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The catalytic effect of platinum on the oxidation of carbon fibres

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Ex-PAN based carbon fibres (5C) were oxidized at 500, 550 and 600 °C in dry air while being contained in both silica and platinum specimen holders. The weight loss measurements taken as a function of time revealed that those fibres oxidized in platinum exhibited a much higher oxidation rate than those exposed in silica. Additionally, those fibres oxidized in platinum underwent unusual changes in fibre morphology. "Spheres" formed along the longitudinal axis of many fibres, and in one instance, a fibre underwent bifurcation, with a sphere forming on each remaining fibril. Likewise, severe surface pitting occurred. It is believed that these changes in microstructure combined with the increased oxidation rate are a result of a catalysed oxidation reaction(s) caused by the presence of platinum, or perhaps by a co-catalytic reaction between platinum and impurities found on the surface of the fibres.

1. Introduction

With the constant need for high-temperature, high-strength lightweight materials, a concentrated effort has been developing over the last 20 years to manufacture carbon fibre-based composites that can be exposed to elevated temperatures. The major drawback of these composites is that if the fibres are exposed to oxygen, they will oxidize, and the mechanical integrity of the composite will be severely degraded.

Thus, it is necessary to understand the oxidation behaviour of the fibres prior to being placed in a high-temperature matrix. On examining the carbon fibre oxidation literature, it becomes evident that many factors have a significant influence on the oxidation process. These factors include fibre precursor, fibre modulus, processing temperatures during manufacturing, etc. Saito and Ogawa [1], Sheppard [2], Eckstein and co-workers [3, 4] and McMahon [5] have shown that various types of carbon fibres which exhibit different material properties behave differently in oxidation. Additionally, it has been shown that the presence of certain elements such as the transition and alkali metals [6–10]; and substances such as colloidal platinum, platinum black [11] and silver oxide [12] have been observed to have a catalytic effect on the oxidation of carbon. The purpose of this investigation is to examine the effects of platinum on the oxidation behaviour of PAN-based 5C carbon fibre.

2. The structure of carbon fibres

Before undertaking a detailed discussion of the catalysis of carbon fibres, it is first necessary to understand the physical structure of the fibres. The discussion will be limited to PAN-based fibres, as this was the material used in this investigation. (The steps involved in the production of these fibres have been described elsewhere [13–15].) Fig. 1 shows a schematic cross-section of a typical PAN-based fibre. The fibre is not homogeneous in structure, but rather exhibits a "skin–core" heterogeneity [16]. The core is comprised of amorphous carbon arranged in a ribbon-like structure (Fig. 2). The skin of the fibre consists of oriented crystallites of graphene – a two-dimensional sheet of carbon atoms (hexagonally packed), often containing vacancy–cluster defects (Fig. 3). Butler and Diefendorf [17] have reported the skin to be between 100 and 150 nm thick. Wicks and Coyle [18], however, have reported this skin thickness to be in excess of 1 μm.

Fig. 4 is an artist's impression of a typical high-modulus PAN-based fibre, which shows both the oriented skin and the ribbon-like fibre core. Originally, it was believed that this heterogeneous structure was found in material where the core was not fully oxidized in the precarbonization steps [19]. Later studies by Knibbs [20], however, showed a skin–core

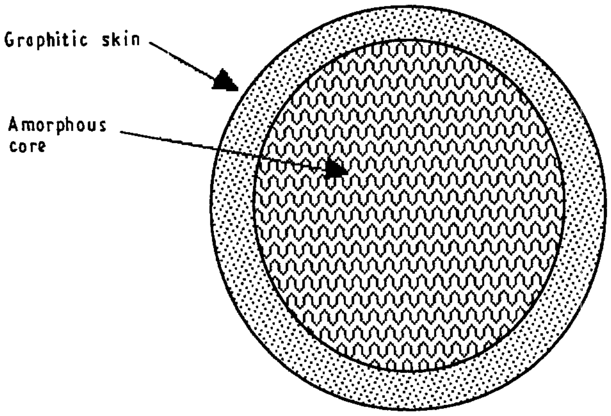

Figure 1 Schematic cross-section of a typical PAN-based fibre (after Johnson [16]).

