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Effect of magnesium on the composition, microstructure and mechanical properties of carbon fibres

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This work was undertaken in order to provide more detailed information on the chemical and mechanical behaviour of carbon fibres during the elaboration of graphite–magnesium composite materials. For this purpose, PAN-based T300, pitch-based P55 and P100 carbon fibres were isothermally heat treated, at temperatures ranging from 450 to 700 °C, under a saturated vapour pressure of magnesium. The composition, microstructure and tensile strength of the resulting samples were characterized by chemical and electron probe microanalysis, Raman spectrometry, X-ray diffraction and mechanical test of single filaments. From the results obtained, it has been concluded that highly graphitized fibres such as pitch-based P55 or P100 are not affected by long-time annealing in the presence of magnesium vapour, whereas impure and disorded fibres such as PAN-based T300 undergo some chemical and microstructural modifications decreasing their mechanical properties.

1. Introduction

Composite materials made of a magnesium matrix reinforced with carbon fibres appear to be very attractive candidates for aerospace applications. Owing to the low density of the metal matrix ($d = 1.74$), such materials could effectively combine high longitudinal tensile and compressive specific strength with good transverse thermal and electrical conductivity. Moreover, the use of high modulus carbon fibres in large volume fraction could result in an exceptional specific stiffness and a near-zero coefficient of thermal expansion [1–3].

Carbon–magnesium composites have been manufactured either by solid state diffusion bonding of fibre tapes previously metallized by ion plating [1–4] or by liquid phase pressure infiltration of fibre tows with pure magnesium or magnesium alloys [2–6]. The mechanical properties reported for these materials and their deviations to the rule of mixture appear to be highly dependent on the elaboration procedure. Up to now, the best results have been obtained on test pieces manufactured by liquid phase processes from fibres precoated with titanium [2], titanium borides [7], amorphous carbon and silica [3] or oxygenated compounds of titanium and zirconium [8]. Such surface treatments were initially developed in order to facilitate the penetration of molten metal into the fibre tows. Whether these coatings only promote wetting or also protect the fibres against chemical interaction with magnesium still, however, remains unanswered. Bringing out response elements to this question would permit a better understanding of the interface chemistry in carbon–magnesium composites and, thereby, contribute to the optimization of these materials. It is with this end in view that we have undertaken the present work, focused upon the chemical and mechanical behaviour of carbon fibres in magnesium.

Chemical interaction between magnesium and graphite could proceed in three different ways. Firstly, these constituents could form intercalation compounds analogous to those which exist with alkali metals and have the chemical formulae: $C_{40}M$, $C_{24}M$, C_8M (M = Rb, Cs, K), $C_{64}Na$, C_4Li [9]. In terms of electronegativity and heat of vaporization, magnesium is a poor candidate for the formation of binary intercalation phases with graphite and, at present, such Mg–C phases are unknown. Impurities and/or disorder could, however, facilitate intercalation of magnesium in graphite: in this respect, a ternary compound $C_{32}Mg(NH_3)_2$ has been isolated [9]. Secondly, carbon and magnesium could react and give the magnesium carbides, MgC_2 and Mg_2C_3. Although it has never been clearly demonstrated that these compounds could form by direct synthesis [10, 11], this hypothesis must not be ruled out since a detailed investigation conducted by Hajek *et al.* has shown that MgC_2 and Mg_2C_3 are thermodynamically stable phases at temperatures lower than about 485 and 670 °C, respectively [12, 13]. Lastly, magnesium could react with impurities contained in the fibres, more especially oxygen and nitrogen, giving rise to the formation of magnesium oxide MgO and magnesium nitride Mg_3N_2.

These reactions should induce chemical and microstructural changes in the fibres and affect their mechanical properties. Different techniques were thus used

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in order to find evidence of such modifications in PAN- and pitch-based carbon fibres heat treated for a long time in magnesium vapour at temperatures ranging from 450 to 700 °C.

2. Experimental procedure

Three different kinds of carbon fibre were used in the present study, the main characteristics of which are reported in Table I.

(i) High strength PAN-based T300 fibres graphitized at a rather low temperature (about 1500 °C) and made of porous, impure and highly disordered graphite.

(ii) Medium modulus pitch-based P55 fibres, denser, purer and more graphitized than T300 fibres.

(iii) Very high modulus pitch-based P100 fibres, still more graphitized than the former.

T300 and P100 fibres were delivered unsized; P55 fibres were desized in an ultrasonic bath for 15 min in dichloromethane.

