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Pitch-based carbon fibres derived from thermoset fibres oxidized with Cl_2 containing air

T. TOMIOKA*, Y. ARAI, T. HAMADA‡
Advanced Materials and Technology Research Laboratories, Nippon Steel Corporation, 1618 Ida, Nakahara-ku, Kawasaki, 211 Japan

Mesophase pitch-based carbon fibres thermoset with Cl_2 containing air were studied for their microstructures and physical properties. Carbon fibres thermoset with Cl_2 containing air and heat-treated at 2000 °C ($Cl_2$2000) possessed slightly smaller mean sizes of crystallites $L_c(002)$*s*, lower densities, lower tensile moduli of elasticity, and higher tensile strengths than those thermoset with air. X-ray diffraction measurements revealed a somewhat lower degree of preferred orientation of a carbon fibre which was thermoset with Cl_2 containing air. The Cl_2 thermosetting partly disordered the periodic arrangement of crystallites and reduced the crystallite size $L_c(002)$ of a carbon fibre heat-treated at a lower temperature. A strong temperature dependence of resistivity was shown for $Cl_2$800, suggesting much disorder in its microstructure due to the Cl_2 thermosetting, and $Cl_2$1000 and $Cl_2$1200, respectively showed specific temperature dependencies of resistivities.

1. Introduction

Mesophase pitch-derived precursor fibres are usually thermoset by mild oxidation with air before heat-treatment at higher temperatures [1–3]. The thermoset process converts a thermoplastic pitch precursor fibre infusible and, at the same time, introduces microscopic disorder to the precursor fibre; the degree of preferred orientation of molecules along the fibre axis becomes lower and the molecular stacking height $L_c(002)$ estimated by X-ray diffraction technique (XRD) gets shorter [4]. The thermosetting with air, however, hardly changes the degree of graphitization of the resultant carbon fibre heat-treated at 2500 °C [5].

Arai *et al.* studied mild oxidation of mesophase pitch-derived pitch precursor fibres with O_2 gas mixed in inert gas, by differential scanning calorimetry (DSC) measurements combined with computer simulation, and proposed a simple model suitable in lower temperature thermosetting such that a pitch precursor fibre possesses a constant number of active sites to react with oxygen, oxygen diffused from the fibre surface reacts with a molecule selectively at the active site, and no further reaction occurs after the all active sites are consumed [6]. They developed the model by assuming two kinds of active sites with different activation energies of oxidation, to give quantitative predictions on the DSC data, the oxygen contents as functions of the distance from the fibre surface, and the density of fibres thermoset at a variety of conditions of temperature and time [7, 8].

Chlorine gas is an oxidizer and can be used in the thermosetting process, being seeded in oxygen and inert gas mixtures or in air [9]. The radical oxidation by adding Cl_2 gas needs a completely different model for the thermosetting simulation. Preliminary examinations by EPMA (electron probe microanalyser) and DSC measurements combined with computation suggested an almost infinite number of active sites which means a zero-order reaction on the active site number or an oxidation independent of active site number, and very located chlorine atoms in the skin part of the thermoset fibre [9]. The distinctive Cl_2 gas containing thermosetting should also affect the resultant carbon fibres in both their microstructures and physical properties [9].

In this article, density at room temperature (d(RT)), tensile modulus of elasticity (TM), tensile strength (TS), interlayer spacing (d_{002}) and crystallite size ($L_c(002)$) will characterize the effects of the thermosetting with Cl_2 containing air on pitch-based carbon fibres heat-treated at 2000 °C. Second, detailed XRD measurements will give further information on the microstructures of carbon fibres which have been thermoset with Cl_2 containing air and heat-treated at lower temperatures [10, 11]. Finally, these carbon

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* *Present address*: Tohoku Kyowa Carbon Corporation, 62-6, Kawauchi, Aza, Nakasoneyama, Osato-cho, Kurokawa-gun, Miyagi, 981-35 Japan
‡ *Present address*: Materials Characterization, Technical Development Bureau, Nippon Steel Corporation, 20-1, Shintomi, Futtsu, Chiba, 299-12 Japan

fibres will exhibit different resistivities as functions of temperature from those derived from air-thermoset fibres [12, 13].

2. Experimental details

2.1. Sample preparation

A mesophase pitch with a softening point of about 304 °C (when the viscosity becomes 2.0×10^4 P) and mesophase content of about 94% determined by polarized light microscopy was spun to form pitch precursor fibres. The pitch viscosity during spinning was about 1.0×10^3 P and the mean diameter of the spun fibres was about 13 μm.