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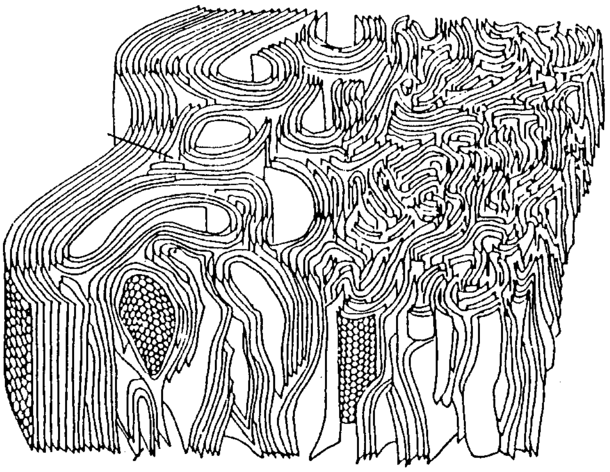


Figure 2 Sketch showing ribbon-like structure of the core of a PAN-based fibre [21].

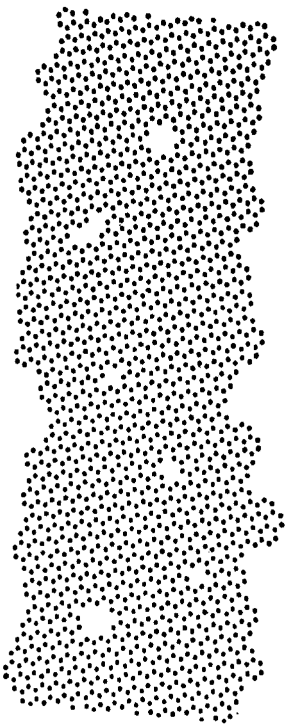


Figure 3 Schematic diagram of two-dimensional graphene, showing vacancy clusters and defects [21].

heterogeneity even for fully stabilized fibres. As the oxidation behaviour of carbon is directly linked to its structure, this dual-phase microstructure may have a marked effect on the fibre morphology of carbon fibres oxidized in the presence of platinum foil.

3. Theories of catalysis

Several theories have been put forth to explain the catalytic effects of certain compounds on the oxidation of carbon: the electronic interaction of the catalyst with carbon [23], the intermediate compound theory, and theories which are based on the concept of active surface areas.

The electronic interaction theory asserts that during oxidation, catalysts affect the nature of chemical bonds between carbon atoms. When an oxygen atom is adsorbed at a potential reaction site on the carbon surface, two different bonding scenarios are possible: Types I and II. Type II is more favourable for the evolution of carbon monoxide, because the carbon–carbon bonds which must be broken are weaker. Likewise, the carbon–oxygen bonds in Type II more closely resemble the bonding found in a molecule of carbon monoxide. It has been suggested by Long and Sykes [24] that catalysts alter the bonding between carbon atoms and make it more like Type II and less like Type I by changing the distribution of π electrons. This change lowers the activation energy and increases the rate of reaction.

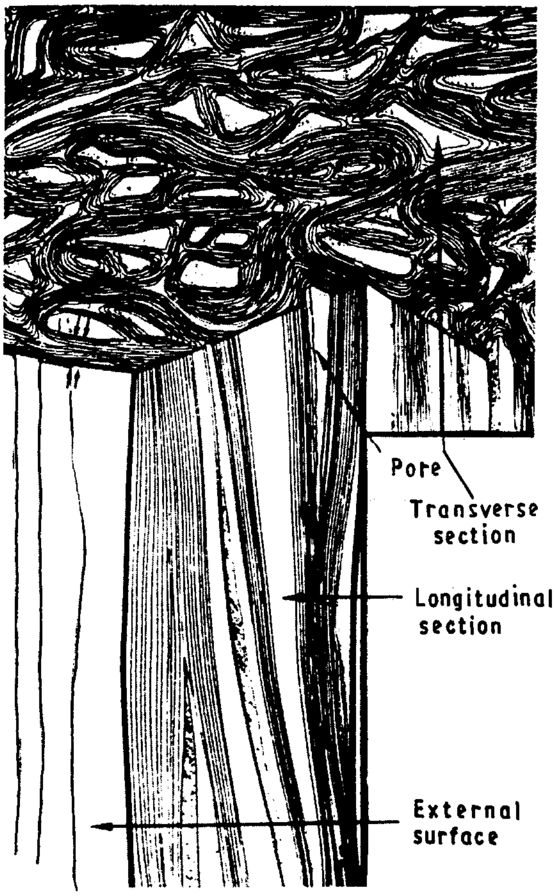
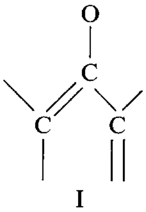


