fibers for use in a reinforced matrix must provide carbon fibers of the highest possible strength, and the applicant has discovered a method by which strong carbon fibers can be produced.

As specified by the present invention one process of producing high-strength carbon fibers with a high modulus is by stretching a carbonaceous polymer fiber in water or water vapor to encourage alignment of molecules in the fiber, and then heating the stretched polymer fiber so that the fiber is first modified into an intermediary form with a high carbon content while maintaining the overall arrangement, and finally by heating the material to a higher temperature so that a graphite structure with a high strength and

modulus of elasticity is produced.

A preferred raw material is polyacrylonitrile fiber.

The stretching stage is performed preferably with the fiber submerged in boiling water or water vapor.

The heating stages are best performed in different furnaces. The first stage which consists in bringing the fibers to a temperature of approximately 1000°C should be carried out in a relatively large furnace which may be fairly simple since large quantities of decomposition products are released and the fiber must be loosely compacted to allow for easy elimination of the decomposition products. The clearing gas may be inert, such as argon, or it may be active. If an active gas is used, it can only be used at a temperature at which the fibers are not destroyed by reaction with the gas; beyond such a temperature an inert gas must be used.

The possibility of coking in this first stage is reduced by gradually increasing the temperature; the combined requirements of light compaction and a slow heating rate both contribute to reduce the rate of production of the first stage. A large, relatively simple, furnace may be used for this stage.

The second stage, in which the fiber is heated to more than 2500°C, does not require light compacting of the fiber and may be carried out fairly quickly. Consequently, the production rate of this stage is relatively high and one can use a smaller heated volume. The required equipment for this stage, which is necessarily quite costly both for the initial investment and the operating expenses, may be

used at full capacity if two furnaces are used for the two different heating stages.

The method used to hold the fiber during the first stage of the heating cycle is not only determinant for the effectiveness of the removal of decomposition products, but also determines the straightness of the finished carbon fiber product. If the fiber is kept from contracting during decomposition, the resulting carbon fiber will be straight.

In some of the examples which follow the fibers are stretched as specified by the invention before undergoing hot processing. In each case the stretching process is the following:

A tow of fiber as supplied by the manufacturer is wound around two bars of circular cross-section and the ends of the tow are tied. In this way a loop of tow is formed around the two bars. The bars and the tow of fibers are then plunged into boiling water and the bars are spread apart in such a way as to stretch the tow by 100% every ten minutes. This operation is continued until the desired degree of stretching is obtained.

The bars are then maintained in this position and the fiber is cooled with 15 to 20°C water. The fiber can

then be removed and placed in a receptacle for heat treatment.

It would obviously be possible to immerse the fibers in water vapor instead of boiling water for this stage of stretching. In this case the temperature of the water vapor should be just over 100°C. The use of water vapor is preferable in large scale production because

water vapor is easier to use on a large scale than boiling water.

The appended figures depict a receptacle in which the fibers are held to prevent contraction during the heat treatment stage directly following the stretching process. The figures are as follows:
Figure 1 is an exploded view of the receptacle;
Figure 2 is a view of a partially assembled receptacle with a tow of fiber wound on;
Figure 3 is a cross-sectional view of an assembled receptacle holding lengths of fiber inside a cylindrical furnace.

In Figure 1 the fiber receptacle comprises gas supply tube 10 having closed end 11 and open end 12 through which an inert gas can be supplied. Gas outlet holes 13 are made in tube 10 to allow for flow of the gas.

Plate 14 is attached to tube 10 and is provided with three holes 15. The purpose of these holes is to accommodate threaded ends 16 which extend beyond ring 17 that is part of spacer 18. Ring 17 is attached by a set of stems 19 to another parallel coaxial ring 20 which is provided with three ends 21. Ends 21 go through holes 22 in a second plate 23 similar to plate 14. Plate 23 has a central hole 24 to receive tube 10.