The pitch precursor fibres were thermoset by mild oxidation in two ways; using dry air or dry air containing 10 mol % of Cl_2 gas. In thermosetting with air, pitch precursor fibres were heated from 200 °C to 300 °C at a rate of about 0.5 °C min^{-1}. and further treated at 300 °C for 60 min. In the case with 10 mol % of Cl_2 in air, the fibres were heated at 200 °C for 10 min, temperature was elevated to the final temperature T_f at a rate of about 10 °C min^{-1}, and the fibres were further treated at T_f for a treatment period Δt. $T_f = 260$ °C and 300 °C and several values of Δt from 0 min to 120 min were tried in the Cl_2 thermosetting. Thermosetting was carried out with an image furnace; pitch precursor fibres put on a china boat were set in a quartz tube, and heated with infrared light. No fusion among the thermoset fibres was observed after the respective thermosetting.

The thermoset fibres were heat-treated at 2000 °C or at other several temperatures lower than 1400 °C for about 15 min in Ar gas by using a tungsten-heater furnace.

2.2. Measurements

The density of a carbon fibre at room temperature (d(RT)) was measured by float–sink method; several ethanol–bromoform mixtures with densities differing by 0.01 g cm^{-3} were prepared, short-cut fibres were put into test tubes containing these respective liquids at room temperature, d(RT) of the sample was determined as the mean value of the highest density of the liquid with sinking fibres and the lowest density of the liquid with floating ones. No clear judgement of whether fibres were floating or sinking was regarded to mean that d(RT) of the fibre tested was equal to that of the liquid.

The tensile modulus of elasticity (TM) and the tensile strength (TS) of single filaments were measured with 25 mm gauge lengths, and about 20 results were averaged for each sample following the standardized method (JIS R 7601-1980) [14]. The filament diameter was measured by using a split image microscope for each filament with an accuracy of about 0.5 μm.

The degree of preferred orientation of crystallites in a fibre was estimated from the half-width at half maximum (HWHM) intensity of the XRD ϕ scan profile, and HWHM was measured as a function of 2θ from 18° to 32° to investigate the crystallite size ($L_c(0\,0\,2)$) dependence of HWHM in the fibre [10]. Wide angle XRD profiles (θ–2θ scan profiles) were measured for some fibre rotation angle ϕ to estimate $L_c(0\,0\,2)$ of the selected crystallites misoriented from the fibre axis by an angle ϕ and to find out whether crystallites in a fibre are periodically arranged or not [10, 11]. Where, the fibre rotation angle, ϕ is the angle between the z-axis and the fibre axis for the experimental set up with the incident X-ray parallel to the x-axis and the X-ray counter in the x–y plane, and $\phi = 180°$ for the fibre axis parallel to the z-axis and $\phi = 90°$ for the perpendicular configuration [10]. Resistivity was measured by using the equipment in refs [12] and [13] with single filaments.

In this article, a pitch-based carbon fibre which was thermoset with Cl_2 containing air and heat-treated at a heat-treatment temperature (HTT) will be noted as Cl_2HTT, and a carbon fibre thermoset by using air and heat-treated at HTT by AirHTT; for example, $Cl_2$1400, $Cl_2$2000, or Air2000, where HTT is in °C. The expression of $Cl_2$2000(260, 60) means a carbon fibre thermoset using Cl_2 containing air with $T_f = 260$ °C and $\Delta t = 60$ min and heat-treated at 2000 °C.

3. Results and discussion

3.1. Density, d_{002}, $L_c(0\,0\,2)$, and mechanical properties

Fig. 1 shows the density d(RT) of $Cl_2$2000(300, Δt) as a function of Δt which is the thermosetting period at the final temperature $T_f = 300$ °C. The d(RT) of Air2000 was about 2.14 g cm^{-3}. The Cl_2 thermosetting effectively decreases the d(RT) of the carbon fibres heat-treated at 2000 °C more than air thermosetting and a heavier Cl_2 thermosetting leads to a lower density of the resultant carbon fibre.

No difference in d_{002} between Cl_2 thermosetting and one without Cl_2 gas was detected for the carbon fibres plotted in Fig. 1, the value being about 0.343 nm for both cases. $L_c(0\,0\,2)$ was slightly depressed by Cl_2 thermosetting as shown in Fig. 1; $L_c(0\,0\,2)$ is about 14 nm for Air2000 and it gradually decreases

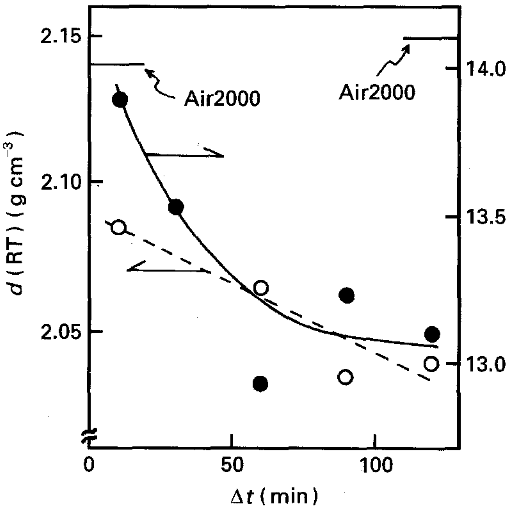

Figure 1 The density at room temperature d(RT) and the crystallite size $L_c(0\,0\,2)$ of $Cl_2$2000(300, Δt) as functions of Δt. The data for Air2000 are also indicated in this figure.

from 14 nm to 13 nm with increase in Δt for $Cl_2$2000(300, Δt).