Figure 4 Artist's impression of a PAN-based fibre [22].



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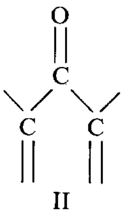

II

The intermediate compound theory proposes that the presence of a catalyst causes the formation of a secondary molecule such as an adsorbed surface oxide, whose decomposition, while in contact with the carbon, leads to the acceleration of the oxidation process. For example, consider the following chemical reactions which occur in the carbon/carbon dioxide system

$$C + CO_2(g) \rightarrow 2CO(g) \qquad (1)$$

$$C + CO_2(g) \rightarrow CO(g) + C(O) \qquad (2)$$

$$C(O) \rightarrow CO(g) \qquad (3)$$

where C(O) is an intermediate surface oxide. According to the intermediate compound theory, the formation of C(O) is promoted by the presence of a catalyst which, in turn, increases the oxidation rate of carbon.

Perhaps the most recent theory of catalytic oxidation to be put forth is based on the concept of active surface areas (ASA) [25, 26]. According to the ASA theory, gas–solid chemical reactions occur at specific surface sites which are more favourable for surface adsorption, both energetically and structurally. Those sites which are more favourable for chemical reaction are labelled "active". A catalyst serves to alter the reacting surface such that a larger fraction of the total surface is an active surface area. There is an upper bound to this process, however. If the concentration of the catalyst exceeds this upper bound, the reaction will be inhibited, or no further catalytic benefit will be realized.

4. Materials characterization

All of the fibres used in this investigation are 5C PAN-based carbon fibres (Fortafil Fibre division of Akzo International). The fibres were received on three large spools, with each spool containing a "tape" of carbon fibres consisting of four fibre tows (50 000 filaments per tow) in width (approximately 100 mm) and 60 m long. The fibres were backed by a strip of paper. By taping the fibres to the paper, the fibres were easily cut. The material properties of the Akzo fibres are given in Table I. An optical micrograph of a polished transverse section of a fibre bundle is shown in Fig. 5. Although they seem to be circular in cross-section the scanning electron micrograph of an "end-on" view of an as-received fibre shown in Fig. 6 reveals that the surface of the fibres is "ribbed" or "fluted".

TABLE I Properties of Akzo 5C fibres

Tensile strength	2760 MPa
Tensile modulus	345 GPa
Ultimate elongation	0.8%
Density	1.8 g cm^{-3}
Filament shape	Round
Filament diameter	≈7 μm

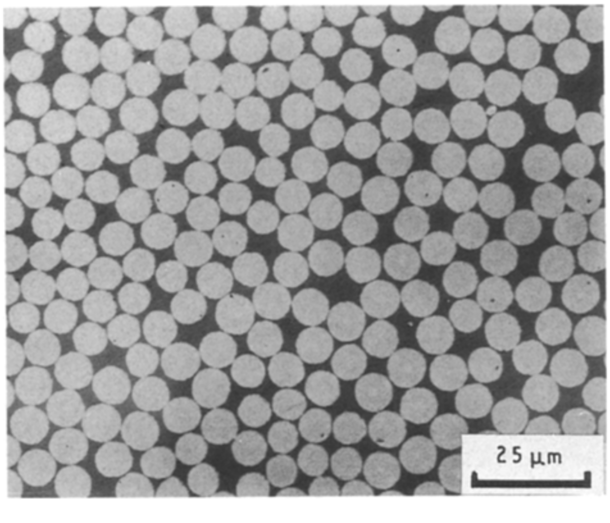

Figure 5 Optical micrograph of as-received fibres.