Heat treatments of these fibres in the presence of magnesium were realized using the experimental device shown in Fig. 1. Fibre tows were introduced with a large excess of magnesium powder (purity > 99%, grain size < 300 μm) inside iron tubes having a length of 70 mm and an internal diameter of 3 mm. These tubes were filled with pure argon (0.1 MPa), sealed and placed in silica ampullae; the latter being themselves sealed under a reduced pressure of argon (0.04 MPa). The sample assemblies were inserted in a horizontal tube furnace regulated to better than ± 3 °C. Four different heating temperatures were selected: 450 °C, at which the compounds MgC_2 and Mg_2C_3 are both stable; 640 and 653 °C, at which only Mg_2C_3 is still stable and 700 °C where the magnesium carbides are both unstable. Under these conditions, each carbon filament constituting the fibre tows was surrounded by magnesium vapour, under a partial pressure varying from 2 Pa at 450 °C to 870 Pa at 700 °C [14]. The duration of the heat treatments was fixed at 1000 h at 450 °C. It was progressively reduced at higher temperatures (400, 260 and 120 h at 640, 653 and 700 °C, respectively) in order to avoid secondary reactions with the internal wall of the sealed iron tubes.

Characterization of the raw and heat treated fibre samples was carried out by different techniques. Surface morphology was systematically examined by scanning electron microscopy (SEM). The amounts of carbon, nitrogen, oxygen and magnesium were determined by chemical microanalysis: combustion at 1800 °C in oxygen for carbon, pyrolysis near 3000 °C in an helium flow for oxygen and nitrogen, dissolution and plasma emission spectroscopy for magnesium. Complementary analyses were performed by electron microprobe analysis (EMA) using a Cameca Camebax apparatus equipped with a wavelength dispersive spectrometer, Raman microprobe analysis (RMA) and X-ray diffraction (XRD). The latter technique was also used for microstructural investigations and more especially for the determination of the graphite cell parameter, *c*, and the evaluation of the crystallite size in the *c* axis direction, *Lc*: this was achieved by considering the angular position and width of the 002 reflection of graphite and by referring to the Bragg and Scherrer formulae, respectively. Finally, the tensile strength of each sample was determined by testing 40 to 45 elementary filaments (gauge length: 20 mm) and analysing the results in Weibull's statistics: the reported values refer to a failure probability of 0.5.

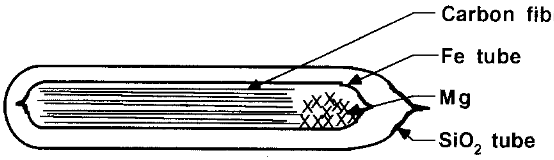

Figure 1 Experimental device used for the heat treatment of carbon fibres in saturated magnesium vapour.

3. Results

3.1. Surface morphology

SEM observations revealed that, apart from small impurity particles, the surface morphology and the mean diameter of magnesium-treated fibres were identical to those of raw fibres, whatever the kind. As an example, Fig. 2 shows T300 fibres before and after heating at 653 °C for 240 h in magnesium vapour: no surface damage can be detected on these fibres. Fig. 3 presents a magnesium crystal condensed from the vapour phase onto P55 fibres. One can observe that fibres drawn out of this crystal have left very long channels, which tends to indicate that the adherence at the metal–fibre interface is very poor.

3.2. Composition

Table II reports the results of chemical microanalyses carried out on fibre samples heated in magnesium

TABLE I Properties of carbon fibres used in this work (manufacturer's data, except for chemical analyses performed in this study)

Fibre type		T300	P55	P100
Precursor		PAN	pitch	pitch
Density		1.76	2	2.15
Manufacturer		Soficar	Un. Carb.	Un. Carb.
Chemical	C	91.8	99.2	99.6
analysis (wt %)	N	8.2	0.02	0.02
	O	0.1	0.2	0.1
Tensile strength (MPa)		3530	1900	2200
Tensile modulus (GPa)		230	380	724