The negligible difference in d_{002} between $Cl_2$2000(300, Δt) and Air2000 cannot be evidence of the equal degree of graphitization between them, because d_{002} exhibits almost equal values for pitch-based carbon fibres heat-treated at 2000 °C in spite of various spinning conditions which result in significant differences in their graphitization [15]. The small difference in $L_c(002)$ between $Cl_2$2000(300, Δt) and Air2000 shown in Fig. 1 suggests a weak depression in the degree of graphitization of the resultant carbon fibres heat-treated at 2000 °C [15].

The tensile moduli of elasticity (TM) of $Cl_2$2000(260, Δt) and $Cl_2$2000(300, Δt) as functions of Δt are shown in Fig. 2, and the values of Air2000 are also indicated in the figure. The Cl_2 thermosetting significantly decreases TM for both T_f values and each Δt, compared to the air thermosetting and a longer Cl_2 thermosetting results in a lower TM. The increasing TM according to the increasing in Δt for shorter Δt as shown in Fig. 2 may be due to insufficient thermosetting; melting of the core part of a fibre during heat-treatment should misorient the crystallite alignment along the fibre axis.

Fig. 3 shows tensile strength (TS) of the carbon fibres studied in Fig. 2. Fig. 3 indicates that some Cl_2 thermosetting much improves TS of the carbon fibres for both $T_f = 260$ °C and 300 °C and that the condition, $T_f = 260$ °C, exhibits a wider range of Δt to improve TS than $T_f = 300$ °C. The improved TS and the lowered TM due to the Cl_2 thermosetting result in a very large strain at tensile break and a toughness improvement of the fibre.

Thus, Cl_2 thermosetting effectively decreases d(RT) and TM of pitch-based graphitized fibres, with their degree of graphitization remaining almost constant for a carbon fibre heat-treated at 2000 °C, in contrast to the transverse cross-section controls in spinning previously reported which significantly depress the degree of graphitization of pitch-based graphitized fibres, while keeping the TM constant [5, 16].

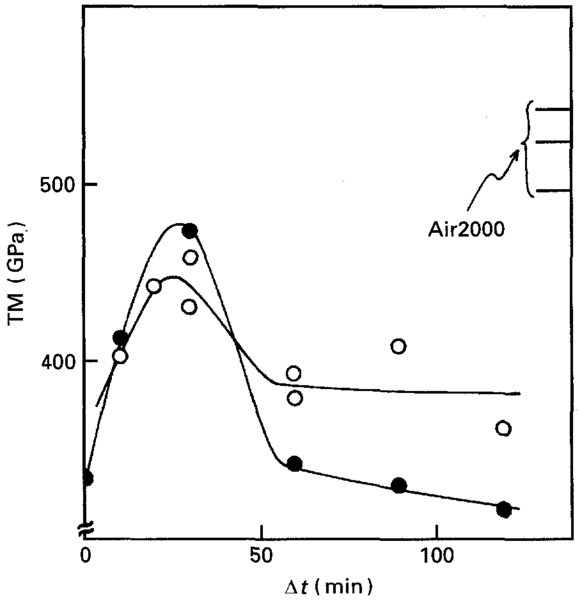

Figure 2 The tensile moduli of elasticity (TM) of $Cl_2$2000(260, Δt) and $Cl_2$2000(300, Δt) as functions of Δt which is the period of thermosetting at T_f. The data for Air2000 are also indicated in this figure. ○, $T_f = 260$ °C; ●, $T_f = 300$ °C.