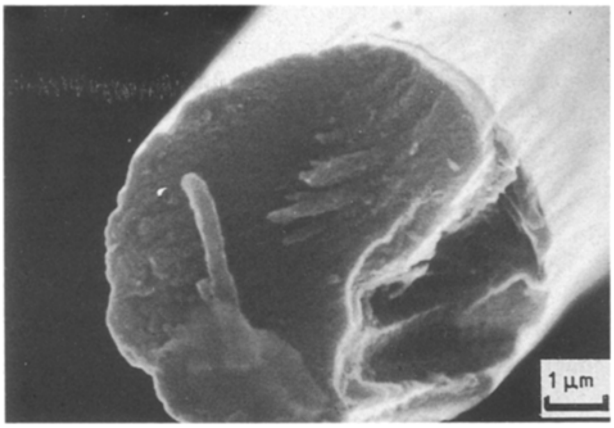

Figure 6 Scanning electron micrograph of an "end-on" view of a fibre showing ribbed fibre surface.

The fibres were analysed using the scanning Auger microprobe. Trace amounts of sodium and chlorine were detected on the fibre surface; however, sputtering for 2 min at an accelerating voltage of 5 kV removed all evidence of these elements.

5. Experimental procedure

The goal of this investigation was to determine the oxidative stability of the Akzo 5C carbon fibres. Because the fibres were to be eventually used in carbon fibre/glass matrix composites, it was important to understand their basic oxidation properties, including the compounds that could possibly act as catalysts. As mentioned previously, a number of investigations have examined the effects of catalytic compounds which were deposited directly on carbon surfaces; however, no work has shown the effect of platinum which was not on the carbonaceous surface, but rather was in close proximity. This is directly applicable to the oxidation testing of carbon. Because of the extreme temperatures encountered in oxidation experiments, it is often necessary to use platinum crucibles/specimen holders to contain the sample. To determine if platinum would effect these experiments, a two-stage experimental programme was proposed.

Fibres were exposed to oxygen-containing environments in vitreous silica and platinum holders. The latter consisted of a piece of platinum foil which was shaped into a "U", while the former was obtained by longitudinally sectioning a quartz tube (i.d. equals 13 mm, length equals 38 mm, wall thickness equals 0.8 mm). All oxidation experiments were done in an environmentally controlled tube furnace comprised of a quartz tube and a stainless steel gas delivery system. These materials were chosen to minimize the possibility of contamination. Likewise, prior to any experiment, the alumina boat used to contain the holder and fibres and the sample holder (either platinum or vitreous silica) were baked out at 800 °C for 3 h to remove any volatile substance and water vapour. The temperature of the furnace was lowered to the desired test temperature, the temperature was allowed to equilibrate, and the fibres were placed in the holder, which was subsequently placed in the alumina boat and pushed into the centre of the furnace. Each oxidation sample contained 20 000–50 000 fibres approximately 5 cm (2 in) long. At periodic times, the fibres and the holder were removed from the alumina boat, placed in a desiccator to cool, weighed on an analytical balance, and replaced in the furnace.

6. Results and discussion

Figs 7 and 8 show the data collected from the oxidation of carbon fibres in platinum and silica holders at 500 and 550 °C, respectively. The data are plotted as change in mass normalized by initial surface area (specific mass loss) versus time. As the reaction between carbon and oxygen occurs on the surface of the fibres, it is reasonable to normalize the changes in mass by the initial surface area of the fibres, where surface area is defined as $2\pi r_0 l_0 + 2\pi r_0^2$, with r_0 equal to the initial radius (≈ 3.5 µm) and l_0 equal to the initial length (5 cm; 2 in). Knowing the fibre dimensions, mass, and density, the number of fibres in each oxidation sample was determined, and the surface area was then calculated. From the data presented in Figs 7 and 8, it is evident that the fibres in the platinum holders are being oxidized more rapidly than those in the silica holders at both 500 and 550 °C.

