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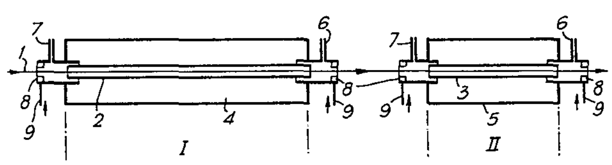
(54) Graphite fibres and process for their manufacture.

(57) Production of high quality graphite fibre is possible by use of a process in which the precursor fibre passes through two heating zones both containing an inert atmosphere in which the temperature profile is independantly controllable. The maximum temperature in the first zone is in the range of about 1500 to 2100° C, and in the second zone from about 2100 to 3500° C.

In the first furnace the weight of the fibre is reduced to about 93 to 95 percent of its initial weight.

The separate first and second heating zones (furnaces) have respectively furnace tubes (2, 3) to which heat is applied in a conventional way. The furnace tubes (2, 3) are surrounded with insulation (4, 5). An inert gas such as nitrogen is supplied to the furnaces (I, II) through pipes (6), and the gas is removed from the furnaces by pipes (7). At each end of each furnace there are furnace seals (8), supplied with inert gas through supply pipes (9).



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GRAPHITE FIBRES AND PROCESS FOR THEIR MANUFACTURE.

Graphite fibres are generally different from carbon fibres in respect of carbon content (purity), structure and physical characteristics. Graphite fibres are preferable to carbon fibres for use in sports equipment such as fishing rods and golf club shafts which require high modulus, for use in electric components such as heaters which require high purity and low resistivity, and for use in the aerospace industry, where parts for aircraft, rockets etc., may have to have high oxidation resistivity and be made to high precision. However, graphite fibres cost much more than carbon fibres and this high cost is largely a result of difficulties in manufacturing processability and productivity. An inert atmosphere is required for production of graphite fibres, and a higher temperature is used than for carbon fibres.

Efforts have been made to increase productivity in manufacturing graphite fibres. For example, it has been proposed to increase the temperature gradient and to shorten the time in graphitizing furnace. However, this produces increased amounts of fuzz on the surface of the graphite fibres and occasional breakage of the fibre strands.

Also, these modifications tend to reduce the tensile strength of the fibres. Further, since the temperature of the inert atmosphere must be higher than that used for manufacturing carbon fibres the wear on the graphitizing furnace, particularly on its heating pipes, is considerably greater. As a result of such wear due to exceedingly high temperatures, deviations from the desired temperature profile tend to increase and the furnace tube must be changed frequently. This seriously interferes with production and processability, and also consumes large amounts of energy, labour and materials.

According to the present invention there is provided a process for the manufacture of graphite fibre by graphitizing precursor fibre characterised in that the precursor fibre or fibres pass successively through separately controllable first and second heating zones, both containing an inert atmosphere, the temperature at the hottest point in the said first heating zone being in the range of about 1500°C to about 2100°C, and the temperature at the hottest part in the said second heating zone being at least about 2100°C.

By use of the present invention it is possible to obtain a stable method of manufacturing high grade and high quality graphite fibres, particularly graphite fibres which have a minimum of surface fuzz. The process may use a shorter heating zone than is usual in conventional processes. Additionally, it is possible to provide a manufacturing process in which the life of parts is lengthened, and their replacement is easier, thereby saving energy, materials and labour.

The term "graphite fibre" as used herein is intended to mean a fibre which is obtained by heating a graphitizable precursor fibre in an inert atmosphere at a temperatue of about 2100°C, or more and which fibre contains about 95% or more by weight of carbon. The term "graphitizable precursor fibre" or "precursor fibre" is intended to mean a fibre which has sufficient structural integrity to maintain its fibrous character and which can be converted to a graphite fibre when heated in an inert atmosphere at a temperature of about 2100°C or more. A typical example of a precursor fibre is an oxidized fibre obtained by heating an acrylic fibre, a cellulosic fibre (rayon), a polyvinylalcohol fibre or a pitch fibre in an oxidizing atmosphere at a temperature of about 200°C to 400°C. Another typical example is a carbon fibre obtained by heating the said oxidized fibre in an inert atmosphere at a temperature above about 400°C. When using the process of the present invention it is preferable to use a precursor fibre obtained from an acrylic fibre comprising about 95 mol % minimum of acrylonitrile (AN) and up to about 5 mol % of one or more ethylene-type vinyl compounds which are copolymerizable with acrylonitrile.