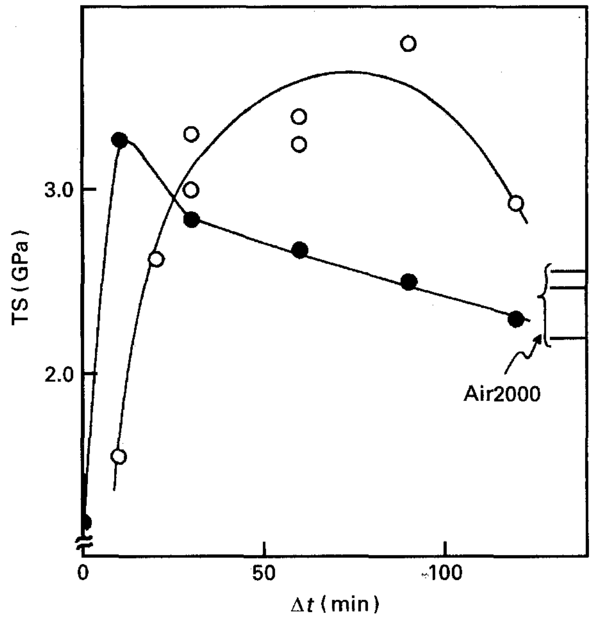

Figure 3 The tensile strengths (TS) of $Cl_2$2000(260, Δt) and $Cl_2$2000(300, Δt) as functions of Δt. The data for Air2000 are also indicated in this figure. ○, $T_f = 260$ °C; ●, $T_f = 300$ °C.

A change in TM of a carbon fibre should generally come from an essential structural modification, though only small changes in $L_c(002)$ of carbon fibres heat-treated at 2000 °C were observed between the two kinds of thermosetting with air and with Cl_2 containing air. In the next section, degrees of preferred orientation of crystallites along the fibre axis will be investigated for pitch-based carbon fibres thermoset with Cl_2 containing air and heat-treated at lower temperatures. The preferred orientation of a carbon fibre should directly contribute to its TM [17–19], and the lower heat-treatment temperatures may affect the microstructural differences of carbon fibres between thermosetting with Cl_2 containing air and with air more than higher temperatures.

3.2. Preferred orientation and θ–2θ scan profiles

Fig. 4 shows HWHM as functions of 2θ for $Cl_2$500(260, 90), and the data of Air500 are also shown in Fig. 4 for comparison. The Cl_2 thermosetting increases the HWHM of the carbon fibre heat-treated at 500 °C, and the difference in HWHM between $Cl_2$500(260, 90) and Air500 is less dependent on 2θ from 18° to 32° as shown in Fig. 4. Thus, the treatment reduces the degree of preferred orientation of crystallites in the carbon fibre heat-treated at 500 °C, independent of their size in $L_c(002)$, because the data around $2\theta = 26°$ shown in Fig. 4 mainly come from crystallites with larger $L_c(002)$ and those far from $2\theta = 26°$ are primarily from smaller crystallites [10].

Fig. 5 shows HWHMs as functions of 2θ of $Cl_2$1400(260, 90) and Air1400, corresponding to Fig. 4. Heat-treatment at 1400 °C significantly reduces

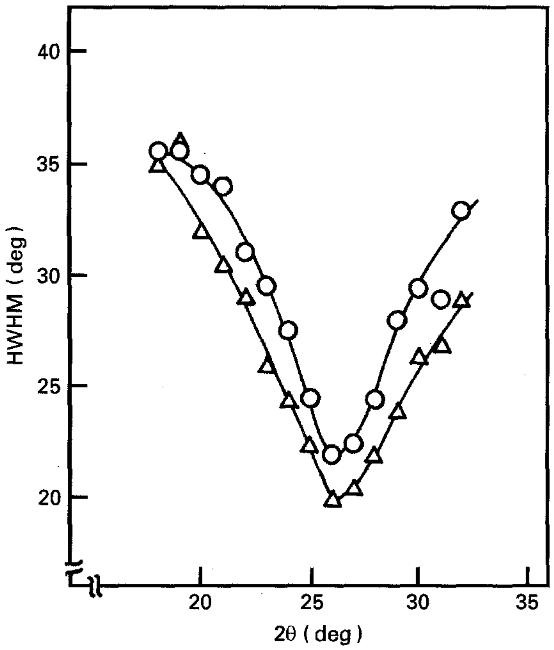

Figure 4 HWHMs as functions of 2θ for $Cl_2500(260, 90)$ (○) and Air500 (△).

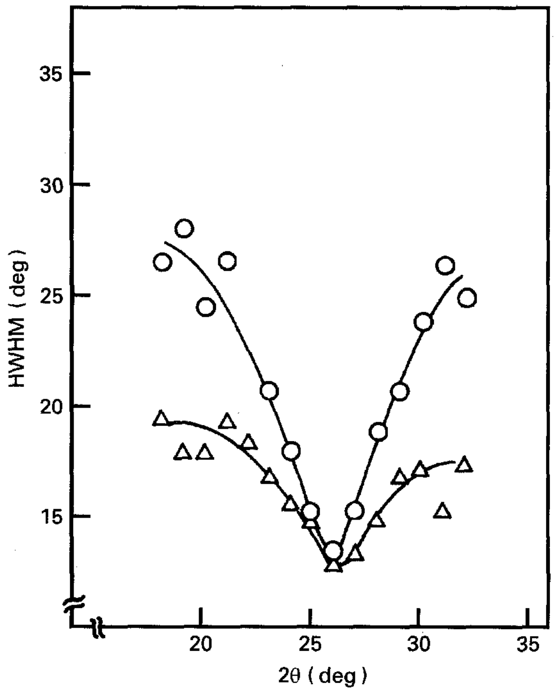

Figure 5 HWHMs as functions of 2θ for $Cl_21400(260, 90)$ (○) and Air1400 (△).

the differences in HWHM around $2\theta = 26°$ between the two kinds of thermosetting observed in the case of HTT = 500 °C, but remains or extends the differences for 2θ far from 26°.

