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The oxidation behaviour of carbon fibres

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The oxidation behaviour of carbon fibres has been studied in air at different temperatures from 550 to 860 °C. A linear relationship has been observed between the carbon fibre size and oxidation time. Experimental results show that the oxidation process is in a mixed control zone, i.e. controlled both by diffusion of the gaseous reactant and product within the boundary layer and by the chemical reaction. The activation energy of carbon burn-off is 140 ± 5 kJ mol^{-1}. The uniform nature of the surface oxidation makes it possible to re-size the carbon fibres to smaller diameters.

1. Introduction

Carbon fibre reinforced composites (ceramics, glass, glass–ceramics and polymers) have received much attention in recent years. Their good mechanical, thermal and chemical properties, especially from the point of view of property/weight and property/cost ratios, make these materials widely applicable in many industries. At high temperatures, however, the composites are restricted to inert atmospheres in order to prevent degradation of the carbon fibres [1, 2]. Once the strong interfacial bond between the fibre surface and the matrix has been debonded by oxidation, a significant reduction in the mechanical properties of the composite is unavoidable [2–4]. The room-temperature bend strength of a carbon fibre reinforced glass–ceramic, for example, could be reduced to nearly zero after 50 h heating in air at above 500 °C [3]. The oxidation behaviour of the fibres is therefore one of the major limiting factors concerning the usage of these materials.

Whilst the degradation of carbon fibres at high temperatures is a drawback for those composites used as structural materials, the uniform nature of the surface oxidation could be an advantage for re-sizing the fibres. Bleay and Scott [2], in studying the oxidation of carbon fibres in Pyrex matrix glass, found that the oxidation took place uniformly around the fibre circumference. The oxidation rate, due to the slow diffusion of oxygen through Pyrex glass, was about 0.5 μm h^{-1} at 500 °C in air. Trumbauer *et al.* [5] also investigated the oxidation rate and microstructure of two different carbon fibres in both as-received and Pyrex glass encapsulated forms. One of the fibres, IM-7, oxidized on all surfaces resulting in a significant reduction of the fibre diameter from 5.5 to 2.5 μm after 60% burn-off.

In the current work the oxidation kinetics of as-received carbon fibres has been studied with the fibres being oxidized in air at different temperatures. Use of diametral measurement and thermal gravimetric analysis (TGA) has allowed the reaction characteristics of the oxidation process to be obtained.

2. Experimental procedure

The high modulus, low ash content carbon fibres used were supplied by Courtaulds Grafil Ltd, Coventry, UK and have a circular cross-section of 7 to 8 μm. The fibre surfaces are smooth but with many fine ridges along the spinning direction with a height of 50 nm or less. The tow size is approximately 10 000. According to the manufacturer, the precursor material was carbonized at 2500 °C and has the lowest metal ion impurity level in the production range of carbon fibres. An approximate elemental analysis gives: C 99.16%, H 0.03%, N 0.40% and ash 0.01%. The sodium content in the fibre was reported as 81 p.p.m.

A muffle furnace was used for the oxidation experiments, no air agitation was employed and the temperature accuracy was estimated as ± 7 °C. The fibres were chopped to about 40 mm in length and two different methods of placing fibres in the furnace were tried. First the fibres were put in a ceramic boat with all the fibres lying close together in a parallel manner, and second the fibres were carefully arranged with spaces left between them and without the use of the boat. The oxidation rate was measured using the second arrangement in order to minimize uneven oxidation due to the boundary layer effect.

A stage microscope attached to a microhardness tester (Model M-400, Leco Corporation, USA) was used for the majority of the size measurements. The

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microscope was calibrated against a standard graticule with 10 μm teils. The uncertainty of the readings was within 0.4 μm. Selective size measurements were also made with a scanning electron microscope (SEM). The disagreement of the reading between the two techniques was within 1% for the as-received fibres. The SEM was also used for investigating the microstructure of the fibres, the samples being prepared by placing the fibres either on a nickel print and then gold coating or on carbon stickers. The oxidation weight loss in relation to firing time was recorded isothermally by TGA. The crystal structure and chemical composition of the fibres were determined by X-ray diffraction using CuK_α radiation and energy-dispersive X-ray analysis (EDX) in the SEM.