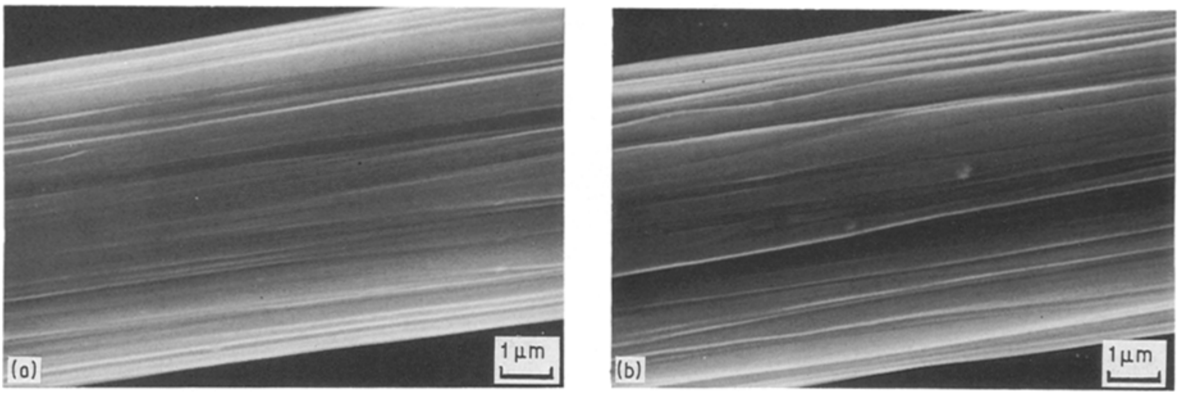

Figure 2 Surface morphology (SEM) of a PAN-based T300 fibre. (a) Raw (b) Heat treated in magnesium vapour for 240 h at 653 °C.

TABLE II Chemical microanalysis of carbon fibres heat treated in magnesium vapour

Fibre type	Heat-treatment		Fibre composition (wt %)				
	Temperature (°C)	Time (h)	C	N	O	Mg	Σ
	untreated		91.8	8.2	0.13	0.0	100.1
	450	1000	81.6	7.2	< 0.1	10.7	99.6
PAN	640	400	73.6	6.45	0.95	18.4	99.4
T300	653	240	77.1	6.2	0.5	18.4	102.2
	700	120	72.8	6.4	< 0.1	20.3	99.6
	700[a]	120[a]	91.7[a]	8.0[a]	< 0.1[a]	0.0	99.8
pitch	untreated		99.2	0.02	0.2	0.0	99.2
P55	700	120	97.8	0.02	0.1	1.8	99.7
pitch	untreated		99.6	0.02	0.1	0.0	99.7
P100	700	120	99.8	0.02	< 0.1	0.2	100

[a] Fibres heated without magnesium.

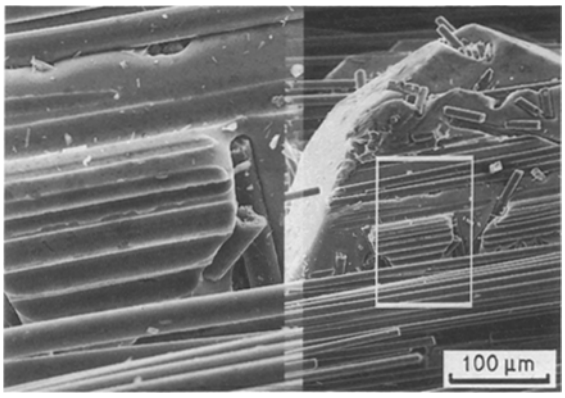

Figure 3 SEM photograph of a magnesium crystal condensed onto pitch-based P55 fibres during a heat treatment at 640 °C for 400 h.

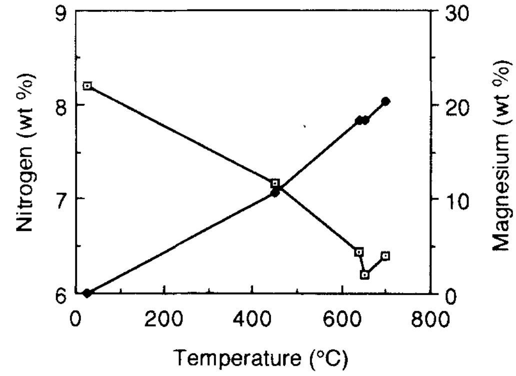

Figure 4 Variations of the nitrogen (□) and magnesium (◆) contents in PAN-based fibres Mg-treated at different temperatures.

vapour, rinsed for 15 h in a 3.6 N solution of hydrochloric acid and dried in air at 110 °C for 4 h. It appears that the amounts of carbon, oxygen and nitrogen remain constant in P55 and P100 fibres, whereas the nitrogen content of T300 fibres significantly decreases from 8.2 wt % in raw fibres to about 6.4 wt % in fibres treated at 640 to 700 °C (Fig. 4). Such a decrease is no more observed for T300 fibres heated under the same conditions, but without magnesium (Table II).

Moreover, it can be seen in Table II that substantial amounts of magnesium are present in treated T300 fibres: the content of this element varies from about 10 wt % at 450 °C to about 20 wt % at 700 °C (Fig. 4). P55 fibres also contain magnesium, but at a level tenfold to twentyfold less, whereas this element is just detectable in P100 fibres.