HWHMs at $2\theta = 26°$ and 32° are plotted as functions of heat-treatment temperature (HTT) in Fig. 6 for both Cl_2 thermosetting and air thermosetting. HWHM at 26° of 2θ is mainly due to crystallites with larger $L_c(0\,0\,2)$ and that at 32° comes from smaller crystallites in $L_c(0\,0\,2)$ as mentioned above. Fig. 6 clearly shows that the difference in HWHM of larger crystallites between Cl_2 thermosetting and air thermosetting is vanishing by higher temperature heat-treatments, but the difference for smaller crystallites remains after heat-treatment at higher temperatures. The low degree of preferred orientation of smaller crystallites may contribute the depressed TM of Cl_22000 which has been mentioned in Fig. 2.

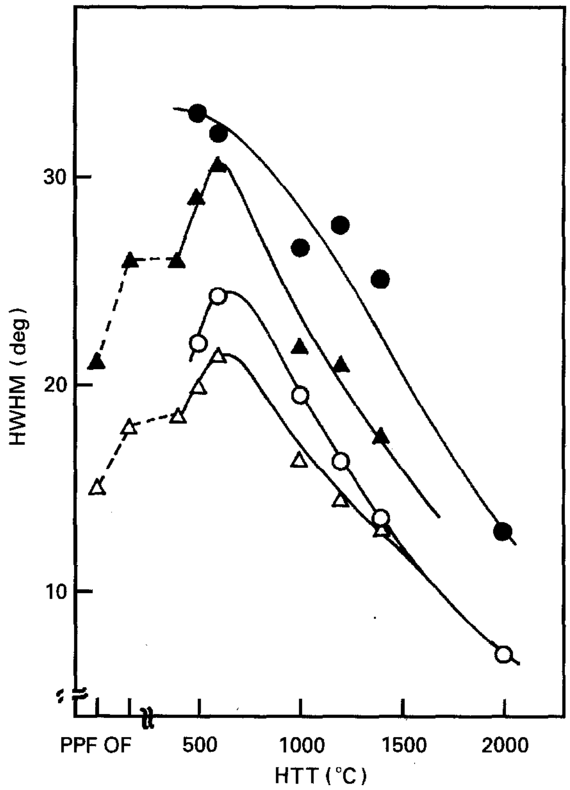

Figure 6 HWHMs at $2\theta = 26°$ and 32° for two kinds of carbon fibres which were thermoset using Cl_2 containing air at $T_f = 260$ °C and $\Delta t = 90$ min or with air and heat-treated at various temperatures. HWHMs are plotted as functions of heat-treatment temperature and the values of HWHM of a pitch precursor fibre and a thermoset fibre oxidized with air are also plotted in this figure. ○, Cl_2 (26°); ●, Cl_2 (32°); △, air (26°); ▲, air (32°).

Figs 7 and 8 show θ–2θ scan profiles as functions of ϕ from 150° to 180° for $Cl_2500(260, 90)$ and Air500 respectively. Air500 exhibits wide peaks around $2\theta = 7°$ corresponding to a periodic arrangement of crystallites [10, 11], but the peaks disappear for Cl_2500. Cl_2500 showed unusual ϕ scan profiles for $2\theta = 4°$, 6°, and 8° which have a minimum at $\phi = 180$, and the Cl_2 thermosetting would partly destroy the periodic structure in crystallite arrangement.

Crystallite sizes $L_c(0\,0\,2)s$ were calculated from the widths of the θ–2θ scan profiles shown in Figs 7 and 8 and are plotted as functions of ϕ for Cl_2500 and Air500 in Fig. 9. Fig. 9 shows that a misaligned crystallite possesses a little smaller $L_c(0\,0\,2)$ than a well-aligned one for both cases [10], and that Cl_2 thermosetting slightly depressed the size $L_c(0\,0\,2)$ of a pitch-based carbon fibre heat-treated at 500 °C, compared to the air thermosetting.

