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Preparation of graphite fibres from a modified PAN precursor

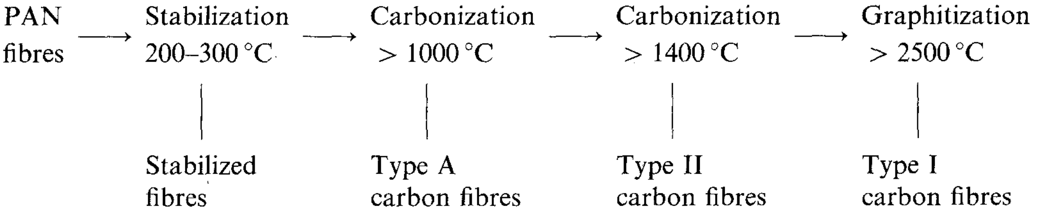
TSE-HAO KO, SING-CHANG LIAU
Department of Materials Science, Feng Chia University, Taichung, Taiwan
MING-FONG LIN
Research and Development Department, China Steel Corporation, Kaohsiung, Taiwan

Graphite fibres were developed from polyacrylonitrile (PAN) fibres modified with potassium permanganate. To our knowledge, this is the first time that the effect of modification on the physical properties, microstructure, elemental composition, electrical resistivity, and mechanical properties of fibres has been examined during the graphitization process. The graphite fibres developed from modified PAN fibres had a higher density, a greater stacking size, L_C, and a higher preferred orientation than those developed from unmodified PAN fibres. The graphite fibres also showed an improvement of 20%–40% in electrical resistivity and modulus.

1. Introduction

Carbon fibres are now important industrially and have gained a wide range of applications from sports products to items used by the aerospace industry. Polyacrylonitrile (PAN) fibres have been found to be the most suitable precursors for making high-performance carbon fibre [1–3]. An important step, the stabilization process, in preparing carbon fibre from PAN fibre is to heat the precursor to between 200 and 300 °C in air (or in an oxygen-containing atmosphere). This process leads to the formation of a ladder polymer in stabilized fibre. Subsequently, carbonization is carried out at a temperature of up to 800–3000 °C in an inert atmosphere. The maximum temperature depends upon the type of carbon fibres ultimately required [4–6].

Typically, the PAN fibres are stabilized in air at 200–300 °C and carbonized in an inert gas at up to 1000 °C. This process produces Type A carbon fibres with a low modulus and a low tensile strength. PAN fibres can also be carbonized at up to 1400 °C to produce Type II carbon fibres, exhibiting high tensile strength and medium modulus. Graphitization, which occurs in heat treatment at temperatures higher than 2500 °C to make Type I carbon fibres, can also be used to increase the modulus. This process, however, often decreases the tensile strength. The following flow chart represents the manufacture of carbon fibres from PAN fibres [4]



Because of their various technological applications in the industrial and engineering fields, the development of high-strain and high-modulus carbon fibres has become necessary. It has been established that the heat treatment of a PAN fibre under a tensile load can improve the fibre quality [4, 7]. Bahl and co-workers pretreated precursors with CuCl to make high-performance carbon fibres [8, 9]. Cagliostro [10] modified precursors with benzoic acid to improve the tensile strength of carbon fibre.

Six previous studies [11–16] presented the results of our process for the modification of PAN fibres with potassium permanganate to produce high-performance carbon fibres. We also discussed the reasons why a PAN fibre modified with potassium permanganate can reduce stabilization time and produce a carbon fibre with improved tensile strength. In the present study, the effect of modification of the precursor with potassium permanganate on the properties and microstructure of the resulting graphite fibres will be discussed. Before this study, we assumed that if this modification process for the precursor was adopted, it would improve the properties and productivity of the graphite fibres more than any conventional process.

2. Experimental procedure

A special grade of acrylic fibre, Courtelle fibre (Courtaulds Ltd, UK), containing 6% methyl acrylate and

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1% (itaconic) acid copolymer was used in this work. A single tow of Courtelle fibre contains 6000 strands of 1.1 denier monofilament. A fibre-wound frame was pretreated by immersing it in a 7% potassium permanganate solution at 85 °C for 2 min, then washed with distilled water and dried to a constant weight in an oven. The manganese content in the resulting carbon fibres was determined using an atomic emission spectrometer. The content of manganese in the fibre had increased about 60 times over its original content after the modification process [11].

Stabilization of the precursor was carried out in a constant temperature zone furnace with a fixed length method at 230 °C for 7 h, in a purified air atmosphere. The stabilized fibres were carbonized to 1300 °C at a rate of 240 °C h^{-1}, from 25 °C to 1300 °C, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The carbonized fibres were graphitized to 2800 °C at a rate 15 °C min^{-1}, from 25 °C to 2800 °C under an argon flow. Neither tension nor load were applied to the fibres during this process. The samples were heated in this way at different temperatures from 1400–2800 °C, at 200 °C intervals.

The mechanical properties of the graphite fibres were measured by an Instron 1122 tensile-testing machine at a crosshead speed of 0.5 mm min^{-1} and a load cell of 10 g, with a testing length of 2.5 cm for graphite fibres. In each sample, at least 25 filaments were tested, and the average value was reported. The diameters of all fibres were measured under an Olympus BHT microscope with a closed circuit television camera which magnified the image of the fibre in order to measure its diameter. The diameters of 30 fibres were measured in each experiment and the average measurement of these fibres was calculated.