3. Results and discussion

3.1. Oxidation rate

The experimentally observed relationships between the carbon fibre size and oxidation time are given in Fig. 1. Some low-temperature experimental points are not shown in the diagram because of the scale limit. Linear relationships were obtained for all the temperatures tested. This means that the effective reaction rate of the oxidation processes:

$$C + O_2 = CO_2$$

and

$$C + 0.5O_2 = CO$$

is of a fixed order at all the temperatures under investigation. The process can then be expressed as

$$\frac{dm}{dt} = -kA$$

where m is the number of moles of a carbon fibre at time t, A the overall fibre surface area and k the generalized reaction rate constant which is a non-negative number dependent on carbon fibre properties, firing temperature, oxygen and carbon oxide partial pressures. Ignoring the surface areas of the fibre ends since the ratio to length to diameter is very large, the following equation is obtained:

$$m = \frac{\pi D^2 L \rho}{4M}$$

where D, L and ρ are the diameter, length and density of the carbon fibres, respectively, and M the molecular weight of carbon. Substituting for m in the differential equation and noting that $A = \pi DL$ we have

$$\frac{dD}{dt} = -K$$

where the coefficient $K = 2kM/\rho$. The integral form of the above equation shows that the fibre diameter changes linearly with the oxidation time:

$$D = D_0 - Kt$$

where D_0 is the original fibre size at $t = 0$.

By using the Arrhenius equation

$$k = k_0 \exp\left(-\frac{Q}{RT}\right)$$

the activation energy of carbon burn-off, Q, can be calculated statistically from the slope of the line. The Arrhenius plot is shown in Fig. 2 and the activation energy for carbon burn-off was found to be 140 ± 5 kJ mol^{-1} where the uncertainty was estimated at the 95% confidence level. The co-relation coefficient of the regression is 0.998 96 ($n = 8$).

Horton [6] measured the pyrolytic graphite oxidation rate in dry air in the temperature range 614 to 1568 °C and found the activation energy to be 138 kJ mol^{-1}, which is very close to the value obtained in this work. Lain *et al.* [7] and Clark *et al.* [8] also reported the activation energies for carbon oxidation of Graphon powder and two types of carbon fibre in the temperature ranges 625 to 675 °C [7], 500 to 600 °C and 394 to 454 °C [8], respectively. They all fall

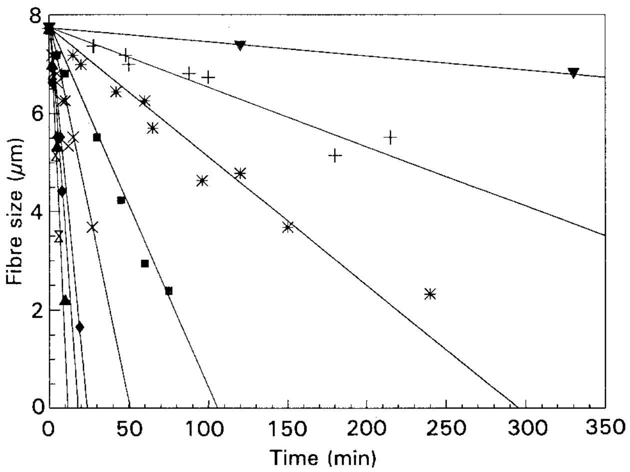

Figure 1 Observed influence of oxidation time and temperature on carbon fibre size. Straight lines are the linear least-squares fits of the experimental points: (▼) 550 °C, (+) 600 °C, (∗) 650 °C, (■) 700 °C, (×) 750 °C, (◆) 800 °C, (▲) 830 °C, (⧖) 860 °C.