3.3. Electrical resistivity

Electrical resistivity ρ of $Cl_2800(260, 90)$ is shown in Fig. 10. The figure shows that the resistivity monotonously decreases with increasing temperature from 3 K to 300 K; the resistivity at 4 K, ρ(4) is about

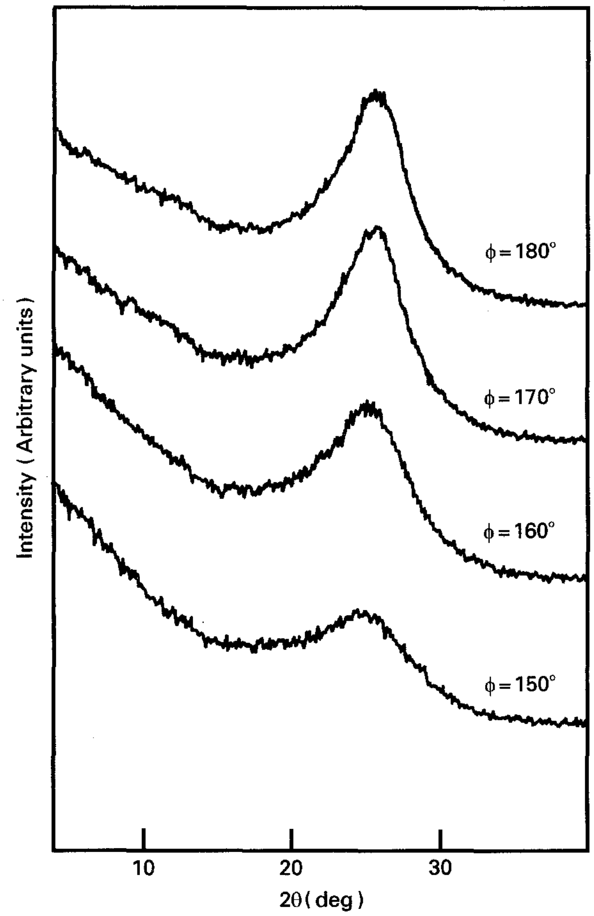

Figure 7 The θ–2θ scan profiles of $Cl_2500(260, 90)$ for ϕ = 180°, 170°, 160°, and 150°.

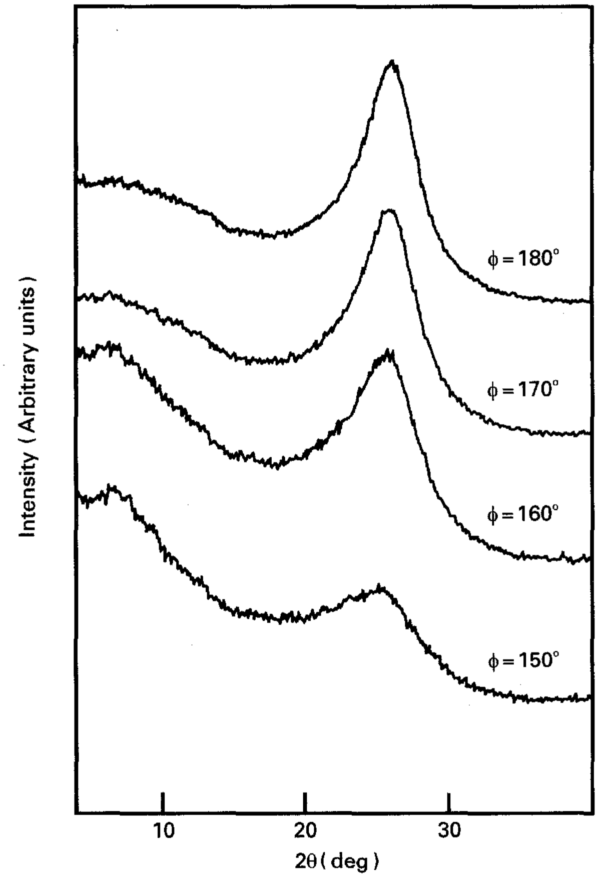

Figure 8 The θ–2θ scan profiles of Air500 for ϕ = 180°, 170°, 160°, and 150°.

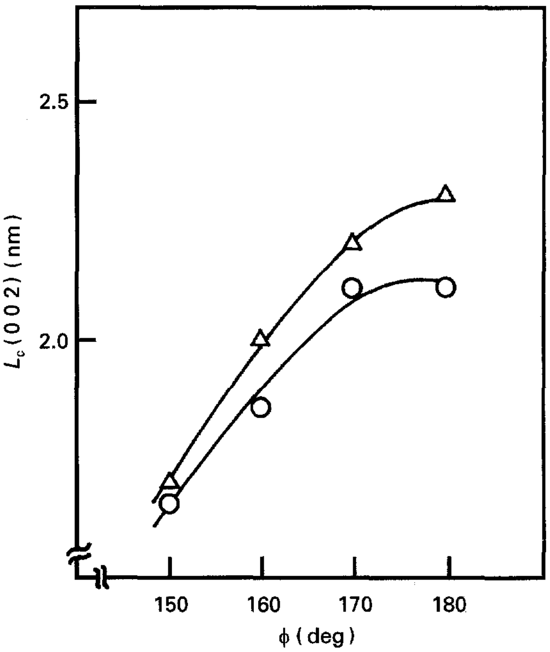

Figure 9 The crystallite size, $L_c(002)$, of $Cl_2500(260, 90)$ (○) and Air500 (△) as functions of ϕ.

