JOURNAL OF MATERIALS SCIENCE 31 (1996) 6189–6193

Some microstructural aspects of vapour-grown carbon fibres to disclose their failure mechanisms

A. MADROÑERO, E. ARIZA
CENIM, Avda Gregorio del Amo 8, 28040 Madrid, Spain
M. VERDÚ
CIDA, C/Arturo Soria 289, 28033 Madrid, Spain
W. BRANDL
Fachhochschule Gelsenkirchen, Neidenburgerstrasse 10, 45877 Gelsenkirchen, Germany
C. BARBA
Centro de Microscopia Electronica, Universidad Complutense, 28003 Madrid, Spain

The microstructure of vapour-grown carbon fibres has been studied by an SEM examination of the transverse section. In this way the duplex structure, of catalytic and pyrolytic carbon, can be differentiated by the fracture of each phase; pyrolytic carbon shows concentric circles, termed *tree trunk* structure, while a glassy appearance characterizes the pyrolytic phase. It was observed that fracture was strongly influenced by the breaking mode of the fibre, because in tensile failure of a thick fibre, fracture similar to the tree trunk appearance can be formed in the outer layer of the pyrolytic phase. Thus it is necessary to study the transverse microstructure of vapour-grown carbon fibres without any failure process. Using a preparation of fibre samples, in slides as thin as necessary for TEM study, the internal structure was disclosed. The pyrolytic phase was constituted of randomly oriented small crystals, while the tree trunk structure was really formed by very elongated crystals with preferential orientation. Electron diffraction of both phases shows a different degree of texture according to the structures. In addition to crystals, TEM examination showed the existence of hollow cavities, that have a clear influence on the failure mechanism. Owing to these faults, the failure process forms parallel grooves, that constitute the tree trunk appearance.

1. Introduction

Vapour-grown carbon fibres (VGCF) are short carbon fibres having a clear potential as reinforcers for composite materials in a wide market, owing to their low cost [1]. They are not yet commercially produced, but their simplicity of production [2] and their mechanical properties [3], besides their exceptional thermal [4] and electrical conductivities [5], suggest a very good industrial future for VGCF.

As in all materials, their optimization requires a good knowledge of the microstructure and the relationship between manufacturing process and microstructure. The VGCF formation was described by Tibbetts and Beetz [6]. Basically it consists of a minute metallic particle of iron or of any other transition metal, that catalyses the decomposition of the gaseous hydrocarbon existing in the atmosphere when fibres are grown. The carbon liberated in this way is at first adsorbed and after exhaustion from the metallic particle, forms a regular filament of the phase named *catalytic*.

At the same time that this catalytic process occurs, the pyrolytic decomposition of the hydrocarbon produces a layer of pyrolytic carbon on the solid catalytic primitive filament.

There is a variation of this model of carburization of the metal seed. It consists of the formation of a liquid drop around the metallic particle, followed by a vapour–liquid–solid (VLS) mechanism [7]. The enlarging of the primitive filament is now quicker, but the structure of the grown fibre is almost the same. In the present work, all the studied fibres were grown by the VLS mechanism.

In any case, when a batch of produced VGCF is examined in a scanning electron microscope (SEM), Model JSM 6400, working at 20 kV, we can see fractures as shown in Fig. 1, a couple of unintentionally broken fibres. In the centre of the fibre, a tree trunk structure can be seen, and then a second layer showing a glassy fracture (without parallel circles) indicates the pyrolytic phase. There is no clear boundary between catalytic and pyrolytic phases.

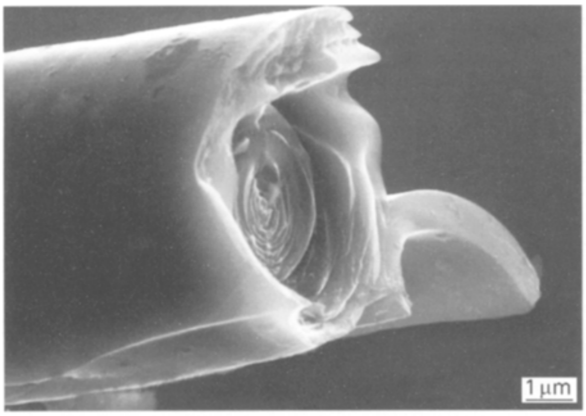

Figure 1 Unintentional failure of a duplex VGCF.