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Figure 2 shows a partially assembled receptacle including a certain number of polymer fibers held in the receptacle. In the partially assembled position, receptacle 18 - made up of rings 20, stems 19 and ends 16 - surrounds tube 10 in the area of gas outlet holes 13. Before fitting receptacle 18 over tube 10, the tow of

polymer fiber 25 is wound around the two rings 17 and 20 in such a way as to extend between the two. Receptacle 18 is then fitted over tube 10 so that ends 16 pass through holes 15 in plate 14; nuts are then tightened onto ends 16 so that ring 17 is pressed against plate 14 to pinch the polymer fibers.

Hole 24 in plate 23 then receives tube 10 and ends 21 fit into holes 22; once again nuts are tightened on ends 22 thereby pinching the fibers between ring 20 and plate 23.

Consequently, as shown in Figure 3, the receptacle holds the fiber tightly when the nuts are tightened on ends 16 and 21 and prevents the fiber from contracting. In Figure 3 receptacle 18 and tube 10 are placed inside cylinder 26 of a furnace having heat element windings 27. Plates 14 and 23 are designed with tabs in order to be installed inside cylinder 26.

Once receptacle 18 and tube 10 have been assembled and placed inside the furnace, a clearing gas, which may be an inert gas, is introduced into open end 12 of tube 10, and passes through holes 13 and then through to the polymer fibers to clear them of reaction products.

The type of receptacle represented in the drawing ensures that the fiber does not contract freely and that the clearing gas is forced to circulate through the harness of fibers. The material,

nimonie 80, and the construction must ensure that the receptacle does not collapse under the extreme forces created during processing of the fiber at 1000°C.

Examples of the manufacture of fibers are given below.

Example 1

A tow of fibers consisting of about 50g of polyacrylonitrile copolymer, sold under the tradename of "Courtelle" is stretched 300% in 100°C water over a period of 15 minutes. The tow is then removed, dried, and wound onto a receptacle of the type described earlier. The specimen is then placed in a furnace for the first stage with an argon flow of about 141 liters per hour through the tow. The temperature is increased by 50°C per day up to 600°C, then by 100°C per day up to 1000°C. Next, the material is cooled, removed from the furnace and taken out of the nimonie receptacle. The fiber is then placed in the second stage furnace, is heated to 3100°C in 100 minutes and then cooled. The average value of the Young's modulus for the fiber is 55 x 10^6 psi (multiply values expressed in psi by 0.07 to obtain the results in kg/cm^2).

Example 2

Acrylic fibers other than "Courtelle" fibers are suitable for preparing carbon fibers with a high modulus. The following pairs of examples show how carbon fibers obtained from pure polyacrylonitrile, form acrilan, and from zefran compare with those obtained from "Courtelle" precursor.

a) Unstretched Courtelle raised to a temperature of 1000°C by 0.5°C/minute in argon, then to 2500°C, yields a carbon fiber with an average modulus of 19.8 x 10^6 psi.

Pure, unstretched, polyacrylonitrile fiber processed as described immediately above results in carbon fibers with an average modulus of 21.0 x 10^6 psi.

Unstretched acrilan fiber raised to 1000°C by 0.5°C/minute in argon and then heated to 3000°C yields a carbon fiber having an average modulus of 53.5 x 10^6 psi.

b) Courtelle fiber stretched 200% and heated to 1000°C by 0.5°C/minute in argon gas and then to 3000°C results in a carbon fiber having an average modulus of 38.5 x 10^6 psi.

Acrilan fiber stretched 200% and processed as described immediately above results in a carbon fiber having an average modulus of 47.5 x 10^6 psi.

c) Courtelle fiber stretched 100% and heated to 1000°C by 0.5°C/minute in argon gas, and then to 3000°C yields a carbon fiber having an average modulus of 36.2 x 10^6 psi.

Zefran fiber stretched 100% and processed as described immediately above yields a carbon fiber having an average modulus of 32.7 x 10^6 psi

Example 3

As a general rule, the more the polymer fiber is stretched before decomposition the greater is the resulting modulus of the carbon. The following samples of Courtelle fiber were heated to 1000°C by 0.5°C/minute, then to 2500°C after being stretched in 100°C water as indicated below.