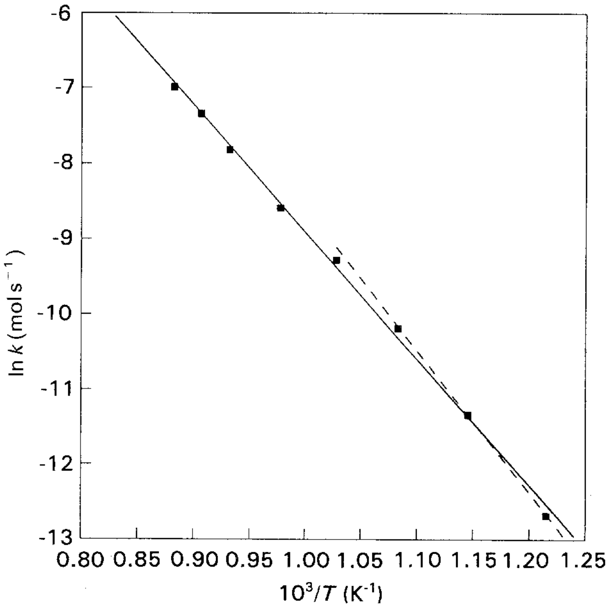

Figure 2 Relationship between ln$k$ and $1/T$: (—) $y = 7.939 - 16.853x$, (- - -) $y = 10.416 - 19.000x$. From the slope of the solid line the activation energy for carbon burn-off was calculated as 140 kJ mol^{-1}. The dashed line shows a possible higher activation energy at the lower temperature range.

into the 190 ± 10 kJ mol^{-1} range. From Fig. 2 it can be seen that the acceleration of the reaction rate slows down at lower temperatures. This introduces a slight curvature to the Arrhenius plot and consequently a higher activation energy for the lower temperature range as shown in Fig. 2 with a dashed line. This may be an indication of a reaction mechanism change, with the transition region being around 600 °C. In Horton's work [6], a similar result was found but at a higher temperature range (about 1000 °C).

The presence of gaseous diffusion boundary layers around the fibre surfaces was observed in the experiments. The fibres heated in the form of a bundle, where the boundary layers will have overlapped each other, experienced a slower and more uneven oxidation rate than when well-separated fibres were heated. This phenomenon indicates that the oxidation process is in a mixed control zone with both mass transport and chemical reaction being the limiting steps of the oxidation process.

The diffusion boundary layer may also have some influence on the observed activation energy. If the oxidation process is in the mixed control zone, the experimentally determined activation energy will represent the energies for both the chemical reaction and gas diffusion. The value will therefore be smaller than that obtained from a pure reaction-controlled process since the activation energy for gas diffusion is always smaller than that for the chemical reactions. With the empirical equation of Fuller *et al.* [9, 10] the diffusivities of CO_2 and O_2 in air were calculated and their activation energies were found to be in the vicinity of 14 kJ mol^{-1}. This value, as expected, is an order of magnitude smaller than the observed one. This may also explain why the activation energy obtained in this work is smaller than the values reported [7, 8]. In the latter references, the boundary layer effect was reduced to its minimum by atmospheric control using flowing gases, and hence larger activation energies were observed.

The carbon consumption rate, according to the linear relationship between the fibre size and oxidation time, has a parabolic relationship with the burn-off fraction s:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -kL\pi D_0(1-s)^{1/2}$$

where s is defined as the ratio of the burnt-off mass to the original mass, i.e. the ratio between the squared fibre diameters:

$$s = \frac{D_0^2 - D^2}{D_0^2}$$

The TGA results, as shown in Fig. 3, agree relatively well with this parabolic relationship although the experimental reaction rate seems to be slower than the calculated rate (the solid line) when the burn-off percentage is higher than about 70%. This rate reduction can be explained by the fact that there was sometimes a white-coloured residue found after the fibres were totally oxidized. These "ashes" were apparently not carbon and they will have affected the reaction rate once the oxidation reached the central part of the fibre. This may suggest that either the crystal structure or the composition of the fibre cores are different from the rest of the fibres as in the case of the T-300R fibres studied by Trumbauer *et al.* [5]. Qualitative EDX analyses of the fibres after being burnt-off by 0 and 90% showed such a tendency.

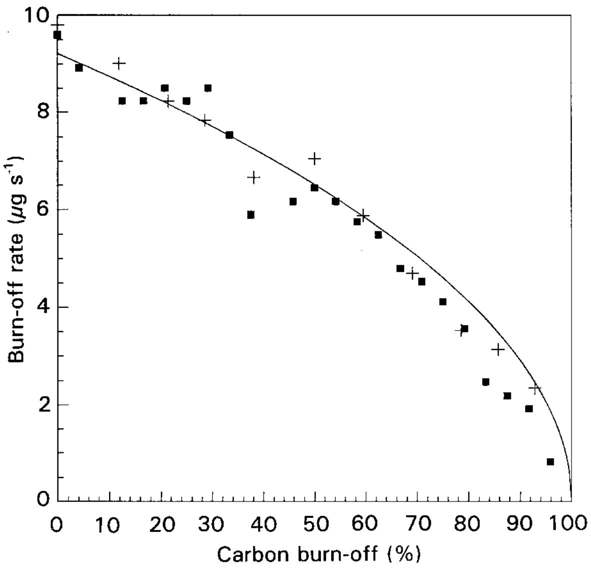

Figure 3 (■, +) Carbon burn-off rate against burn-off percentage determined by two TGA experiments. Sample weight 0.012 g. (—) Parabolic curve based on the uniform surface oxidation assumption and normalized to the TGA results.