Electron microprobe analyses were performed on the transverse section of unrinsed filaments. Results obtained by this technique were in full agreement with the former. More especially, they brought a qualitative confirmation of the decrease in the nitrogen content of treated T300 fibres and showed the presence of magnesium in these fibres, the amount of this element

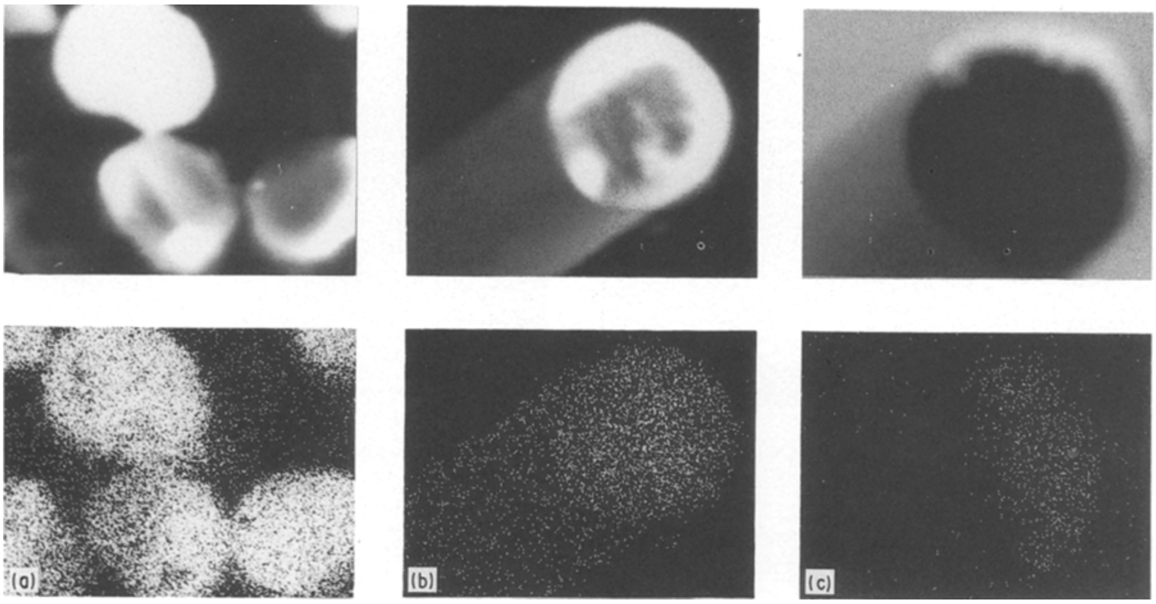

Figure 5 SEM photographs and corresponding magnesium X-ray maps obtained by EMA for treated carbon filaments. (a) T300, 653 °C, 240 h; (b) P55, 653 °C, 240 h; (c) P100, 640 °C, 400 h.

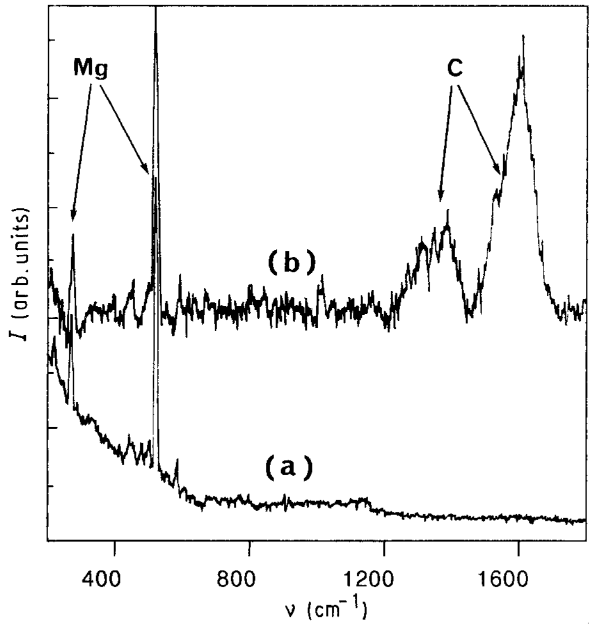

Figure 6 Raman microprobe spectra. (a) Pure magnesium. (b) Transverse section of a T300 filament after heating in magnesium vapour at 653 °C for 240 h.

varying from 10 wt % at 450 °C to 20 wt % at 700 °C. Furthermore, the latter technique revealed that magnesium was not concentrated onto the surface of the fibres but homogeneously distributed in the bulk of each filament (Fig. 5).