The maximum temperature in the first heating zone is preferably in the range of 1700°Cto 1900°C. The second heating zone preferably has a maximum temperature in the range of 2100°C to 3500°C, more preferably in the range of 2300°C to 2700°C.

It has been discovered that if the front and rear heating zones are operated at heating temperatures outside the ranges from 1500°C to 2100°C and 2100°C to 3500°C, respectively, it is difficult to obtain high quality graphite fibre. The quality of the fibre produced is influenced by such things as the type of precursor fibre, whether it was pretreated or not, and the temperature profile of the heating zone; in some instances it is especially sensitive to the maximum temperature of the first heating zone and is reduced if this exceeds about 2100°C. In particular, the fibres tend to develop excessive surface fuzz and tend to break easily.

The rate of heating of the precursor fibre as it passes through the heating zones is preferably within the range of 300°C/min to 2000°C/min in the first heating zone, more preferably within the range of 500°C/min to

1500°C/min, and preferably within the range of 2000°C/min to 10,000°C/min in the second heating zone.

The treatment time of the precursor fibres in the first heating zone, which is defined as the time during which the fibres are in the zone at a temperature above 1000°C. is preferably within the range of 10 seconds to 10 minutes, more preferably 30 seconds to 3 minutes.

An embodiment of the present invention will now be described by way of example with reference to the drawings, in which:

Fig. 1 is a view in longitudinal section of graphitizing apparatus for carrying out the process of this invention;

Figs. 2 and 3 respectively show typical examples of temperature profiles in the furnace tubes used in the respective heating zones.

Referring to Fig. 1, the separate first and second heating zones (furnaces) have respectively furnace tubes (2,3) to which heat is applied in a conventional way. The furnace tubes (2,3) are surrounded with insulation (4,5). An inert gas such as nitrogen is supplied to the furnaces (I,II) through pipes (6), and the gas is removed from the furnaces by pipes (7). At each end of each furnace there are furnace seals (8), supplied with inert gas through supply pipes (9).

As shown in Fig. 1, the precursor fibre (1) is first conducted through the seal (8) into the furnace tube (2) of the furnace (1) which provides the first heating zone. The temperature profile inside this furnace tube (2) is controlled, to produce a profile as shown in Fig. 2. This is done by locally controlling the heat input at selected spots along the tube (2), in a conventional way. When the precursor fibre is a carbon fibre, it is treated in this furnace until its weight is reduced to about 93% to 95% of its previous weight, and then it is conducted into the furnace tube (3) of the furnace (II) which provides the second heating zone. There the fibre is heated again, and is converted into a graphite fibre. Fig. 3 shows a typical temperature profile of the furnace tube (3) of the second heating zone, the maximum temperature of which is set at about 2500°C in this case.

By use of the present invention, a more efficient and therefore more profitable process for the manufacture of graphite fibres is possible. These advantages can be realised for the following reasons:

(a) The heating zone is divided into two independently controlled zones, giving increased flexibility with the rate of heating the fibre. There is also better control of the temperature profile within the furnace;

(b) The weight loss of the precursor fibre during initial heating up to 1500°C is usually large. It has been found that the use of a high rate of heating in the stage up to 1500°C tends to damage the precursor fibre. In the conventional, single heating zone system, the overall rate of heating must be so low that it restricts overall productivity. By use of the present, double heating zone system, it is possible to select optimum rates of heating for the first and second heating zones independently of each other. This allows manufacture of high quality graphite fibres with increased productivity;

(c) With the process of the present invention, it is possible to reduce the overall length of the heating zone by dividing it, and the maintenance and custody of the furnace can thereby be made easier. The life of a furnace tube in the second furnace is much shorter than that of one in the first furnace, because of the higher temperature at which it operates. However, clearly the tube in the first furnace need not be replaced merely because the tube in the second furnace has to be, and also the tube in the second furnace, being relatively short compared with the tube in a single-heating zone furnace, is easier to handle. Thus, costs of time, labour, and materials can be reduced. Surprisingly the energy consumption can also be reduced. This is because it has been found possible to string up the fibres without lowering the temperatue of the furnace.

EXAMPLES.

Carbon fibres were produced from acrylic fibres and carbonized in an inert atmosphere, the maximum temperature of which was 1100°C. They were taken from creels and heated to produce graphite fibres using separate furnaces as shown in Fig. 1. The conditions were varied, there being 3 conditions within the scope of the invention (Examples 1-3) and four conditions outside the scope of the invention (Comparative Examples 1-4). The conditions are shown in Table 1.

TABLE 1.