A Rigaku X-ray diffractometer, providing nickel-filtered CuK_α radiation, was used to measure the crystalline-related properties of the sample. The step-scan method was used to determine the d-spacing and stacking size (L_c, stacking height of layer planes); the step-interval was set at 0.02°. The preferred orientation of the PAN fibres (0 0 1) and the carbon fibres O(0 0 2) was determined by an X-ray diffractometer with a fibre specimen attachment. The precursors were located at around 17° (2θ) and the carbon fibres were set at around 25° (2θ) (the 0 0 2) plane of carbon fibres is thought to have a hexagonal structure). The 360° azimuthal circle was used to allow the fibre axis to be rotated 360° about the vertical. The d-spacing, L_c and O(0 0 2) were calculated by using Equations 1 (the Bragg equation), 2 (the Scherrer equation), and 3 [17], respectively.

$$n\lambda = 2d\sin\theta \quad (1)$$

$$L(hkl)\,(\mathrm{nm}) = K\lambda/B\cos\theta \quad (2)$$

$$\mathrm{O}(hkl)\,(\%) = [(360\text{-}H)/360]\,100 \quad (3)$$

in which $\lambda = 0.154$ nm, K is the apparatus constant (= 1.0), and B is the half value width in the radian of the X-ray diffraction intensity, I, versus 2 θ curve. H is the half value width in degrees of the curve of I versus azimuthal angle [16]. The preferred orientation, O(0 0 2), has a value of 0%, if the specimen is completely unoriented. If the crystals are all arranged perfectly parallel to one another, the orientation is 100%.

Density was measured at 25 °C according to the density gradient column method. The density column was prepared with a mixture of n-heptane and carbon tetrachloride, so that a density gradient of about 1.2–1.6 g cm^{-3} extended from top to bottom. For the measurement of densities from 1.6–2.0 g cm^{-3}, a density gradient column prepared with a mixture of carbon tetrachloride and 1,3-dibromopropane was adopted.

A Perkin–Elmer model 240C Elemental Analyser was used to test the elemental analysis. The samples from the carbonization process were analysed for carbon, hydrogen, and nitrogen. The oxygen content was determined by the difference.

Electrical resistance measurements on the graphite fibres were made using a GW digital milli-ohmmeter. The contact resistance at the point of contact between the measuring probe and the fibre was minimized with silver paint during measuring. At least 30 fibres were measured in each experiment and the average measurement of these data was calculated.

A scanning electron microscope (SEM), Hitachi Model S-520, was used to examine the fracture surfaces of the graphite fibres at 20 kV accelerating potential. The specimens were coated with gold to obtain a better image. The dark-field and electron diffraction patterns of the fibres were recorded by a transmission electron microscope, Hitachi Model H-600.

3. Results and discussion

3.1. Properties of samples

The original PAN fibres and the modified PAN fibres were carbonized up to 1300 °C and were used as samples. Fibre A was developed from the original precursor and fibre B was developed from the modified precursor. The properties and the elemental contents of the fibres before graphitization are given in Tables I and II.

Tables I and II show that fibre B has a greater tensile strength, a higher density, a higher preferred orientation, a greater carbon content, and a lower modulus than fibre A. These findings suggest strongly that the modification of PAN fibres results in improvements in the final properties of carbon fibres. The manganese metal has been found to catalyse the formation of graphitic and turbostratic carbons during the graphitization stage in experiments conducted by Oya and Otani [18]. Another possible reason for this process at the molecular level may be that the manganese, which is contained only in fibre B and not in fibre A, is highly reactive with the carbon element because it has an uncompleted d-electron shell [18]. The manganese forms strong chemical bonds with the π-benzene complex of carbon, which results in a mixed sandwich compound [19]. In the next section, the effect of modification of the precursor on the properties and the microstructure of the resulting graphite fibres during the graphitization process will be discussed.

TABLE I Properties of carbonized fibres

Sample code	Developed from	Tensile strength (GPa)	Tensile modulus (GPa)	Density ($g\,cm^{-3}$)	Preferred orientation (%)
Fibre A	Original PAN fibre	3.61	224	1.756	89.3
Fibre B	Modified PAN fibre	3.93	187	1.772	89.6

TABLE II Elemental contents of fibres before carbonization

Sample code	Elemental contents (wt %)			
	C	N	H	O (diff.)
Fibre A	95.98	2.99	0	1.03
Fibre B	96.18	2.98	0	0.84

3.2. Elemental analysis and density

Table III shows the results of the elemental analysis of the graphite fibres developed from the original and the modified PAN fibres during the graphitization process. Graphitization of fibre A and fibre B is almost completed at 2000 and 1800 °C, respectively. In our previous study [16], all hydrogen of both samples was lost after 1100 °C during carbonization. This finding indicates that all the residual nitrogen and oxygen in both fibres evolved above this temperature. No remarkable difference of elemental composition between fibre A and fibre B was observed during graphitization. However, the formation temperature of the pure carbon elemental composition in fibre B is 200 °C lower than that in fibre A, which was developed from the original PAN fibre.