Complementary analyses by Raman microprobe spectrometry demonstrated that most of the magnesium distributed in the bulk of treated T300 filaments was not combined but in the elemental state (Fig. 6).

Finally, systematic characterization of the different magnesium-treated fibre samples by X-ray diffraction brought evidence neither for the presence of metallic magnesium, which is surprising at first sight, nor for that of oxides, nitrides or carbides such as MgO, Mg_3N_2, MgC_2 or Mg_2C_3. These points will be discussed later.

3.3. Microstructure

Figs 7 to 9 report the values of the graphite cell parameter, *c*, and of the mean crystallite size in the *c* axis direction, L_c, determined from the 002 X-ray reflection for all the magnesium-treated samples. It can be seen in Fig. 7 that T300 fibres undergo microstructural changes when annealed for a long time in

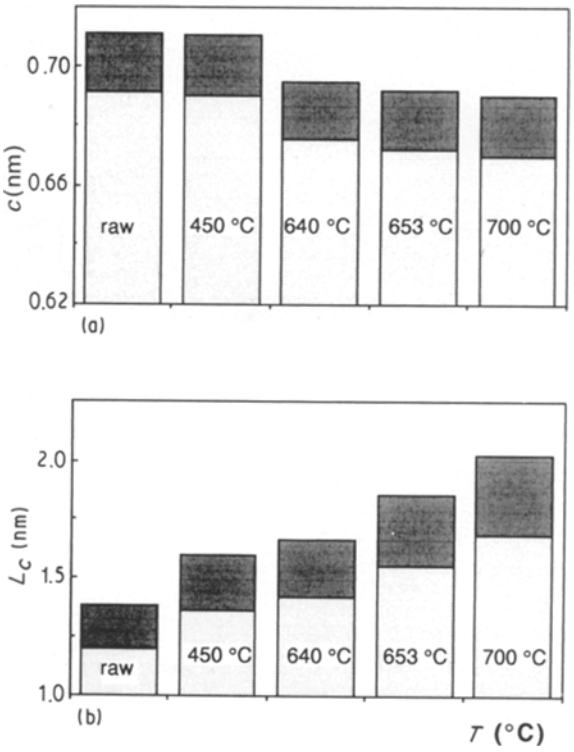

Figure 7 Graphite cell parameter, *c*, and crystallite size, L_c, for T300 fibres heat treated in magnesium vapour at different temperatures.

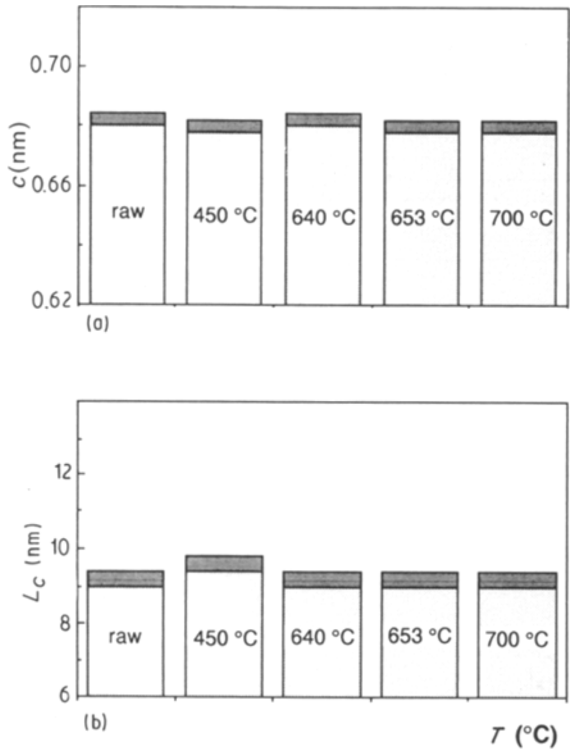

Figure 8 Graphite cell parameter, c, and crystallite size, L_c, for P55 fibres heat treated in magnesium vapour at different temperatures.