The proportionality of the oxidation rate to surface area indicates that the active surface area (ASA) is evenly distributed on all the exposed fibre surfaces and is independent of the amount of oxidation of the fibre. This differs from the work using IM-7 fibres [5]. The typical autocatalytic reaction characteristic, a reaction rate peak with a maximum at about 40% burn-off [5], was not observed in the present work. This difference can be explained by two observations. The first is the difference in surface smoothness between the two types of fibre. For the IM-7 fibres, increased surface roughness accompanying the initial burn-off expands the ASA significantly and therefore the oxidation rate increases. Upon reaching a certain burn-off point, 40% in this case, the reaction rate slows down steadily in accordance with the decreasing fibre size. In the present study, however, the surface quality of the fibres is hardly affected by the oxidation and, as a result, the ratio between the ASA and fibre diameter is not changed. The second observation is the nearly amorphous structure of the carbon fibres as revealed by the X-ray diffraction results. The poorly defined diffraction peaks shown in Fig. 4 are indicative of a relatively low lattice ordering. As a consequence of this near-amorphous nature, the ASA is uniformly distributed on the fibre surfaces without any preference, resulting in an even oxidation on the fibre surfaces.

An additional finding was the occurrence of local excessive carbon oxidation when the fibres were heat-treated in an alumina boat. The impurities in the crucible materials, such as Na_2O, may have acted as a

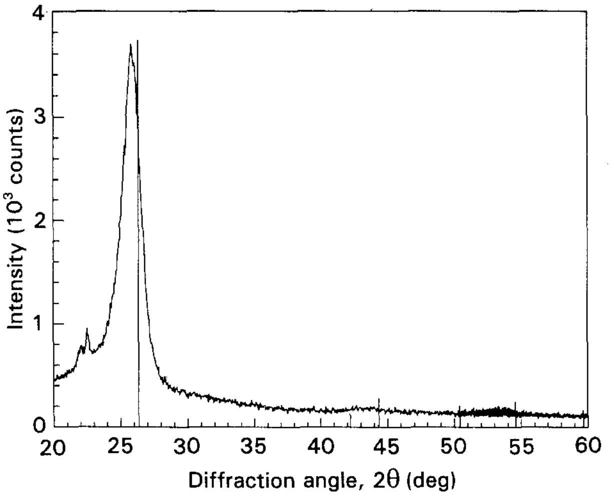

Figure 4 X-ray diffraction of the as-received carbon fibres. The vertical bars show the graphite peak positions.

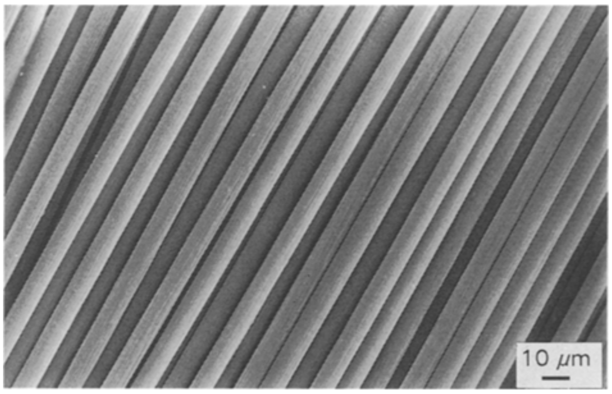

Figure 5 As-received fibres with an average diameter of 7.72 ± 0.08 μm.

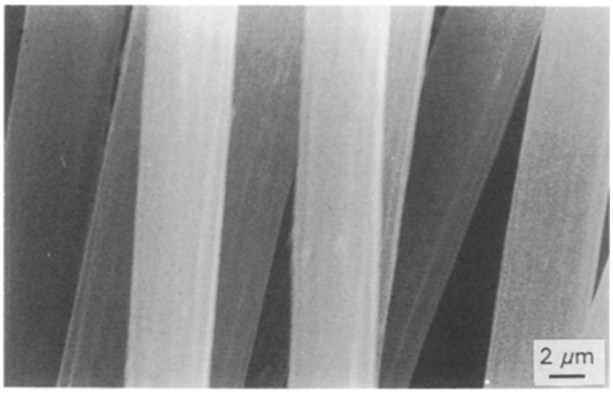

Figure 6 Detailed view of the fibres after being heat-treated at 700 °C with weight loss of about 50%. The fibre size is about 5.5 μm.