	Maximum Temp. First Furnace	Maximum Temp. Second Furnace	Rate of heating from 1300 C to 1500 (First furnace)(C/min)
Comparative Ex.1	not used	2450	----
Comparative Ex.2	1400	2450	6000(Second furnace)
Example 1	1600	2450	450
Example 2	1800	2450	750
Example 3	2000	2450	1200
Comparative Ex.3	2250	2450	2100
Comparative Ex.4	2450	not used	----

The resulting data are shown in Table 2. Moreover, the usual temperatures, the periods of time between changes of furnace tubes and the number of days required to change them, with respect to both first and second furnaces, are shown in Table 3. Some of the properties of the fibres made in these examples are shown in Table 2.

Table 3 gives an indication of the lifetime of the furnace tubes, at different operating temperatures, and the time taken to change them.

TABLE 2.

	Tensile Strength (kg/mm^2)	Young's Modulus ($10^3/kg/mm^2$)	Surface Fuzz (amount formed)	Fibre Breakage	Weight Yield/Weight of precursor fibre (%) After first heating Zone	Weight Yield/Weight of precursor fibre (%) After Second Heating Zone
Comparative Example 1	171	37.3	very much	frequent	----	93.5
Comparative Example 2	183	39.0	very much	none	95.8	93.2
Example 1	249	40.0	very little	none	94.1	93.0
Example 2	260	40.5	very little	none	93.7	93.1
Example 3	244	40.6	very little	none	93.4	92.8
Comparative Example 3	212	40.4	much	none	93.5	93.0
Comparative Example 4	177	41.2	much	considerable	92.9	----

TABLE 3.

	Maximum Temperature	Period between Changes	Days for Changing
First furnace	1800°C	6 months	2
First furnace	2450°C	20 days	2
Second furnace	2450°C	1 month	0.5

CLAIMS:

1. A process for the manufacture of graphite fibre by graphitizing precursor fibre characterised in that the precursor fibre or fibres pass successively through separately controllable first and second heating zones, both containing an inert atmosphere, the temperature at the hottest point in the said first heating zone being in the range of about 1500°C to about 2100°C, and the temperature at the hottest part in the said second heating zone being at least about 2100°C.

2. A process according to claim 1 in which the two heating zones are constituted by separate furnace tubes separately heated and furnished with inert atmosphere.

3. A process according to claim 1 or claim 2 in which the said temperature at the hottest point in the first heating zone is in the range of from 1700°C to 1900°C.

4. A process according to any one of claims 1 to 3 in which the said temperature at the hottest point in the second heating zone is in the range of 2100°C to 3500°C.

5. A process according to claim 4 in which the said temperature at the hottest point in the second heating zone is in the range of from 2300°C to 2700°C.

6. A process according to any one of the preceding claims in which the average rate of heating of fibre in the first heating zone is in the range of from 300°C/min to 2000°C/min.

7. A process according to any one of the preceding claims in which the average rate of heating of fibre in the second heating zone is in the range of from 2000°C/min to 10,000°C/min.

8. A process according to any one of the preceding claims in which the precursor fibre is a converted polyacrylonitrile fibre.

9. A process according to claim 8 in which the precursor fibre is a carbon fibre obtained from an acrylic fibre comprising at least 95 mol % of acrylonitrile and up to 5 mol % of one or more ethylene-type vinyl compounds copolymerizable with acrylonitrile by heating and oxidizing the said acrylic fibre in an oxidizing atmosphere at a temperature in the range of about 200°C to about 400°C, and then heating the oxidized fibre so formed in an inert atmosphere at a temperature of from 400°C to 1500°C.

10. A process according to claim 8 in which the precursor fibre is an oxidized fibre obtained from an acrylic fibre comprising at least 95 mol % of acrylonitrile and up to 5 mol % of one or more ethylene-type vinyl compounds copolymerizable with acrylonitrile, by heating and oxidizing the said acrylic fibre in an oxidizing atmosphere at a temperature of from about 200°C to about 400°C.

Fig.1.