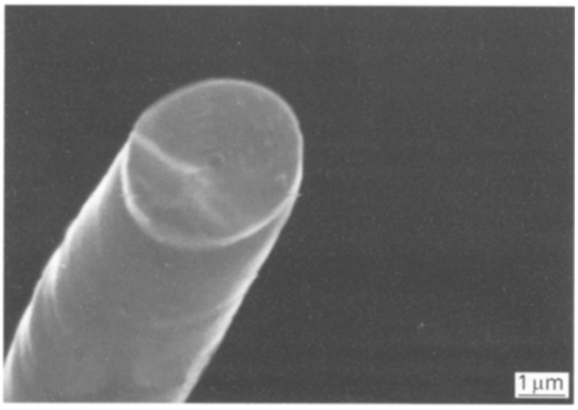

Figure 2 Unintentional failure of a single-phase VGCF.

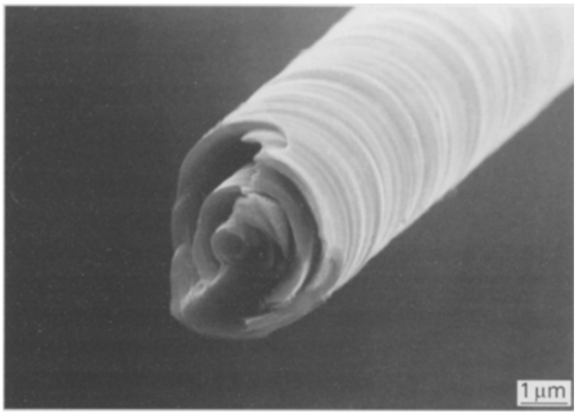

Figure 3 Fracture of a thick VGCF after cutting with scissors.

As the manufacturing time was extremely long, one-third of the layer of pyrolytic carbon coated the duplex fibre, achieving a common wrapping for two neighbouring complete fibres. The adhesion of this last layer appears to be extremely weak.

If we attempt to study the core of the tree trunk structure, without the pyrolytic addition, it is necessary to produce VGCF with such a short manufacturing time that the cortical layer could be negligible. In Fig. 2, a fibre of this type is shown. Surprisingly, the tree trunk structure is no longer clearly displayed, suggesting that the tree trunk structure is crudely formed during the catalytic enlargement of the first filament body, and during the later times of fibre forming it becomes more markedly established.

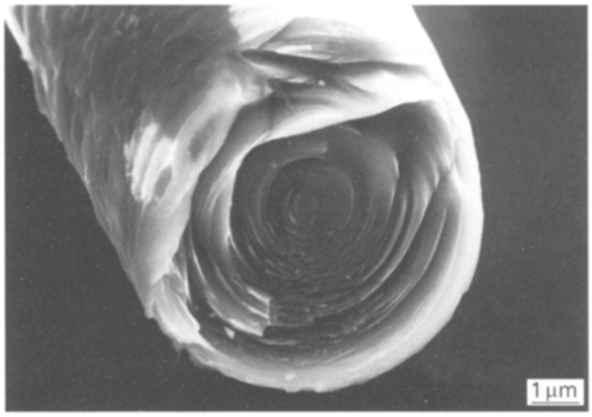

Figure 4 Tensile fracture of a thick VGCF.