The variety in density tested during graphitization by a density gradient column method for both fibres is shown in Fig. 1. The difference between the two fibres is very remarkable below the graphitization temperature of 2200 °C. The density of fibre A increases very slightly over the range up to 2200 °C, and then begins to increase sharply. Conversely, the density increase is followed by a sharp drop at 1800 °C for fibre B, then the density begins to increase remarkably. Fibre B has a greater density than fibre A above 2000 °C.

It is probable that the microstructural changes are mostly due to growth in the widths of the microfibrial crystallites presented as elongated ribbons in the graphitization temperature range from 1500–2800 °C [20]. During the graphitization process, there will also be some elimination of the structural defects that were caused by the evacuation of substitutional nitrogen. The substitutional nitrogen was incorporated into the ladder structure at temperatures of 300–500 °C and finally eliminated at 1500 and 1700 °C. According to above discussions, the size of sharp-edged voids among the complex three-dimensional interlinking of layer planes forming crystallites also increases with increasing graphitization temperature. Therefore, two factors affect the density change of the graphitized fibres during the graphitization process. The first factor is due to carbon layer planes packed side by side to form the basic structural unit (BSU) of graphite fibre [21]. The formation of the BSU will increase the density of fibres. Another factor is the formation of defects and voids during graphitization, which decreases the density.

Because of the above two factors, and because of the purity of the carbon obtained at 2000 °C (in Table III), the density of fibre A increases very slightly below 2200 °C. Above 2200 °C, more and more BSUs are formed, which makes the increase in density remarkable. For fibre B, all of the residual nitrogen and oxygen evolve at 1800 °C, as shown in Table III. The density showed a sharp drop at 1800 °C, as shown in Fig. 1. Above 1800 °C, the density increased very remarkably. This finding indicates that the elimination of nitrogen and oxygen leads to the rearrangement and consolidation of structure in fibre B in the temperature range 1600–1800 °C during graphitization. These reactions lead to the drop in density during this heat-treatment range. Above 2200 °C, fibre B has a greater density than fibre A. This indicates that fibre B has more ordered graphite-like structure than fibre A.

3.3. Preferred orientation and the degree of randomness

Fig. 2 shows the variation in preferred orientation of both fibres during graphitization. Preferred orientation of fibre A increases very rapidly below a graphitization temperature of 1800 °C, and then begins to increase very slightly from 1800–2200 °C, and then shows a sharp increase above 2200 °C.

Preferred orientation increases 1.08% at 1400–1800 °C, only 0.21% at 1800–2200 °C, and 1.44% at 2200–2800 °C. From the last section, we know that the density of fibre A increased very slightly below 2200 °C and all elements except carbon evolved at 2000 °C. Also, the preferred orientation of fibre A increased very slightly from 1800–2200 °C. Those findings indicate that the formation of the ordered graphite-like structures transformed from the less-ordered structures has a transitional temperature range, 1800–2200 °C. During this transitional stage, the non-carbon elements evolve from fibre A and the structures in fibre A undergo rearrangement and consolidation. After this stage, the high-ordered graphite-like structure, the basic structural unit (BSU), is formed in graphite fibre, leading to increases in density and preferred orientation.

In the case of fibre B, the preferred orientation increases gradually up to 2200 °C, and then increases quite sharply from 2000–2800 °C. All of the residual

TABLE III Elemental analysis of the carbon fibres during graphitization

Graphitization temperature (C°)	Fibre A (from PAN fibres, wt %)				Fibre B (from modified PAN fibres, wt %)			
	C	N	H	O (diff.)	C	N	H	O (diff.)
1400	98.3	1.3	0	0.4	98.4	1.2	0	0.4
1600	98.9	0.2	0	0.1	99.0	0.2	0	0.8
1800	99.8	0.1	0	0.1	100	0	0	0
2000	100	0	0	0	100	0	0	0

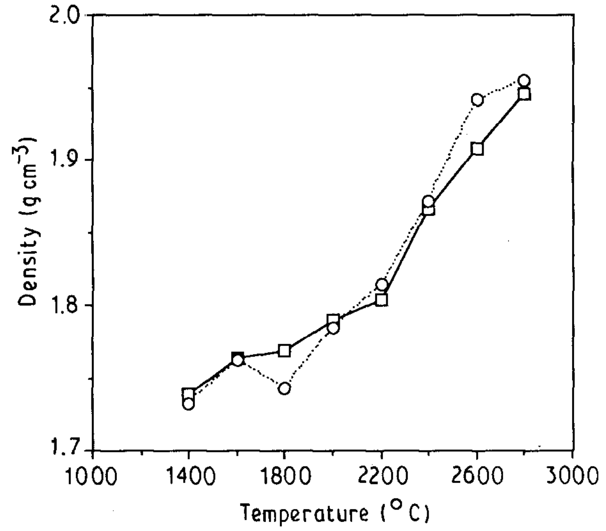

Figure 1 Relation between density of graphite fibres and graphitization temperature; graphite fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