0% stretching results in an average modulus of 30.1 x 10^6 psi
50% stretching results in an average modulus of 30.3 x 10^6 psi
100% stretching results in an average modulus of 42.6 x 10^6 psi
400% stretching results in an average modulus of 42.9 x 10^6 psi

It is thought that the stretching process favors initial

alignment of the polymer molecules, which is at least partially maintained until the fiber reaches its final carbon form. The water or water vapor that is used as a stretching atmosphere acts through solvation of the polymer fibers and reduces their resistance to alignment while thus reducing the

temperature level necessary for stretching of the fibers.

Example 4

The slower the rate of temperature increase to 1000°C the higher the final modulus of the carbon.

Unstretched Courtelle fiber heated to 1000°C by 3.3°C/minute in argon gas, and then to 2500°C, results in an average modulus of 7.3×10^6 psi for the carbon fiber.

Unstretched Courtelle fiber heated to 1000°C by 0.5°C/minute in argon gas, and then to 2500°C, results in an average modulus of 19.8×10^6 psi for the carbon fiber.

Example 5

The higher the maximum processing temperature, the higher will be the final modulus of the carbon. The following samples were all prepared using unstretched Courtelle fiber heated to 800°C by 0.13°C/minute, and then heated to the final temperatures indicated below.

A max. temp. of 1690°C results in an average modulus of 14.6×10^6 psi

A max. temp. of 2005°C results in an average modulus of 17.0×10^6 psi

A max. temp. of 2200°C results in an average modulus of 20.7×10^6 psi

A max. temp. of 2475°C results in an average modulus of 21.2×10^6 psi

A max. temp. of 2740°C results in an average modulus of 22.9 x 10^6 psi
A max. temp. of 3300°C results in an average modulus of 28.0 x 10^6 psi

Example 6

If the rate of temperature increase during the second stage of the heat treatment is not greater than 40°C/minute, then the duration has little effect on the modulus of the carbon fiber.

Three samples of unstretched Courtelle fiber were processed under similar conditions with the exception that the maximum temperature of 2500°C was maintained for 0, 15, and 60 minutes, respectively. The resulting moduli of the carbon were 21.1, 21.2, and 20.3 x 10^6 psi. The average rate of temperature increase

during the second stage was 40°C/minute in all three cases.

A sample was treated up to 1000°C in the same way as the three samples above, but was then heated to 2500°C at an average increase rate of 170°C/minute, and then maintained at that temperature for 15 minutes: an average modulus of 18.9 x 10^6 psi was obtained for the carbon.

This drop in the final modulus of the carbon caused by a high rate of temperature increase during the second stage may, however, be compensated for by maintaining the fiber at its final maximum temperature for a duration of not less than 40 minutes.

The formation of a graphite fiber with a high Young's modulus in the direction of the axis of the fiber depends on the development of a fiber containing a high proportion of graphitic crystallites with their layer planes (that is, their direction of high stiffness)

aligned longitudinally with the fiber.

It is considered that the creation of such a fiber is favored in the present process by including the stages described herebelow.

Firstly, a polymer fiber having a high degree of alignment in its supramolecular structure along the axis of the fiber is obtained by selecting a fiber which is or can be aligned by stretching. Acrylic fibers can be so aligned as is indicated by the results of diffraction to x-rays (other polymer fibers can also be obtained in a highly aligned form). This alignment must be maintained within the basic carbon structure of the fiber during the first stage of heating to 1000°C, when producing a fiber with a high carbon content. By correctly selecting the conditions of the first stage it is possible to convert the initial hydrocarbon polymer into a highly stable structure having a high carbon content

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without incurring, in the process, an extensive degree of scission in the polymer chain. If scission in the chain is substantially limited, then the relatively immobile chains will keep their respective positions in the fiber during the first stage of heating, resulting in the conservation of the overall anisotropy of the fiber. In acrylic fibers this stabilization of the structure is assisted by the formation of a closed cyclic structure along the polymer chain at relatively low temperatures. This structure, which is that of a polynaphtyridine, is relatively stable.

At higher temperatures, the subsequent development of the aligned structure of the carbon chain into a graphite structure results in an

aligned polycrystalline structure with the layer planes of the graphite crystallites aligned in the direction of the fiber's axis. This is demonstrated by the results of diffraction to x-rays. The higher the final treatment temperature, the greater is the degree of development of the graphite structure.