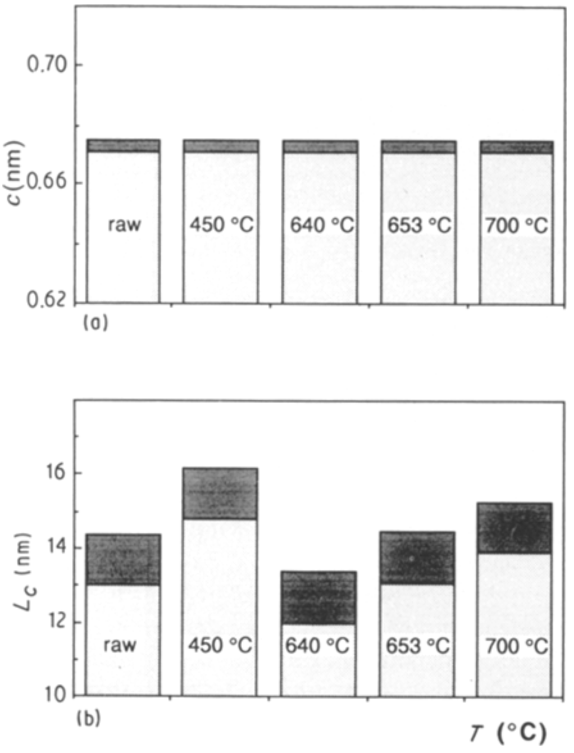

Figure 9 Graphite cell parameter, c, and crystallite size, L_c, for P100 fibres heat treated in magnesium vapour at different temperatures.

magnesium vapour: as the temperature is raised, the cell parameter, c, continuously decreases from 0.701 to 0.685 nm while the crystallite size, L_c, increases from 1.29 to 1.75 nm. Such variations, that do not occur when the fibres are heated without magnesium, characterize an ordering in the microstructure of the fibres. These changes are not detected in Mg-treated P55 fibres (Fig. 8) and P100 fibres (Fig. 9), for which the c and L_c parameters retain their initial values, whatever the treatment temperature.

3.4. Mechanical properties

Results of mechanical tests carried out on the three kinds of carbon fibre before and after long time annealing in saturated magnesium vapour at the four selected temperatures are listed in Table III. The variation of the tensile strength of the fibres with the heating temperature is illustrated in Figs 10 to 12.

It can be seen in Fig. 10 that the tensile strength of PAN-based T300 fibres varies with the treatment temperature. This strength is unchanged when heated at 450 °C for 1000 h, but begins to decrease after 400 h at 640 °C. Correlatively, Weibull's parameter, characterizing the dispersion of the results, decreases. These tendencies become more and more pronounced for T300 fibres heated in magnesium vapour for 240 h at 653 °C. At that temperature, only a half of the initial tensile strength is retained, whereas fibres annealed for the same time and at the same temperature but without magnesium are not affected. After 120 h at 700 °C in magnesium vapour, the tensile strength of T300 fibres is lower than that of untreated specimens but higher than that measured at 653 °C. Complementary experiments (Table III) were realised at 655 °C (240 h) and at 662 °C (120 h): the results obtained confirmed the anomalous decrease in tensile strength of T300 fibres heated in magnesium in the temperature range 650 to 660 °C. Changes with the treatment temperature were also observed for the tensile modulus of T300 fibres. An accurate determination of this parameter from stress–strain curves is quite hazardous, thus these changes were not considered.

Significant variations of the tensile strength with the annealing temperature in magnesium vapour are specific for T300 fibres. For P55 fibres, a slight decrease of this parameter seems to occur at 653 °C (Fig. 11) but the extent of this change is lower than in the former case. Finally, for P100 fibres, the tensile strength values appear largely scattered, due to the brittleness of the filaments, but remain approximately constant, whatever the treatment temperature, as shown by Fig. 12.

4. Discussion

Of the three types of carbon fibre studied in this work, PAN-based T300 is the only one that undergoes significant modifications in mechanical properties, microstructure and composition when heated in magnesium vapour at temperatures ranging from 450 to 700 °C. It can thus be concluded that fibres made of dense, pure and well crystallized graphite are chemically inert towards magnesium, whereas fibres made of porous, impure and highly disorded graphite can chemically interact with this metal. This interaction appears however very limited, on account of the long duration of the heat treatments in magnesium vapour and of the small amplitude of the observed modifications. Moreover, no reaction product has been characterized. Only hypotheses can, therefore, be proposed

TABLE III Mechanical properties of carbon fibres heat treated in saturated magnesium vapour

Fibre type	Heat-treatment Temperature (°C)	Heat-treatment Time (h)	Tensile strength (MPa)	Tensile modulus (GPa)	Weibull parameter
	untreated		3350	200	6.0
	450	1000	3530	230	5.5
PAN T300	640	400	2880	190	3.6
	653	240	1770	175	3.1
	655	240	1460	220	2.9
	662	120	2075	210	4.8
	700	120	2610	245	4.4
	untreated		2220	370	4.5
pitch P55	450	1000	2420	370	3.8
	640	400	2830	350	2.7
	653	240	2100	290	3.2
	700	120	2520	380	4.0
	untreated		2600	–	3.6
pitch P100	450	1000	2300	–	3.7
	640	400	2720	–	3.9
	653	240	2550	–	3.5
	700	120	2350	–	3.4