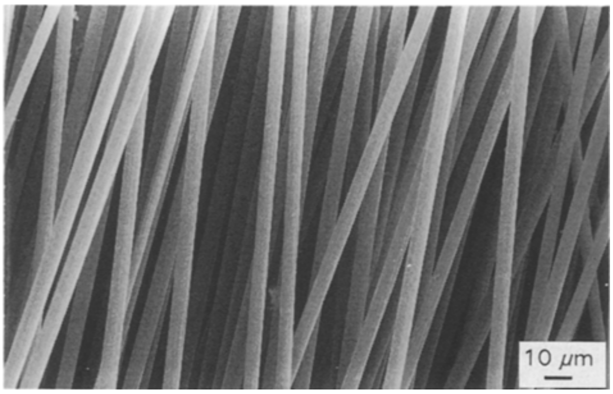

Figure 7 The same oxidation conditions as in Fig. 6. The size variation along the length of the fibres is fairly small.

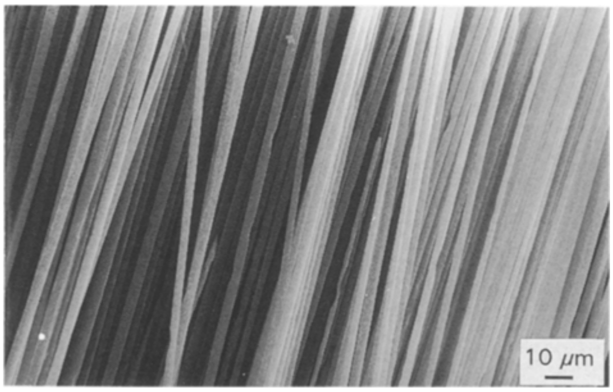

Figure 8 Fibres oxidized down to 3 μm at 700 °C. The surface quality of the fibres is still reasonably good but defects also start to develop.

catalyst, as reported by others [5, 11]. The Na_2O oxide converts to the peroxide and reacts rapidly with carbon at temperatures close to its melting point (733 K).

3.2. Fibre microstructure

Figs 5 to 8 show SEM micrographs of the carbon fibres at different stages of the burn-off process. The as-recieved fibres are shown in Fig. 5. They exhibit smooth outer surfaces and circular cross-sections. About 100 measurements of the fibre size by both the stage microscope and SEM gave an average fibre diameter of 7.72 ± 0.08 μm.

After oxidizing the fibres at 700 °C for 30 min the fibre size reduced to about 5.5 μm, corresponding to an approximate 50% burn-off. The details of the fibre surfaces are shown in Fig. 6; generally they are still flawless and smooth. Longitudinally, the fibres were oxidized uniformly with very little size variation as shown in Fig. 7.

Fig. 8 shows the fibres after 85% burn-off at 700 °C, the size being reduced to about 3 μm. Both longitudinal and cross-sectional size distributions are still relatively uniform, although degradation of the fibres resulting from defects and the non-homogeneous central core became more apparent. Some surface imperfections and two broken fibres are also shown in Fig. 8. At and above this level of burn-off, the very fine fibre sizes achieved mean that any local fluctuation of temperature and atmosphere will cause a noticeable size change along the length of the fibres and possibly even a breakage. Any defects within the fibres will also start to enlarge, leading to the deterioration of the fibres with randomly distributed voids on the fibre surfaces.

The mechanical strength of the fibres also falls as the fibre size decreases. A noticeable change occurs when the fibre size is reduced down to about 3 μm. At this point the fibres become very difficult to handle.

4. Summary

This investigation has shown the ability to reduce carbon fibre size uniformly via oxidation. Linear relationships between the size reduction and heat-treating time at all the temperatures tested were observed and the activation energy of carbon burn-off was found to be 140 kJ mol^{-1}. The cross-sectional shape and the surface quality of the fibres are not affected by the degree of oxidation up to approximately 85–90% burn-off.

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