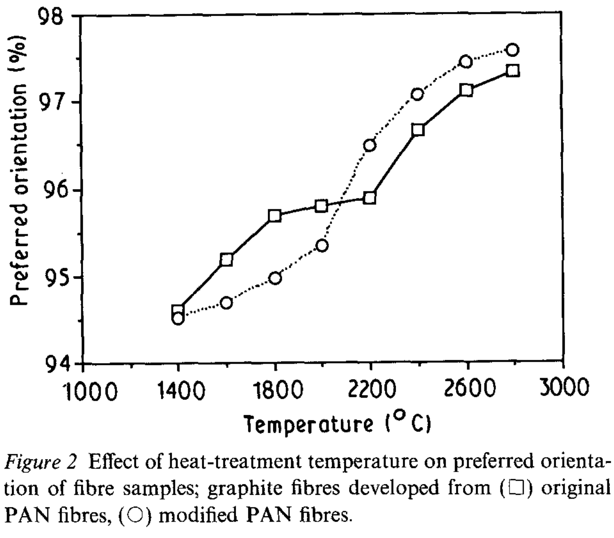

Figure 2 Effect of heat-treatment temperature on preferred orientation of fibre samples; graphite fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

nitrogen and oxygen in this fibre evolve before 1800 °C, as shown in Table III. In Fig. 1, the density of fibre B shows a drop at 1800 °C. These findings indicate that the ordered graphite-like structures are formed gradually and steadily in fibre B, which developed from the modified PAN fibre. Therefore, above the graphitization temperature of 2200 °C, the graphite fibres developed from fibre B have a greater density and a higher preferred orientation than those fibres developed from fibre A.

The degree of ordering within graphite material has been the subject of extensive studies. The pioneering work of Franklin [22] has been modified several times, but her equation relating the *d*-spacing between the graphite layers is still valid. The degree of randomness in the alignment of the graphite layers, *P*, was measured using the formula

$$d_{(0\,0\,2)} = 3.440 - 0.086(1 - P^2) \qquad (4)$$

The degrees of randomness in the alignment of both graphite fibres are shown in Fig. 3. The degrees of randomness for both fibres decrease linearly with the graphitization temperature. This indicates that the formation of the ordered structure was steady during the graphitization temperature. Below 2000 °C, the structure in fibre A is more ordered than that in fibre B; but above 2000 °C, fibre A is more disordered in structure than fibre B. As shown in Figs 1–3, the density, the preferred orientation, and the degrees of randomness have a transition point at about 2000–2200 °C. These findings indicate that manganese catalyses the formation of graphite and turbostratic carbon in fibre B during the later stage of graphitization. This reaction improves the density, the preferred orientation, and the formation of ordered structure in fibre B.

3.4. Stacking size and electrical resistivity

In this research, the microstructure parameters of graphite fibres developed from two different precursors were studied by X-ray diffraction techniques. The Scherrer equation is used to calculate the values of L_c (stacking height of graphene planes, stacking size) from the width of the 002 reflection. The stacking height of graphene planes, L_c, of the carbon fibres as a function of the graphitization time are shown in Fig. 4. The stacking height of graphene planes, L_c, in the graphite fibres increases rapidly with graphitization temperature. For both fibres, the L_c value is almost the same below 2000 °C, but a significant difference is observed above 2000 °C. Graphite fibres developed from the original PAN fibres have a greater L_c at about 2000–2600 °C and a lower L_c above 2600°C than those developed from the modified PAN fibres.

The progression of changes in the room-temperature electrical resistivity is plotted as a function of the graphitization temperature in Fig. 5. As shown in Fig. 5, sharp inflections occur for fibre A and fibre B

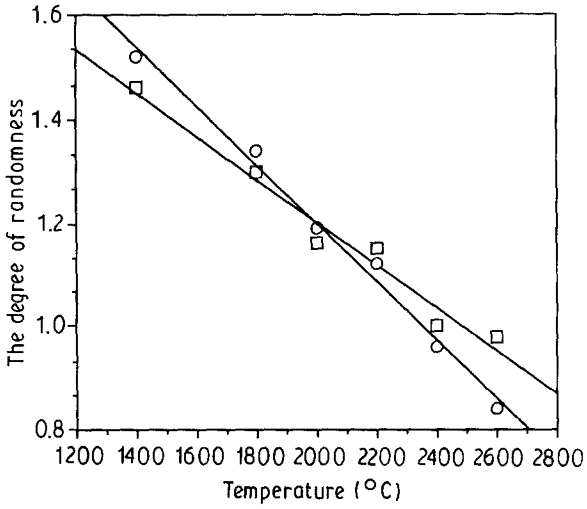

Figure 3 Relation between the degree of randomness of graphite structure and graphitization temperature; graphite fibres developed from (□) original PAN fibres; (○) modified PAN fibres.