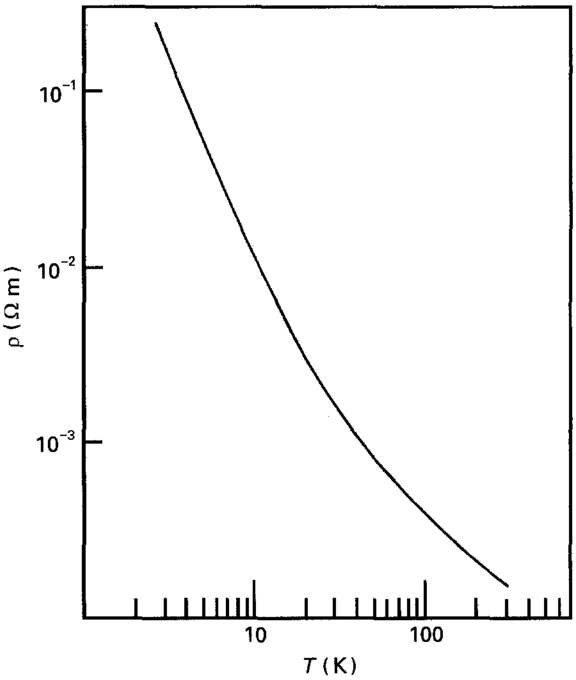

Figure 10 The temperature dependence of the electrical resistivity, ρ, of $Cl_2800(260, 90)$.

5.3×10^2 times larger than that at 300 K, ρ(300). On the other hand, Air800 exhibited a monotonous and much weaker temperature dependence of ρ, the ratio ρ(4)/ρ(300) was about 1.9. The strong temperature dependence shown in Fig. 10 of Cl_2800 corresponds to a non-metallic electrical conductivity and suggests that Cl_2800 is a more disordered system than Air800 [20–24].

The ratio ρ(4)/ρ(300) of a pitch-based carbon fibre heat-treated at lower temperatures is less affected by a transverse cross-section control in spinning [13]: Air800 with a diameter of about 10 μm and one heat-treated at 800 °C with a 25 μm diameter which was noted as #A800 and investigated in ref. [13] showed almost the same value of ρ(4)/ρ(300), and Air1000 and Air1200 respectively showed almost identical temperature dependencies of ρ with corresponding #A1000 and #A1200 having about 25 μm of diameters studied in refs [12] and [13], where #A800, #A1000 and #A1200 were thermoset by using air at the same conditions with Air800. Thus, the Cl_2 thermosetting would change the microstructures of a carbon fibre in a shorter scale than the cross-section control in spinning related to a scale of several tens of nanometres [5, 25].

$Cl_2$800 showed a stronger temperature dependence of ρ than Air700 with a rate ρ(4)/ρ(300) of about 6.9×10^1 and a weaker one than a carbon fibre (#A600) thermoset by using air at the same conditions with Air800 and heat-treated at 600 °C with a diameter of about 25 μm which was studied in [13] as #A800, #A1000 and #A1200 mentioned above. The ratio ρ(4)/ρ(300) suggests that $Cl_2$800 should correspond to an air-thermoset carbon fibre heat-treated at a temperature between 600 °C and 700 °C.

The resistivities of $Cl_2$1000 and $Cl_2$1200 are shown in Fig. 11 and the detailed temperature dependence of ρ at lower temperatures is exhibited in Fig. 12 for $Cl_2$1200. The ρ of $Cl_2$1000 monotonously decreases with increasing temperature, although Air1000 and #A1000 had a maximum around $T = 20$ K, and the temperature dependence of $Cl_2$1000 was significantly stronger than those of Air1000 or #A1000 [12, 13]. The stronger temperature dependence of $Cl_2$1000 may inherit the resistivity of $Cl_2$800 which was more disordered and non-metallic.