If we prepare thick fibres (their manufacture requires only a very large manufacturing time, in order to allow the coating to reach a large thickness) and break them in a different controlled manner, in order to produce a transverse section easy to examine in the SEM, the results are surprising. Fig. 3 shows a fibre cut by scissors. As a consequence of the non-uniform shear stress during the cut, the outer pyrolytic layer shows a wide range of different local fractographies. Fig. 4 shows a tensile fracture of a wholly similar fibre, from the same batch. In contrast with Fig. 3, the tensile process yields, in the outer layer, a fracture that resembles the tree trunk structure.

The examination of these two last fractures could be interpreted as if the tensile process enhances the formation of parallel ring fracture. On the other hand, shear breaking does not. So, the SEMs evaluation of a fracture requires distinction to be made between real aspects of the fibre phases, and aspects originated by the failure process.

2. Experimental procedure

Transmission electron microscopy and electron diffraction studies were carried out on a Jeol, Mod. JEM 2000FX, working at 200 kV, the microdiffraction method being used. To perform TEM observations, the obligatory first step was to obtain ultrathin sections, ultramicrotomy being a good method for that purpose. The sample preparation was an important factor to bear in mind. Samples were embedded, prior to sectioning, in an epoxy resin (Epon 812) to obtain transverse cuts. Ultramicrotome sections, 60 nm thick, were cut with diamond knives in an ultramicrotome Reichert, Model Ultracut E. The effort required to prepare these samples was extremely tedious, because most of the samples are destroyed during the second cut. Therefore, it was necessary to produce a large number of sample preparations to achieve the necessary number of samples for this study.

In Fig. 5 we can see a transversel section of the core area of a VGCF. The very elongated and reasonably parallel flakes, translated to a ribbon structure if we think in three-dimensional terms, suggest a structure similar to Ruland's model [8]. Between the ribbon (about 800 nm according to Fig. 5) there are empty

Figure 5 Core zone of a VGCF.

spaces or cavities, observable at higher magnification, as we can see in Fig. 6.

The most important consequence is that there is no microscopic architecture that substantiates the hypothesis of circularly bent planes as suggested by the tree trunk structure of Fig. 1. In fact, the microstructure of the core of a VGCF is more similar to a rope than to a trunk tree, according to the TEM image in longitudinal section published by Tibbetts [9].

In contrast, the cortical structure, according to Figs 7 and 8, shows small crystals, sized about 150 nm, randomly oriented and having no sharp shape, as occurs in the core area crystals. The difference in appearance between both these figures is that in thick cortical areas (Fig. 8) there are more hollow spaces than in thin cortical ones (Fig. 7).

Fig. 9 shows an electron beam diffractogram in which a more pronounced (0 0 2) texture can be seen in the core area than in the cortical one, according to Figs 6 and 8.

The last aspect to be studied here is the boundary between phases in VGCF. In Fig. 10 it is possible to see a boundary between the core area (bottom right corner) and the cortical area (upper part of the picture). The boundary is rather coherent. The hollow intergranular spaces are small and narrow in the core area, but in the cortical one they are irregular.

In Fig. 11 we can see a boundary between two pyrolytic sublayers in the cortical area; the accumulation of large faults is equivalent to a weakness wall.

Figure 6 Core zone of a VGCF.