Although the process of producing intermediary carbon fibers was described as employing an argon atmosphere in the preceding examples, it is possible to use other inert gases as the treatment atmosphere. Furthermore, it has also been found that an oxidizing or reducing atmosphere can be used with advantageous results provided that the atmosphere is changed from a reducing or oxidizing one to an inert one before reaching the temperature at which the fibers would be completely destroyed.

A reducing atmosphere, of which hydrogen is the simplest example, was used for treatment up to 450°C, at which point the hydrogen was replaced with argon for heating from 450 to 1000°C. The use of a reducing atmosphere has various advantages.

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For example, it was found that although the use of a reducing atmosphere may lead to a slight drop in the modulus of elasticity in the final graphite fibers, it imparts a considerable increase to the mechanical strength of the fibers, an increase that can constitute a major advantage in certain engineering applications where these fibers are used as a reinforcement material in a matrix.

Other advantages that are attributed to the use of a reducing atmosphere are that the reducing atmosphere controls the carbonization

reaction so as to limit the quantity of reaction products given off in a volatile form. The fibers can therefore be compacted more tightly and more fibers can be carbonized in a given furnace. When using a reducing atmosphere the heating rate can also be substantially increased during this stage without prejudice to the fibers produced. Consequently, the fiber production rate of a given furnace can be increased considerably.

The reduction of volatile decomposition products also leads to additional conservation of carbon in the fibers, resulting in a better final product.

Although it is possible to obtain carbonized fibers while maintaining a hydrogen atmosphere up to a temperature of 1000°C, it was found that this results in a substantial drop in the modulus of the final fibers and that it is better to replace the hydrogen atmosphere with an argon atmosphere at a temperature below 450°C. It is preferable to maintain the hydrogen atmosphere to as high a temperature as possible without considerably affecting the properties of the fiber produced. In this way, a minimal amount of time is devoted to the use of argon as the clearing gas, thus consuming a minimal amount of argon and making possible considerable reductions in costs.

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When an oxidizing atmosphere is used, the best known example being oxygen, the final fibers end up having a considerably higher modulus than that obtained in an inert atmosphere.

An additional advantage obtained by the use of an oxidizing

atmosphere is that it is possible to obtain strong final fibers by the use of a carbonization temperature of approximately 700°C instead of the usual 1000°C. This results in considerable savings in the time devoted to carbonization and consequently a great improvement in the fiber production rate.

Reducing and oxidizing atmospheres could be used together to impart to fibers certain required properties from a range of possibilities. In this way fibers could be manufactured for use in a matrix in order to obtain a predetermined variation in the properties of the structure of a single part; this represents a useful particularity for engineering applications.

The following examples concern the effect that the gaseous environment during thermal decomposition of the polymer fiber has on the Young's modulus and the tensile strength of the final carbon fibers.

Examples 7, 8, and 9 were obtained starting with Courtelle fibers by increasing the temperature at a rate of 0.5°C/minute up to 1000°C in the atmospheres indicated below, and then to 2500°C for 15 minutes in argon gas.

Ex. 7: heated to 1000°C in argon, average modulus = 19.8×10^6 psi

Ex. 7: heated to 1000°C in hydrogen, average modulus = 11.8×10^6 psi

Ex. 7: heated to 1000°C in a vacuum (0.03 mm Hg), average modulus = 23.8×10^6 psi

Examples 10, 11, 12, 13, and 14 were obtained with

Courtelle fibers that were stretched in 100°C water and heated to 1000°C

at a rate of 0.5°C/minute in the atmospheres indicated below, and then heated to 3000°C in 60 minutes in argon.

Ex. 10: heated to 1000°C in argon, average modulus = 53.2×10^6 psi

Ex. 11: heated to 400°C in oxygen and then to 720°C in argon, average modulus = 66.3×10^6 psi

Ex. 12: heated to 400°C in air and then to 1000°C in argon, average modulus = 65.4×10^6 psi

Ex. 13: heated to 1000°C in nitrogen, average modulus = 40.9×10^6 psi

Ex. 14: heated to 450°C in hydrogen and then to 1000°C in nitrogen, average modulus = 37.0×10^6 psi

The peak value obtained in example 11 was 85×10^6 psi.