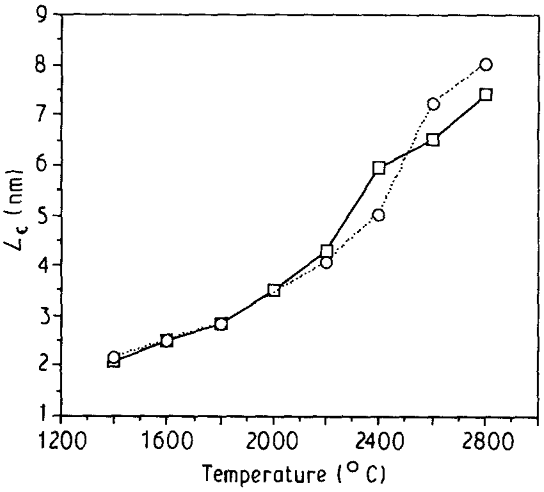

Figure 4 Variation of stacking size, L_c, of graphite fibres with different graphitization temperatures; graphite fibres developed from (□) original PAN fibres; (○) modified PAN fibres.

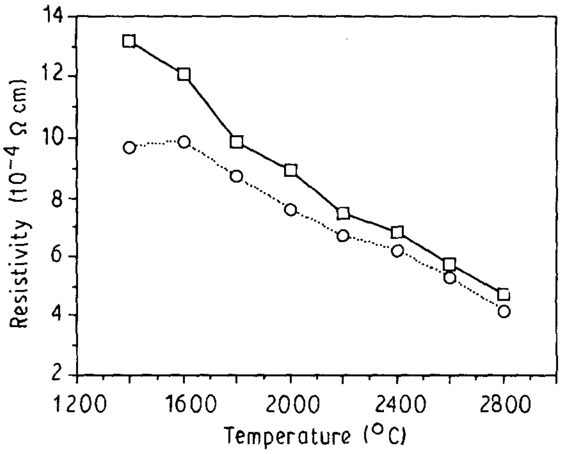

Figure 5 Variation of electrical resistivity of graphite fibres with different graphitization temperatures; graphite fibres developed from (□) original PAN fibres; (○) modified PAN fibres.

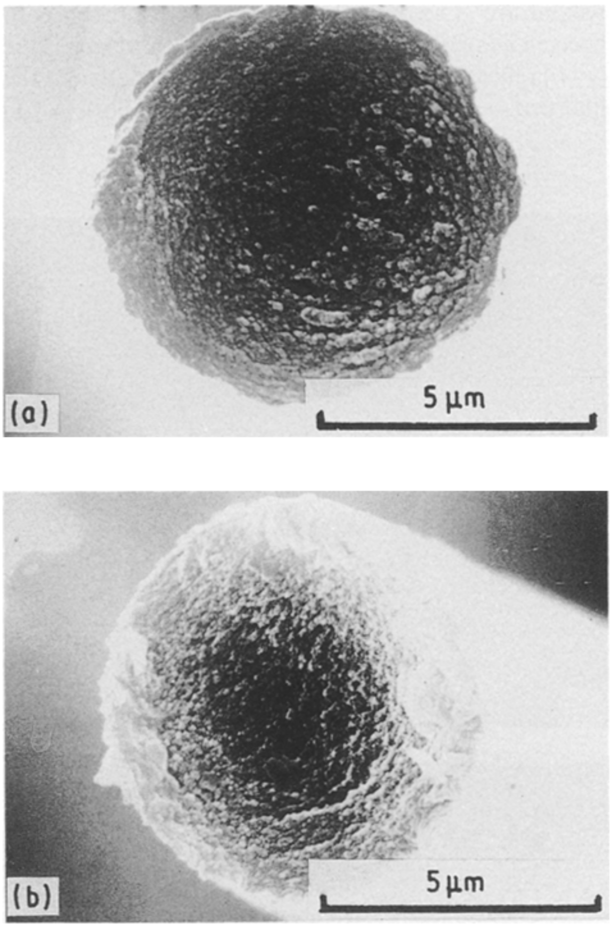

Figure 6 Scanning electron micrographs of the fracture surface of graphite fibres, developed from (a) original PAN fibres, graphitized at 2200 °C, (b) modified PAN fibres, graphitized at 2600 °C.

above the graphitization temperature of 1800 and 1600 °C, respectively. These results are significant, indicating that major changes are occurring in the electronic structure of the fibres in those temperature ranges. Marchand and Zanchetta [23] have shown that nitrogen has a definite inhibitive effect on graphitization; thus, when the nitrogen is eliminated from the fibre, the degree of graphitization increases and hence the electronic structure of the fibre abruptly changes. As shown in Table III, nitrogen is eliminated from fibre A at about 1800–2000 °C and from fibre B at about 1600–1800 °C. These changes in the electronic structure correlate well with the observation that the residual nitrogen is evolved from both fibres at about the same graphitization temperature.

The resistance falls from 13×10^{-3} Ωcm to 4.7 $\times 10^{-4}$ Ωcm for fibre A and 9.8×10^{-4} Ωcm to 4.2 $\times 10^{-4}$ Ωcm for fibre B when the temperature is raised to its maximum of 2800°C. Fibre B has a lower electrical resistivity than fibre A during the graphitization process. The electrical resistivity of fibre A and fibre B decrease linearly with the increases in the graphitization temperature above 1800 and 1600 °C, respectively. This finding indicates that the formation temperature of the electronic structure of fibre B is about 200 °C lower than that of fibre A. This finding also reveals that manganese would catalyse the formation of the electronic structure in fibre B during the graphitization process.