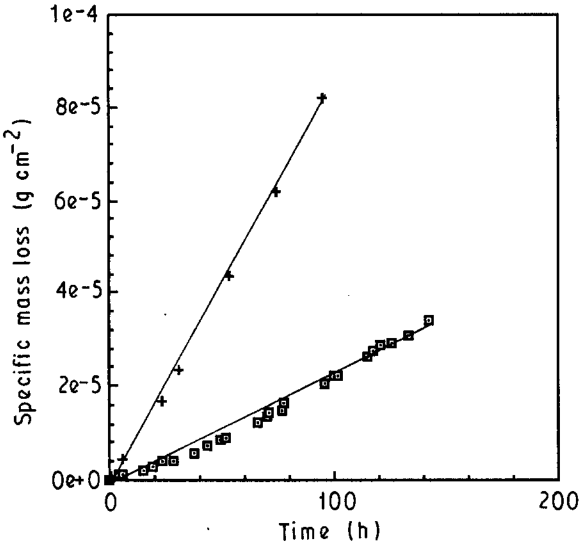

Figure 7 Plot of specific mass versus time for fibres oxidized in (+) platinum and (⊡) silica holders at 500 °C in dry air.

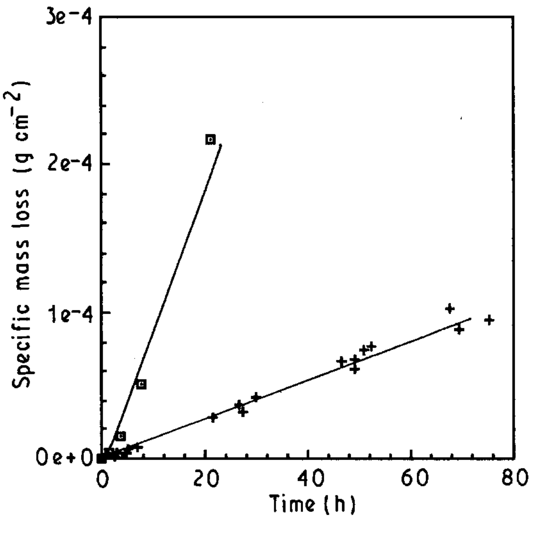

Figure 8 Plot of specific mass versus time for fibres oxidized in (⊡) platinum and (+) silica holders at 550 °C in dry air.

Attempts were made to oxidize fibres at 600 °C in platinum; however, the oxidation rate was too rapid to permit periodic weight measurements over a long enough period of time. The portion of the fibres which were surrounded by the platinum was totally consumed in approximately 24 h. Data were collected at 600 °C for fibres oxidized in the silica holders.

The catalytic effect produced by the presence of platinum also produced some very unique morphological changes in the fibres. Fig. 9 shows another micrograph of the as-received material, taken on the scanning electron microscope. Fig. 10 shows a scanning electron micrograph of the fibres after being oxidized in dry air at 500 °C in platinum. Notice the extreme pitting. This effect was not manifested in the fibres oxidized under the same environmental conditions in a silica holder, as shown in Fig. 11.

Further evidence of the catalytic effect of platinum is shown in Fig. 12. The fibres in this micrograph show the formation of "spheres" along the longitudinal axis of the individual filaments. The diameter of these spheres is approximately the same size as the diameter of the original fibre (7 µm). Fig. 13 shows a low-magnification scanning electron micrograph illustrating that the formation of these spheres is not an isolated event, but rather a widespread occurrence.

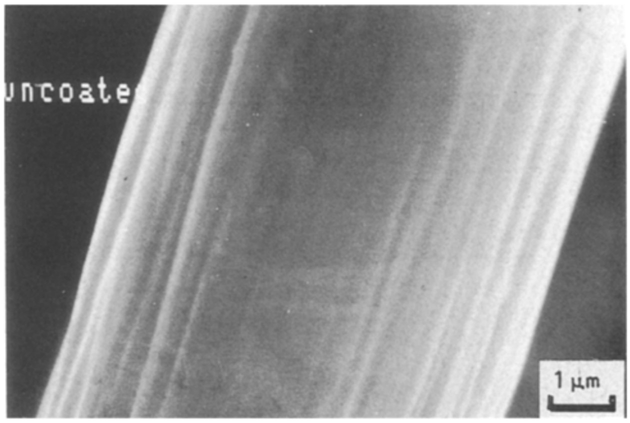

Figure 9 Micrograph of the as-received fibres.