In examples 15 and 16 Courtelle fibers were stretched 300% in 100°C water, and heated to 600°C at a rate of 0.03°C/minute, then to 1000°C at a rate of 0.14°C/minute in the type of atmosphere indicated, then to 3000°C in 60 minutes.

Example 15: heated to 430°C in hydrogen, then to 1000°C in argon. Tensile strength = 240,000 psi.

Example 16: heated to 1000°C in argon. Tensile strength = 170,000 psi.

Examples 7 and 9 indicate that the decomposition of the polymer fiber in a vacuum produces a carbon fiber with a higher modulus than when decomposition occurs in argon.

Examples 10 and 13 show that decomposition in nitrogen produces a fiber with a lower modulus than decomposition in argon.

Examples 7, 8, 13, and 14 show that the presence of hydrogen during decomposition reduces the modulus to below that obtained with nitrogen or argon.

Examples 10 and 11 show that the presence of oxygen up to 400°C

results in higher modulus values than those obtained with just argon. Example 11 also indicates that the use of oxygen up to 400°C enables the process

of the first stage to be stopped at around 700°C. Example 12 shows that a similar increase in the modulus is obtained by using air up to 400°C.

Examples 15 and 16 show that the substitution of argon with hydrogen up to 430°C results in an increase in tensile strength in the final carbon fibers.

Note that the density of the fibers produced in the last ten examples does not exceed 1.8 g/cm^3.

Oxidation of the polymer structure during the decomposition process is believed to result in stabilization of the original polymer chain and consequently a higher degree of molecular alignment conservation. This therefore results in a higher-modulus fiber. Reduction of the structure has an opposite effect from that of oxidation because a less thermally-stable molecular structure is produced during decomposition, resulting in less alignment and a lower modulus. The most mobile structure produced under these conditions will lead to a more reduced carbon-fiber structure. The carbon structure will contain less discontinuity creating stresses and probably fewer permanent stresses. The fiber will consequently be stronger when it is produced in reducing conditions than when produced from a more stable oxidized structure.

The choice of the gaseous atmosphere to be used in any of the

stages of the decomposition process will depend upon the particular modulus and tensile-strength properties required.

CLAIMS

1. Process for producing high-strength and high-modulus carbon fibers, characterized

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by the stretching of carbonaceous polymer fiber in water or water vapor to encourage alignment of the molecules within the fiber. The stretched polymer fiber is heated so that the fiber is first modified into an intermediary form with a high carbon content while keeping its overall alignment. Next the material is heated to a higher temperature in order to produce a graphitic structure with a high strength and high modulus of elasticity.

2. Process as in claim 1, characterized by a carbonaceous polymer fiber consisting of polyacrylonitrile.

3. Process as in claims 1 and 2 characterized by the stretching stage being performed with the fiber immersed in boiling water or water vapor.

4. Process as in claims 1 through 3 characterized by an initial heating stage where the fibers are brought to a temperature of 1000°C.

5. Process as in claims 1 through 4 characterized by a second heating stage bringing the fibers to a temperature of at least 2500°C.

6. Process as in claim 1 characterized by the use of a relatively

low-temperature furnace and a relatively high-temperature furnace, with heating to modify the fiber into a high-carbon-content intermediary form taking place in the former while heating at higher temperatures takes place in the latter.

7. Process as in claim 1 characterized by the first heating stage taking place with the fibers in an inert atmosphere.

8. Process as in claim 1 characterized by the first heating stage taking place with the fibers in an active atmosphere during the initial part of the heat treatment,

and then the active atmosphere being replaced with an inert atmosphere when a temperature of approximately 400°C is reached.

9. Process as in claim 8 characterized by an active atmosphere consisting of hydrogen or oxygen.

10. High-strength and high-modulus carbon fiber produced by the process according to claims 1 through 9.

11. Process for producing high-strength and high-modulus carbon fiber in substantially the same way as the method described, in particular as in the text which precedes.

Brussels, November 23, 1966
Filed by Rolls-Royce Limited