3.5. Electron microscope studies

The fractured ends of both graphite fibres have been examined on a stereoscan. Typical fractured ends of the graphite fibres are shown in Fig. 6. Both fibres have a wraparound basal plane structure in the cross-section. Because both fibres were developed from fully stabilized PAN fibres, the cross-section of the fibres showed no sheath–core structure under a transmission optical microscope. Our finding agrees with previous studies [24–29], indicating a circumferential crystalline orientation on the circular cross-section of those carbon fibres which were developed from fully stabilized fibres, and a radial orientation on the cross-section of those fibres which were developed from partially stabilized fibres.

Electron diffraction micrographs of both fibres are shown in Fig. 7. Both fibres are graphitized at 1400 °C and, as shown in Fig. 7a and c, each shows three diffraction arcs. The first diffraction at $2\theta \approx 25^\circ$ corresponds to the (0 0 2) planes of the hexagonal cell. The second arc is attributed to the (1 0 l) plane and connects in a foggy arc to form a ring. The third ring is the (1 1 0) reflection arc. The equatorial arc length and the line broadening of the (0 0 2) planes for fibre A are shorter than that for fibre B. This indicates that fibre A has a greater preferred orientation and a higher stacking size than fibre B. The result from the TEM agreed with the result from the wide-angle X-ray diffractometer, as shown in Figs 2 and 4.

When the fibres were graphitized at 2800 °C, they showed a diffraction arc at $2\theta \approx 55^\circ$, corresponding to the (0 0 4) planes, as shown in Fig. 7b and d. This finding indicated that three-dimensional interplanar correlations existed in both fibres. With heat-treatment at this temperature, fibre B had a greater stacking size and a higher preferred orientation than fibre A.

Fig. 8 shows the 0 0 2 dark-field image of a longitudinal section for both fibres. Both fibres give similar results, showing small bright domains. Each of these bright domains corresponds to a stack of planar aromatic structures. The bright areas are areas of 0 0 2 reflection and the units seen vary in size, although the large units may be composed of two or more smaller unresolved units. The sizes of bright domains increase from 2 nm to 70–80 nm when the graphitization temperature rises from 1400 ° to 2800 °C. After this temperature increase, the preferred orientation of the