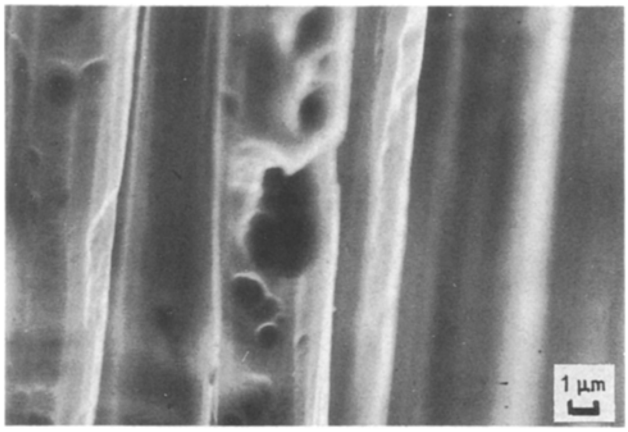

Figure 10 Micrograph of fibres oxidized in a platinum specimen holder showing pitting on the fibre surface.

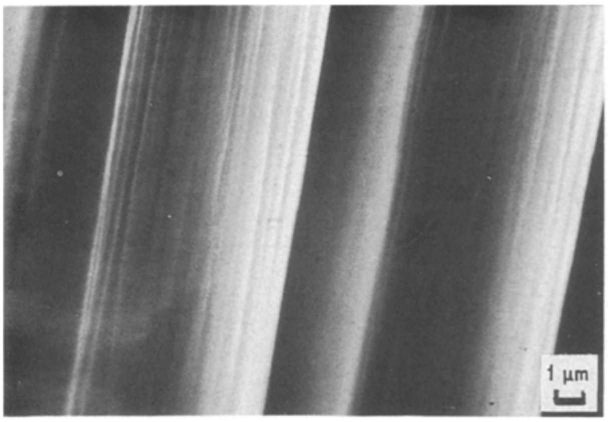

Figure 11 Micrograph of fibres oxidized in a silica specimen holder.

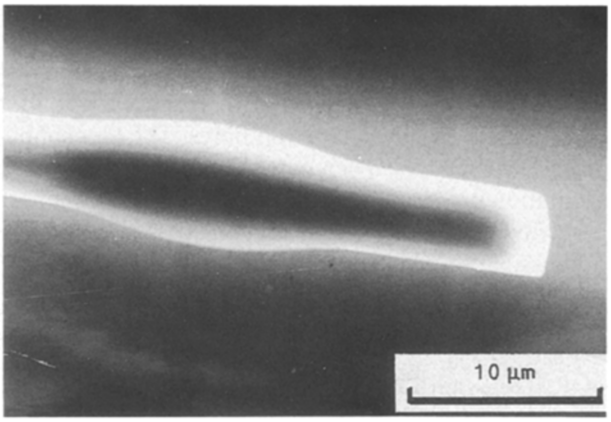

Figure 14 Micrograph of a sphere in its preliminary stages of formation.

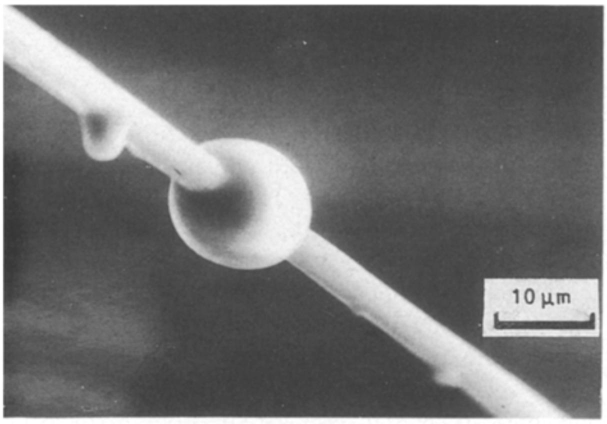

Figure 12 Micrograph of a fibre oxidized in a platinum holder showing the formation of a sphere along the longitudinal fibre axis.