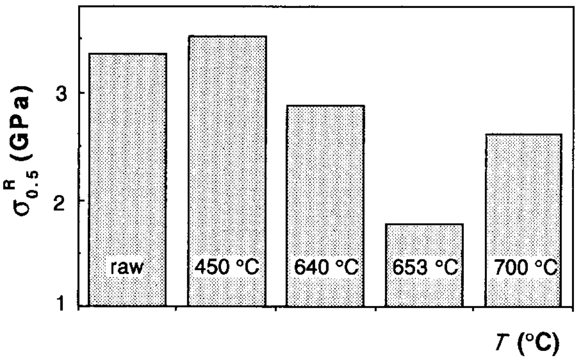

Figure 10 Tensile strength, $\sigma_{0.5}$, measured for T300 fibres heat treated in magnesium vapour at different temperatures.

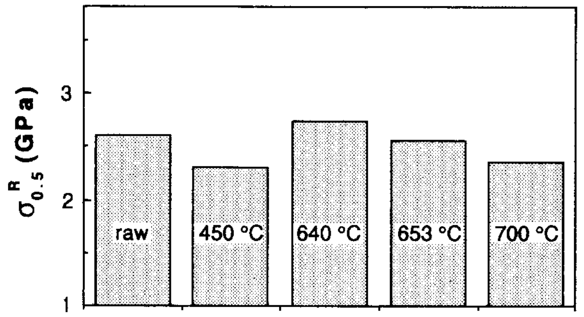

Figure 12 Tensile strength, $\sigma_{0.5}$, measured for P100 fibres heat treated in magnesium vapour at different temperatures.

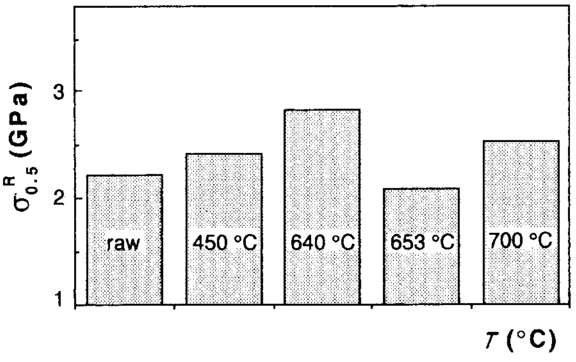

Figure 11 Tensile strength, $\sigma_{0.5}$, measured for P55 fibres heat treated in magnesium vapour at different temperatures.

to describe the chemical behaviour of PAN-based T300 fibres in magnesium.

Let us first consider the possible formation of graphite–magnesium intercalation compounds. As a general rule, insertion of electropositive elements in graphite considerably increases the spacing of the layer-planes of this phase. Intercalation of magnesium in graphite constituting T300 fibres should obey this rule and result in a dilatation of its lattice parameter, *c*. Now a variation of this parameter is effectively observed, but this variation is a decrease, not an increase. In consequence, formation of stable magnesium–graphite intercalation compounds in T300 fibres is very unlikely. One could further suppose that unstable intercalation compounds would have formed on heating and decomposed on cooling, which would be consistent with the presence of large amounts of non-crystalline metallic magnesium inside treated T300 filaments and with the low values measured at room temperature for the lattice parameter, *c*. Such chemical reactions would, however, give rise to exfoliation in the fibres and to modifications of their mechanical properties much more striking than those observed. The latter hypothesis, therefore, also appears very unlikely.

Another type of chemical interaction that could occur between magnesium and T300 fibres is the formation of magnesium carbides. Taking into account the thermodynamic stability of these compounds, temperatures just lower than 485 and 670 °C would correspond to the most suitable conditions for the synthesis of MgC_2 and Mg_2C_3, respectively. The fact that the mechanical properties of T300 fibres are entirely retained after heating for 1000 h at 450 °C in magnesium vapour tends to indicate that, contrary to previous assumptions [15], formation of MgC_2 must be ruled out. One cannot be so categorical as regards the possible formation of Mg_2C_3. On one hand, no evidence of the presence of this compound has been found in T300 fibres. On the other hand, however, complementary experiments we have recently undertaken have shown that small amounts of Mg_2C_3 could be synthesized by heating at 662 °C for 240 h amorphous carbon from acetylene pyrolysis and magnesium vapour. As T300 fibres contain porous and highly disorded graphite, formation of undetectable traces of this compound at temperatures slightly lower than 670 °C is then not impossible.