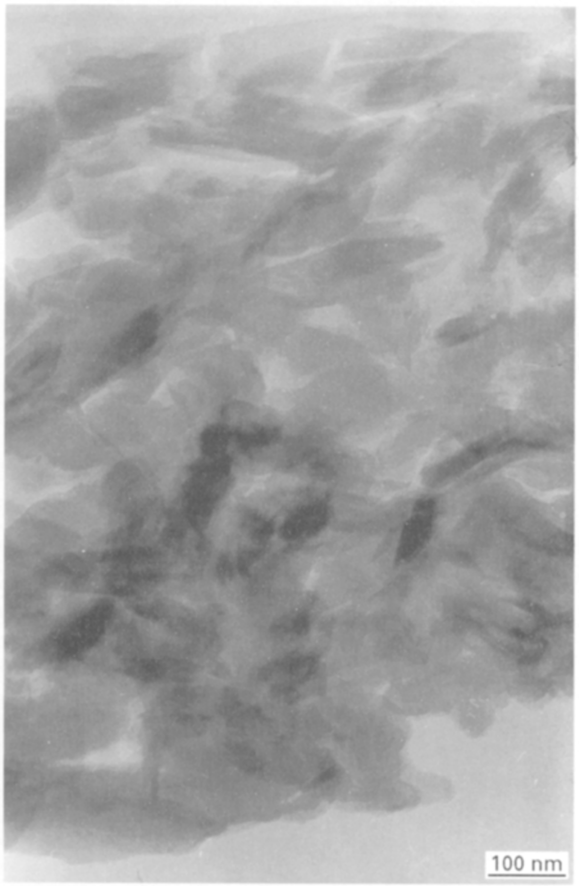

Figure 7 Cortical zone of a thin VGCF.

Figure 8 Cortical zone of a thick VGCF: (a) cortical area, (b) core area.

Figure 10 Boundary between pyrolytic and catalytic phases.

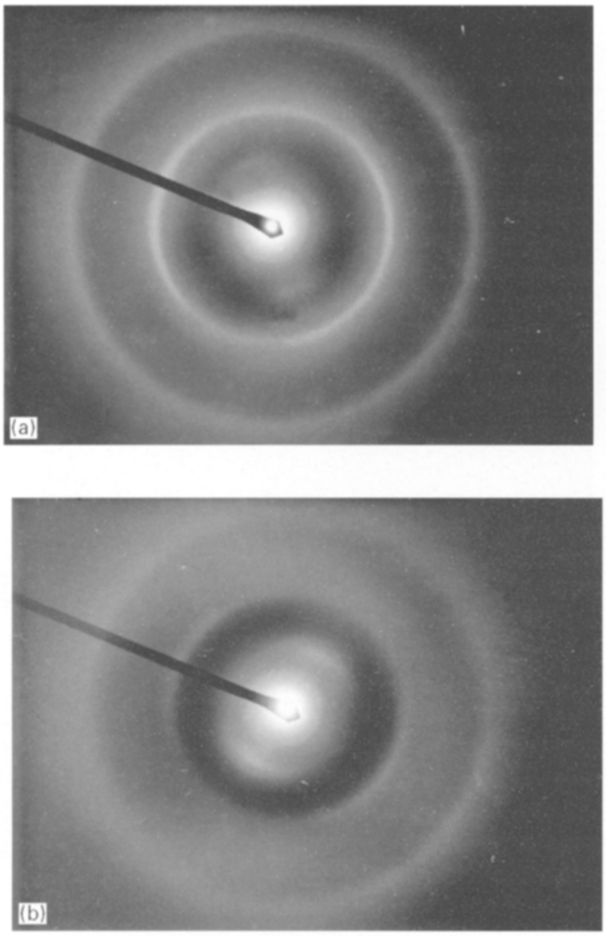

Figure 9 Electron diffraction in VGCF.

Figure 11 Boundary between two pyrolytic layers in the cortical area.

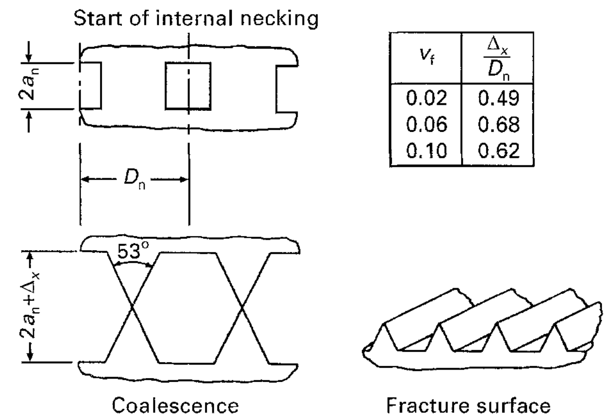

Figure 12 Displacements and internal neck profiles for coalescence of cavities, and resulting fracture surface, from [12].