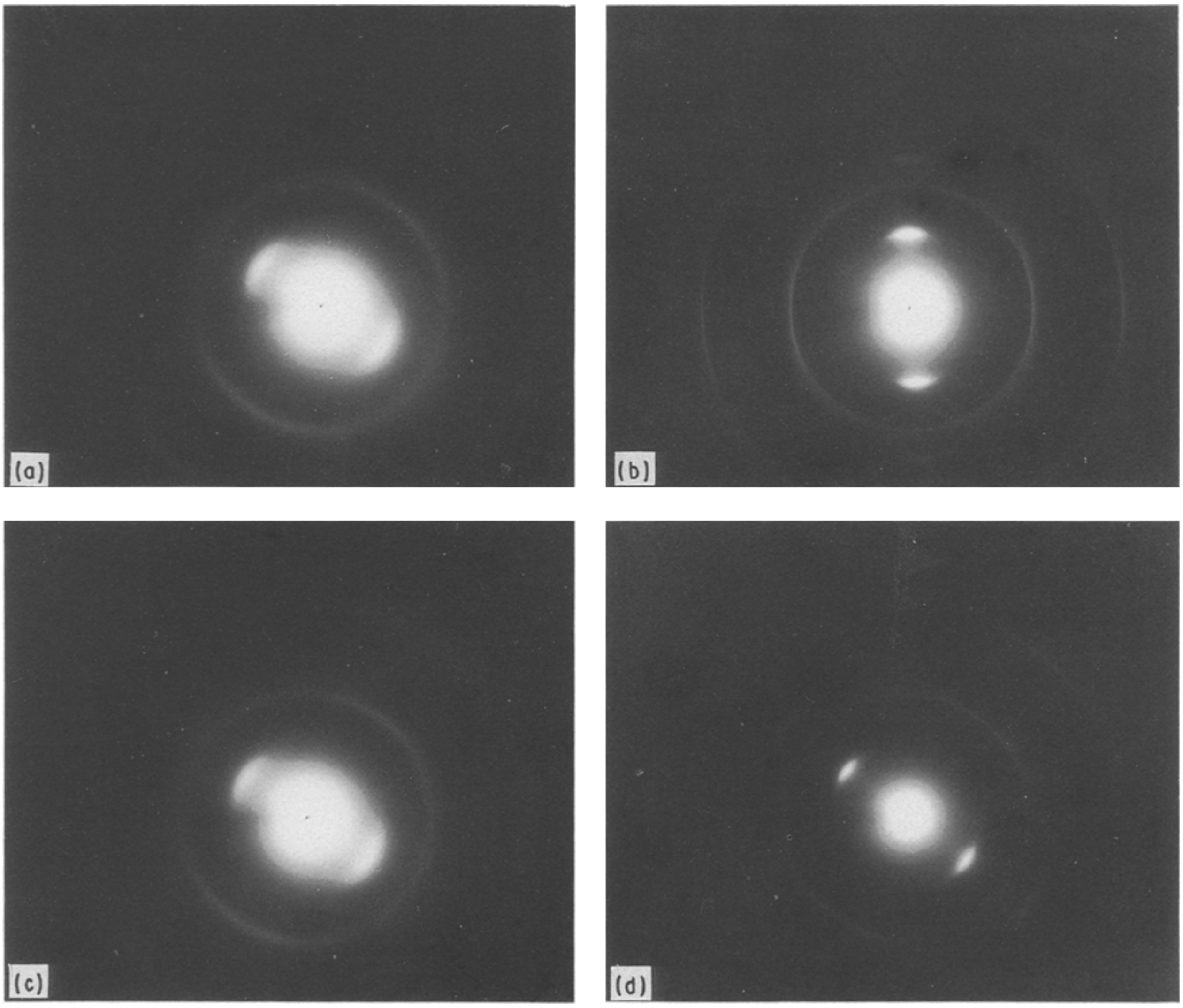

Figure 7 Electron diffraction TEM pattern of graphite fibres, developed from original PAN fibres, graphitized at (a) 1400 °C, (b) 2800 °C, and developed from modified PAN fibres, graphitized at (c) 1400 °C, (d) 2800 °C.

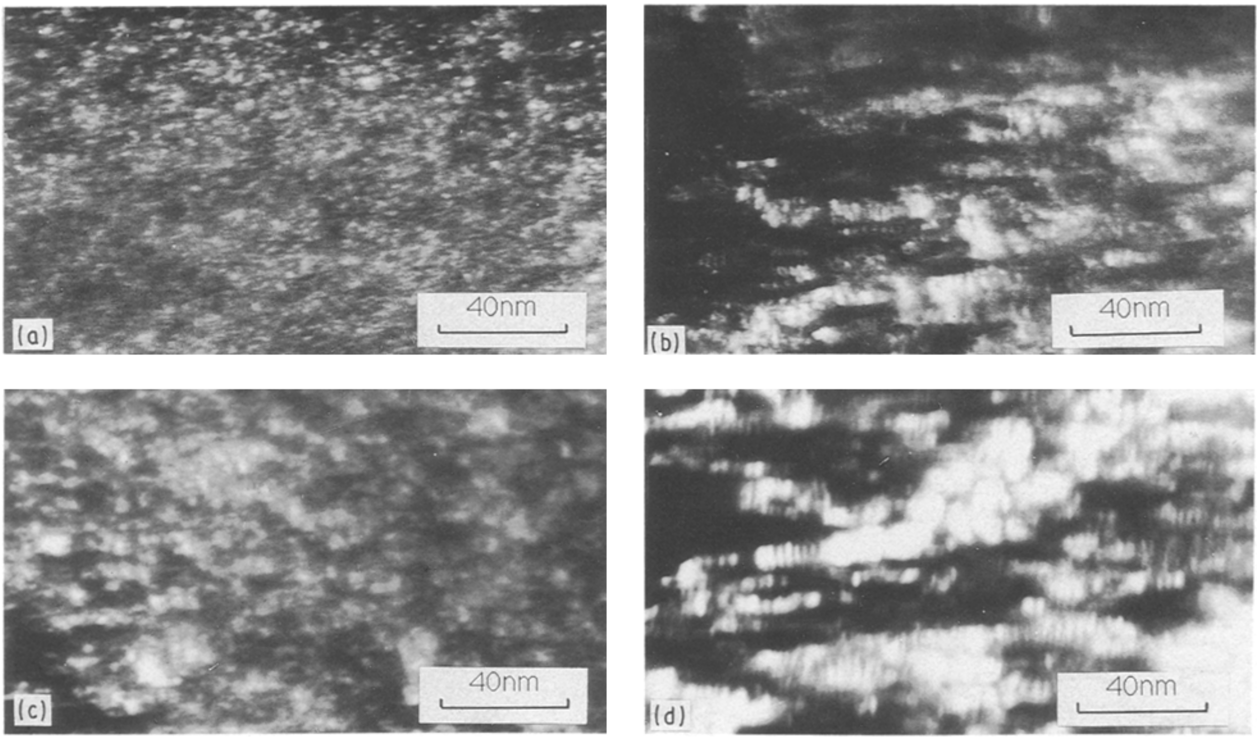

Figure 8 Dark-field (0 0 2) TEM image of graphite fibres, developed from original PAN fibres, graphitized at (a) 1400 °C, (b) 2800 °C, and developed from modified PAN fibres, graphitized at (c) 1400 °C, (d) 2800 °C.

layer planes appears to lie preferentially parallel to the fibre axis, as shown in Fig. 8b and d. The increase in orientation will promote the increase in modulus.