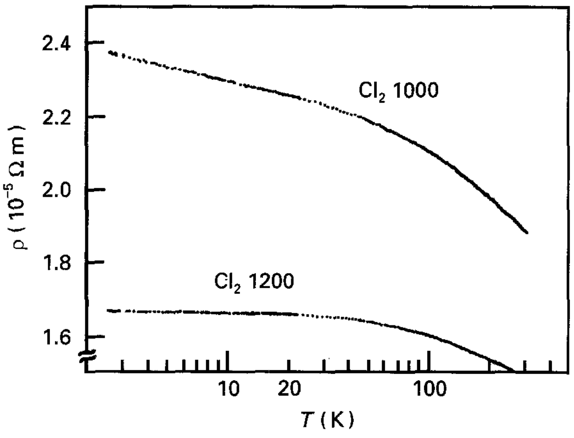

Figure 11 The temperature dependence of the electrical resistivities, ρ, of $Cl_2$1000(260, 90) and $Cl_2$1200(260, 90).

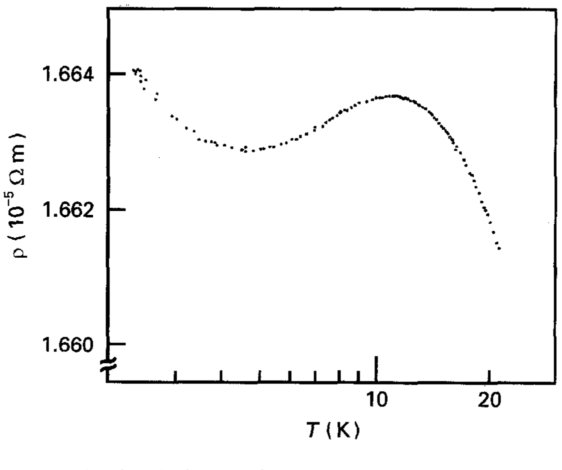

Figure 12 The electrical resistivity, ρ, of $Cl_2$1200(260, 90) as a function of temperature from about 3 K to about 30 K.

$Cl_2$1200 shows a very weak temperature dependence of ρ, especially in the lower temperature region and possesses a maximum at about $T = 12$ K and minimum at about $T = 5$ K as shown in Figs 11 and 12. Air1200 and #A1200 exhibited a maximum at about $T = 20$ K and no minimum for T higher than 2 K, similar to Air1000 or #A1000 [12, 13].

Koike and Fukase studied resistivities of carbon fibres derived from pitch and heat-treated at 1200 °C [26]. They showed that the temperature dependencies of the carbon fibres at temperatures below 10 K under a magnetic field or without magnetic field can be quantitatively explained by electron–electron interaction [27, 28], and the Kondo effect in a disordered three-dimensional system [29, 30]. A strong magnetic field applied to the carbon fibre depressed the Kondo effect and shifts a minimum position in ρ as the function of temperature to higher temperatures [26]; minimum at about $T = 1.5$ K without magnetic field and minimum at about $T = 5$ K under a magnetic field of 56 kOe. Thus, the minimum of ρ at about $T = 5$ K of $Cl_2$1200 might be due to the small Kondo effect. The increase in ρ with increasing temperature from about 5 K to about 10 K would be due to electron–phonon scattering [26], and a small electron–phonon scattering may be another explanation of the minimum at the higher temperature and the maximum at the lower temperature of $Cl_2$1200.

4. Conclusions

Thermosetting using Cl_2 containing air caused a lower density, a slightly depressed graphitization, a significantly lower tensile modulus of elasticity, and a much improved tensile strength of resultant carbon fibres heat-treated at 2000 °C. The lower tensile modulus of elasticity with an almost constant degree of graphitization by the Cl_2 thermosetting makes contrast with a constant tensile modulus and significantly lowered graphitization induced by transverse cross-section control in spinning.

The Cl_2 thermosetting misaligned crystallite orientation along the carbon fibre axis for a carbon fibre heat-treated at 500 °C, independent on the crystallite size $L_c(0\,0\,2)$. The misoriented crystallites with smaller sizes were less easily well-aligned than larger ones by further heat-treatment at temperatures higher than 1400 °C. The small crystallites which remained less oriented would partly contribute to the lower tensile modulus of elasticity of a carbon fibre thermoset with Cl_2 containing air and heat-treated at higher temperatures.

The Cl_2 thermosetting partially destroyed the periodic arrangement of crystallites and reduced the crystallite size $L_c(0\,0\,2)$ of a carbon fibre heat-treated at 500 °C.

The Cl_2 thermosetting introduced microstructural disorders to a carbon fibre heat-treated at 800 °C, and the resistivity, ρ, showed a strong temperature dependence. A carbon fibre thermoset with Cl_2 containing air and heat-treated at 1000 °C had a monotonously decreasing ρ with increasing temperature, and one Cl_2 thermoset and heat-treated at 1200 °C exhibited ρ as a function of temperature with a maximum at $T = 12$ K and a minimum at $T = 5$ K, while both carbon fibres thermoset with air and heat-treated at 1000 °C and 1200 °C showed a maximum at $T = 20$ K and no minimum in the temperature range higher than 2 K.

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