This explains the delamination between pyrolytic layers in Fig. 1.

3. Results and discussion

The most relevant aspect of the pre-exposure results is the absence of the curved planes (Fig. 1) in centre of the core area. The formation of such planes was explained by Tibbetts [10] as a peculiarity of the exhaust process of the carbon from the carburized seed by precipitation in the seed–filament interface. This kind of curved crystallographic plane is similar to other proven structures frequently found in natural graphites [11]. Nevertheless, we think that the formation of such rings is an effect of the tensile stress, as is suggested by the outer skin of Fig. 4. In the technical literature there is some description [12] of the formation of parallel grooves during failure by the effect of pre-existing cavities; such jutted out tracks are the result of internal necking between adjacent cavities (see Fig. 12). So, as the cavities are more elongated and regular in the core zone than in the cortical one, the tree trunk appearance after failure is characteristic of the core zone.

It is possible to think also that the parallel grooves formed in Fig. 4 could be produced by cavities similar to those shown in Fig. 8. So, in not very thick fibres, as Fig. 7 shows, the grooving of the outer layer of Fig. 4 does not take place.

In any case, achieving a complete knowledge of the relationship between failure mode and fracture in VGCF would require further studies.

4. Conclusions

1. From the crystalline point of view, core and cortical phases are distinguishable by the different grain shapes and preferential orientation.

2. In the core area there is a significant texture as a consequence of the preferential orientation of their grains parallel to the fibre axis, and such texture can be evidenced by electron beam diffraction.

3. When the pyrolytic coating is extremely thick, the number of faults increases and weakness walls could exist.

4. The appearance of circularly bent planes, labelled tree trunk structure, in addition to Tibbetts's explanation, admits a justification as an internal necking between adjacent cavities. From this point of view, tree trunk structure is a non-pre-existing structure, formed during tensile failure.

Acknowledgement

The present work was realized as an action of the Human Capital and Mobility Network "Productions and Applications of Vapour Grown and other Ceramic Fibres and Filaments" (Contract CHRX-CT-94-0457). We thank the Commission of the European Communities for the financial help to perform this study.

References

1. S. BECK, in "How to apply advanced composites technology", ASM International Congress, Dearborn, MI (1988) p. 463.
2. M. ENDO, *Chem. Technol.* **7** (1988) 568.
3. G. G. TIBBETTS, *Carbon* **27** (1989) 745.
4. B. NYSTEN and J. P. ISSI, *Composites* **21** (1990) 339.
5. J. HEREMANS, *Carbon* **23** (1985) 431.
6. G. G. TIBBETTS and C. P. BEETZ, *J. Phys. D Appl. Phys.* **20** (1987) 292.
7. A. MADROÑERO, *J. Mater. Sci.* **30** (1995) 2061.
8. W. RULAND, *Appl. Polym. Symp.* **7** (1969) 293.
9. G. G. TIBBETTS, in "Vapor-grown carbon fibers", edited by J. L. Figuereido, C. A. Bernardo, R. T. K. Baker and K. J. Hüttinger, NATO AISI, Series E, "Applied Science", Vol. 177 (Kluwer Academic Press, Dordrecht, The Netherlands, 1990) p. 73.
10. *Idem*, in "Physical modelling of carbon filament growth", edited by J. L. Figuereido, C. A. Bernardo, R. T. K. Baker and K. J. Hüttinger, NATO AISI, Series E, "Applied Science", Vol. 177 (Kluwer Academic Press, Dordrecht, The Netherlands, 1990) p. 525.
11. U. B. HEZEL, E. ZELLMANN and D. HOFFMEISTER, in "Proceedings of the 42nd Annual Meeting of the Electron Microscopy Society of America", edited by G. W. Bailey (San Francisco Press, San Francisco, CA, 1984) p. 276.
12. P. F. THOMASON, *J. Inst. Metals* **96** (1968) 360.

Received 2 October 1995
and accepted 2 July 1996