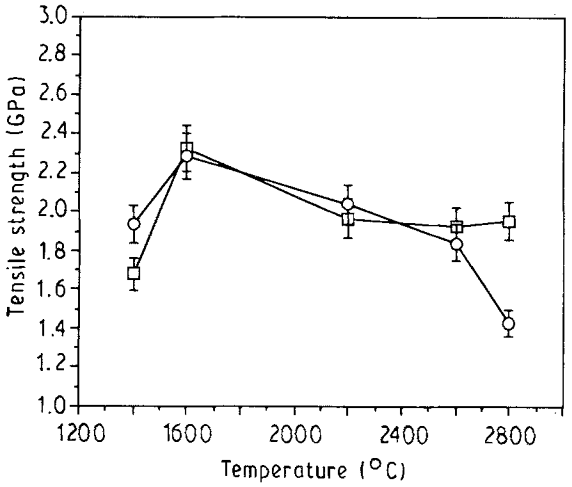

Figure 9 Relation between tensile strength of graphite fibres and graphitization temperature; graphite fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

3.6. Mechanical properties of graphite fibres

To observe the influence of the modification process on the tensile strength of graphite fibres, both fibres were graphitized to 2800 °C under similar conditions. The results are plotted in Fig. 9. The tensile strength of both fibres increases rapidly and then falls off sharply, showing a peak at 1600 °C; above this temperature the strength decreases gradually with rise in temperature. This is probably due to the volatilization of impurities as suggested by Sharp and Burnay [30] and Reynolds and Moreton [31].

In our recent study [16], the carbon fibre which was developed from the modified PAN fibre and carbonized at 1300 °C showed an improvement in tensile strength from 20% to 40%. In this article, the carbon fibres which were graphitized at 1400 °C exhibited similar results. However, the tensile strength of fibre B, which was developed from the modified PAN fibre, was lower than that of fibre A above 2600 °C. However, fibre B had a higher density, greater preferred orientation, and a greater stacking size than fibre A. This finding indicates that the cavities were formed mainly at high temperatures by the volatilization of inclusions, and that this was the cause of the decreases in tensile strength after heat-treatment above 2600 °C for fibre B.

Fig. 10 shows the variation in densities of graphite fibres during graphitization. The modulus of both fibres increase with temperature throughout the graphitization process. It is known that the moduli of carbon and graphite fibres increase when the preferred orientation is improved [20]. However, this is not a satisfactory explanation for the modulus of fibre B, the fibre developed from the modified PAN fibre. For example, within the temperature range 1400–2000 °C, fibre B has a significantly higher modulus than fibre A, as shown in Fig. 10, even though fibre B has a lower preferred orientation, as shown in Fig. 2. The reason for this is not known. Our measurements on the resistivity of fibre B showed that manganese modification has the effect of decreasing the resistivity of the resulting graphite fibre, as shown in Fig. 5. One possible reason for the improvement in modulus is that the manganese forms strong chemical bonds with the π-benzene complex of carbon, which results in a

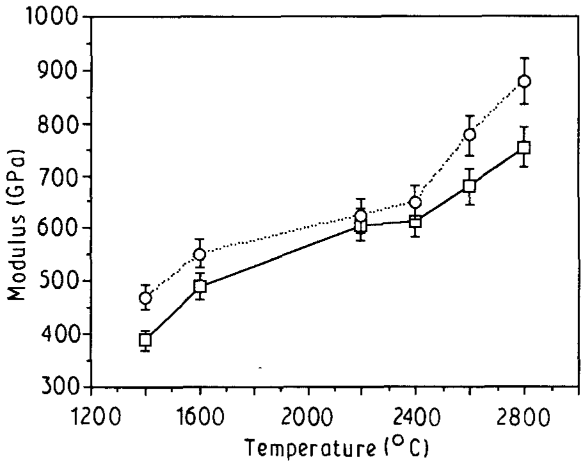

Figure 10 Effect of the graphitization temperature on tensile modulus of graphite fibres; developed from (□) original PAN fibres, (○) modified PAN fibres.

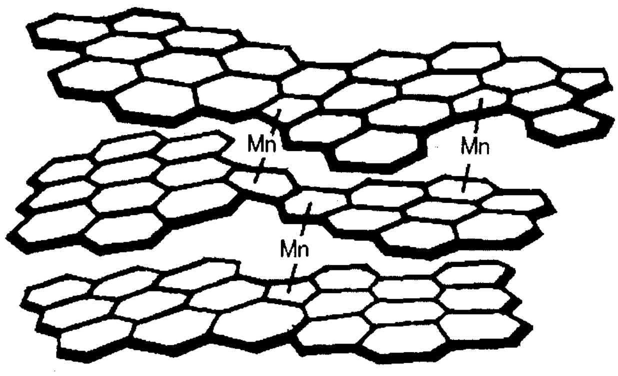

Figure 11 Structural model of sandwich compound in the graphite fibres, developed from modified PAN fibres.

mixed sandwich compound. We believe it is possible that the manganese are positioned between the boundaries of crystalline planes and form strong chemical bonds between two of these boundaries. The structural model of the sandwich compound in the graphite fibre is shown in Fig. 11. This would increase the stiffness of fibre B relative to fibre A. This hypothesis would explain the increase in modulus and an improvement in resistivity.

4. Conclusions

Modification of the polyacrylonitrile (PAN) fibres with potassium permanganate has increased the desirable physical properties of the graphite fibres. The resulting graphite fibres developed from modified PAN fibres have a higher density, a greater stacking size, L_c, and a higher preferred orientation than those developed from unmodified PAN fibres. The graphite fibres also showed a lower electrical resistivity and a greater modulus than those fibres developed from the original PAN fibres. It is possible that the manganese formed strong chemical bonds with the π-benzene complex of carbon between two carbon layers. Experiments show that the modification process brought about an improvement of 20%–40% in electrical resistivity and modulus of the graphite fibres.

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