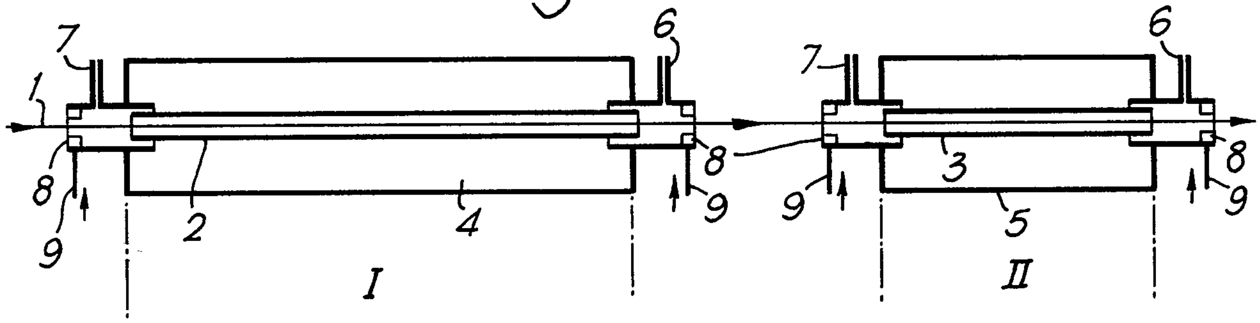


Fig.2.

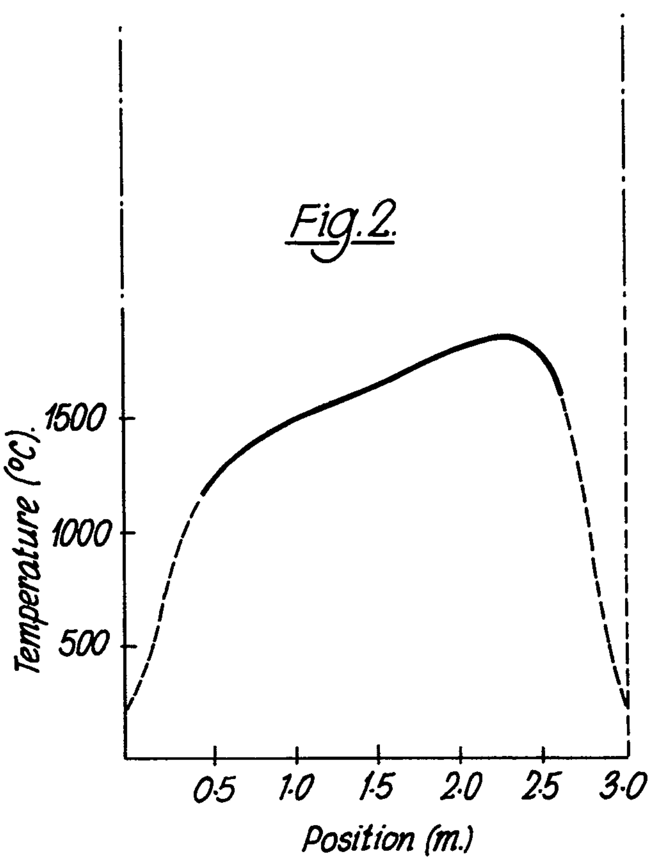
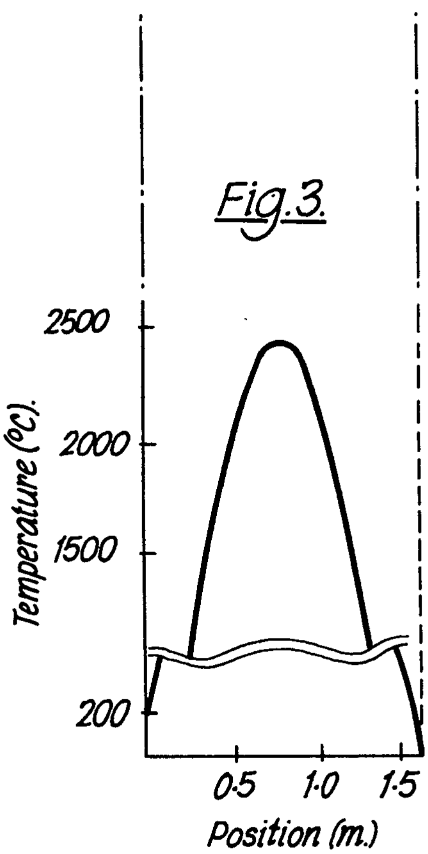


Fig.3.



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EUROPEAN SEARCH REPORT

Application number
EP 79 30 1690

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	DE - A - 2 178 193 (UNION CARBIDE) * Claims; page 20, line 33 - page 25, line 8 *	1,2,4, 5	D 01 F 9/22 9/20 9/14
	--		
	FR - A - 2 006 543 (ROLLS-ROYCE) * Claims; page 3, lines 12-31 *	1,2,4, 5,8	

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

D 01 F 9/14
9/12
9/20
9/22

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10-06-1980	HELLEMANS

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