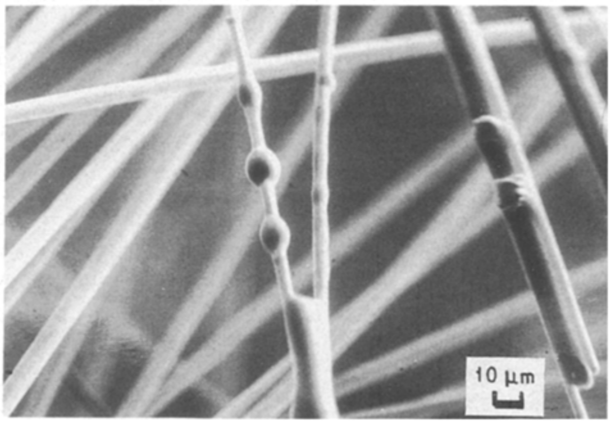

Figure 15 Micrograph of a fibre which has bifurcated. Spheres have formed on each of the remaining filaments.

Figure 13 Micrograph showing the widespread nature of the formation of the "spheres".

Fig. 14 shows what appears to be a sphere in its "embryonic" stages of formation. The sphere is just beginning to pinch off.

Perhaps the most unusual structure caused by the apparent catalytic effect of platinum is shown in Fig. 15. The original fibre has bifurcated into two separate filaments, and the aforementioned spheres have formed on each strand.

This pitting shown in Fig. 10 has been reproduced under different test conditions. Frischknecht [27] observed pits on the surface of fibres that had been oxidized at 700 °C in air. The presence of platinum caused this pitting to occur at a temperature 200 °C lower than those observed by Frischknecht.

Perhaps the formation of the pits themselves, may be analogous to aqueous corrosion. In corrosion, pits form because certain compounds/elements obtain abnormally high concentrations at certain locations along the surface. Trace amounts of sodium, a known catalyst in the oxidation of carbon, were detected on the fibre surface of the as-received fibres using the scanning Auger microprobe. Perhaps at places on the fibre contaminated with sodium, the platinum and sodium act as reinforcing catalysts.

The formation of the spheres and the splitting of the fibres as shown in Figs 12–15 are not as easily explained. The fibres used in this investigation did not receive any post-manufacturing surface treatment of any kind. It can be stated, therefore, that the spheres are not formed by the "pinching off" of a foreign coating. The sphere shown in Fig. 12 appears to have the same diameter as the as-received fibres, approximately 7 μm, which is the original diameter of the as-received fibres. Perhaps these very specific locations did not oxidize, either because of the proximity of the fibre segment to the platinum, or because of local changes in fibre structure which give rise to small, more oxidation-resistant regions.

Fig. 15, however, is rather puzzling. The fibre in this scanning electron micrograph has bifurcated, and spheres have formed on each fibril. It is possible that these fibrils are the remains of the partially graphitic skin present in the as-received fibres. The amorphous core seems to have been completely consumed in the oxidation process. This fibre morphology has not been reported in the literature previously; therefore it is impossible to determine a direct explanation of these phenomena.

6.1. Calculation of activation energies

In knowing the values of the specific mass loss as function of time, activation energies can be calculated for the oxidation of carbon fibres in platinum and silica. The slopes of the lines in Figs 7 and 8 are directly proportional to the rate of reaction of carbon with oxygen. Knowing that these reactions are thermally activated, it is reasonable to assert that they can be adequately described by a classical Arrhenius relationship

$$\text{Rate} = Ke^{-Q/RT} \qquad (4)$$

where K is a constant, Q is the activation energy, T the absolute temperature, and R the ideal gas constant. By plotting the log (reaction rate) versus T^{-1}, the slopes of the lines will be $-Q/R$, and the y intercept will be the constant K. Fig. 16 shows this plot for fibres oxidized in the silica holders at 500, 550, and 600 °C. The calculated activation energies and pre-exponential terms for the fibres oxidized in silica and platinum are shown in Table II.