To finish with chemical reactions, let us now examine the possible combination of magnesium with impurities contained in T300 fibres and more especially, with nitrogen and oxygen. Unlike magnesium carbides, magnesium nitride Mg_3N_2 and magnesium oxide MgO are thermodynamically very stable phases. Conversion of nitrogen and oxygen initially present in the fibres into Mg_3N_2 and MgO appears, therefore, very likely. As concerns nitrogen, chemical microanalyses and EMA have revealed a decrease in the content of this element in magnesium-treated T300 fibres, from 8.2 to 6.4 wt % N at 700 °C (Fig. 4), whereas such a variation has not been observed for fibres annealed under the same conditions without magnesium. It can thus be concluded that magnesium promotes the extraction of nitrogen from the fibres. Only a small part of nitrogen initially present in these fibres is, however, concerned. Then, only little amounts of Mg_3N_2 can be produced, which would explain why this compound has not been characterized by X-ray diffraction. As for oxygen, its content in raw fibres is much too low for further characterization of MgO.

If one cannot refer to chemical interaction to explain the presence of large amounts of metallic magnesium inside magnesium-treated T300 filaments (Fig. 4), how can it be accounted for? In this respect, it must be remembered that T300 fibres are very porous, due to their low graphitization temperature ($d = 1.76$). Magnesium vapour can then penetrate into the opened pores of these fibres. A simple condensation of this vapour on cooling can explain the presence of metallic magnesium inside the filaments, but not the large amounts found. The only phenomenon that can account for such large amounts (Fig. 5) is the capillary condensation of solid or liquid magnesium, from its saturated vapour, during the whole course of the heat-treatment. Such a phenomenon only occurs in pores having a mean diameter lower than about 50 nm; then, magnesium crystals formed in these pores cannot be larger. These would be the reasons why, although abundant, these crystals were not attacked by an acidic solution which does not sufficiently wet carbon to infiltrate the pores and why metallic magnesium has not been detected by X-ray diffraction. Capillary condensation can also occur in P55 fibres, but to a far lesser extent since these fibres have a much lower porosity than T300. As for P100 fibres, the opened porosity appears negligible.

Capillary condensation is essentially a physical phenomenon involving very small energy exchanges. It is thus very unlikely that it induces notable modifications in the mechanical behaviour of the fibres. This assumption is supported by the fact that, although fairly rich in magnesium, T300 fibres entirely retain their mechanical properties when heated for 1000 h at 450 °C in saturated magnesium vapour.

On the contrary, extraction of nitrogen via a chemical reaction is a highly energetic process. It effectively involves the breaking of strong carbon–nitrogen bonds within C–N heterocycles. Now, it is generally assumed that nitrogen is a graphitization inhibitor in PAN-based fibres [16]. Extraction of nitrogen by heating in magnesium would then be the reason for the low-temperature ordering of the layer-planes observed in T300 fibres (Fig. 7) and, thereby, for a significant decrease in their tensile strength. It can, however, be seen in Fig. 7 that the microstructural parameters, c and L_c, regularly vary with the temperature of the heat treatment. If recrystallization was the only factor affecting the mechanical properties, the tensile strength of T300 fibres should regularly decrease for increasing treatment temperatures. As the tensile strength of these fibres and, to a lesser extent, their modulus go through a minimum near 653 °C (Fig. 10), another contribution must be considered. This contribution could be the formation of traces of the magnesium carbide Mg_2C_3 just below its decomposition temperature, i.e. 670 °C.

5. Conclusion

From the foregoing results, it is clear that highly graphitized carbon fibres such as pitch-based P55 or P100 exhibit an excellent chemical inertness towards magnesium, at temperatures ranging from 450 to 700 °C, whereas impure and low graphitized fibres such as PAN-based T300 undergo some modifications in composition, microstructure and mechanical properties that can be attributed to chemical reactions. These reactions, however, appear to proceed very slowly.

It can thus be concluded that degradation of carbon fibres by chemical interaction with magnesium cannot be the major cause for large deviations to the rule of mixture in carbon–magnesium composites, especially if highly graphitized fibres are used. It can be thought that the excellent chemical inertness of graphite towards magnesium is responsible for a poor wettability between fibres and liquid metal and for a weak interfacial bonding. Consequently, fibre surface treatments or addition to magnesium of carbide formers would be needed to reinforce the metal–fibre adherence and improve the mechanical properties of these composites.

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