TABLE II Activation energies for carbon fibres oxidized in platinum and silica holders

Sample holder	Pre-exponential constant, K ($\text{g cm}^{-2}\text{s}^{-1}$)	Activation energy (kJ mol^{-1})
Platinum	1.6×10^{14}	301
Vitreous silica	1.1×10^{8}	177

A true catalyst should lower the activation energy of a chemical reaction(s). In this investigation, even though the overall reaction rate is higher for the fibres reacted in platinum foil, the calculated activation rate is larger than the activation energy calculated for the fibres oxidized in silica. If the data for the fibres oxidized in the platinum and silica holders shown in Table II are plotted on an Arrhenius plot, the lines intersect at a temperature of 785 °C (Fig. 17). Mathematically, this indicates that above this temperature, oxidation in the platinum and silica holders should proceed at the same rate.

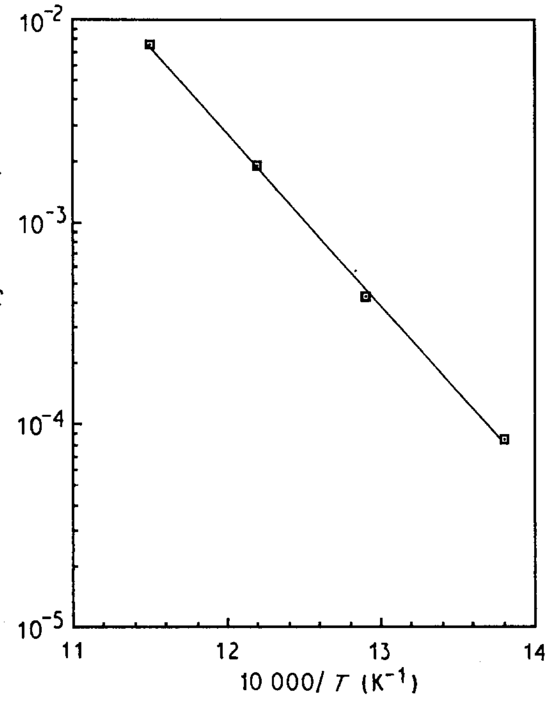

Figure 16 An Arrhenius plot for reaction rates of fibres oxidized at 500, 550, and 600 °C (for fibres in silica holders only) in dry air.

7. Conclusion

The effect of platinum on the oxidation of carbon fibres is manifested in both the reaction rate and morphology of the fibres. The exact cause of these manifestations, beyond what has already been proposed, is unclear.

The presence of platinum did produce an increase in the reaction rate in the oxidation of the carbon fibres. The fibres oxidized in platinum, however, exhibited a higher activation energy than those oxidized in silica. The pre-exponential term for the fibres oxidized in platinum, was six orders of magnitude larger than the fibres oxidized in the silica holders. This is responsible for the increase in oxidation rate.

As mentioned previously, the unique changes in fibre morphology can be caused by several factors such as localized differences in fibre structure and localized concentrations of impurities. A confirmation of either of these explanations as the true cause for the formation of "pods" would require a very detailed analysis of the atomic structure of these fibres. The

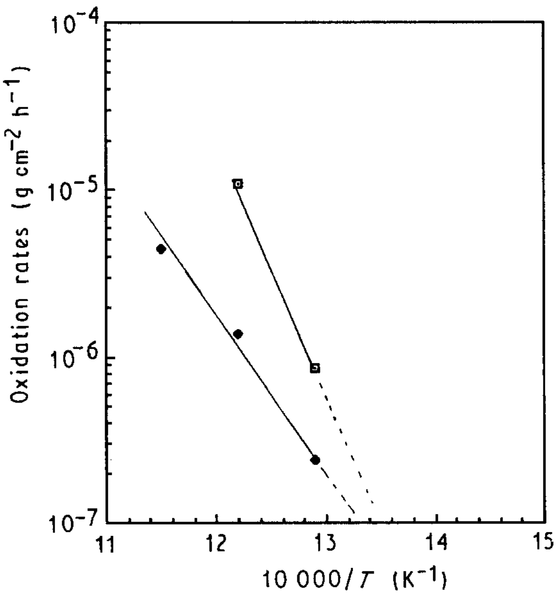

Figure 17 An Arrhenius plot for oxidation data of fibres oxidized in (□) platinum and (◆) silica specimen holders.

significance of these experiments, however, is that these changes in reaction rate and fibre morphology are only observed in the presence of platinum.

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