Possibilities for the vapour–liquid–solid model in the vapour-grown carbon fibre growth process

A. MADROÑERO
CENIM, Avda Gregorio del Amo 8, 28040 Madrid, Spain

Vapour-grown carbon fibres are very promising as composite reinforcers due to their low cost, about $ 10/kg. They are currently produced on a laboratory scale, but to reach an industrial production volume, it would be necessary to increase their final length up to the centimetre range. Current literature describes how the catalytic growth of such short fibres is finally poisoned by the carbon-deposition pyrolytic process, so the achievement of fibres larger than a very few millimetres, is rather difficult. A slight change in the habitual routine production process, however, it makes possible to grow this type of fibre by an as-vapour–liquid–solid growth model, which yields grown fibres with a very attractive length. In this model, hydrogen plays an important role.

1. Introduction

The substitution of conventional materials by new materials for high market-volume applications, is an option that depends, first and principally, on the relative saving in weight that their use offers, and secondly, the penalty in cost/kilogram that their use imposes.

In a comparative study in the automotive industry carried out by Beetz et al. [1], where steel was substituted by glass fibre-reinforced plastics (GFRP)-type composite materials, by aluminium alloys and by carbon fibre-reinforced plastics (CFRP), it was found that while GFRP offered a 27% mass saving (MS) with a cost penalty (CP) of $ 0.68/kg, and the aluminium alloy gave a 35% MS with a CP of $ 0.60/kg, the CFRP offered an MS of 45% but with a CP of $ 2.87/kg. The CP/MS ratio is 3.7 times worse in CFRP than in GFRP. This means that the use of carbon fibre (CF) in the automotive industry is still very limited and only a 6% CF produced in the World is intended for the land-transport industry.

The CP/MP ratio of CFRP can only be improved by decreasing the price of the CF, which is impossible with the manufacturing technology of current ex-polyacrylonitrile (PAN) fibres, mainly due to the high energy consumption. The most promising possibility that has appeared on the industrial horizon for the most economical types of CF is vapour-grown carbon fibres (VGCF) to which Beck [2] assigned a cost of $ 10/kg. This new type of CF is defined by Daumit [3] as: "A non-continuous CF. For its production, a hydrocarbon vapour is combined with a catalyst source (e.g. iron particles) and hydrogen. In an elevated temperature environment, the hydrocarbon gas decomposes, yielding carbon which dissolves in catalytic particles and initiates the growth of primary fibres. Such primary fibres are subsequently thickened through additional carbon deposition to a diameter of several micrometres and then heat-treated to enhance crystal structure and properties".

In the present paper, formation process of VGCF and its relationship with the internal structure of VGCF, are reported.

2. Models of formation and internal structure

The processes for forming VGCF fibres have been widely studied [4–6] and are based on a catalytic vapour–solid (VS) process to absorb the atomic carbon that is produced in the atmosphere as a consequence of the reduction of hydrocarbon in the form of vapour. The absorbed carbon saturates the seed that is always constituted by a minute metal chip from group VIII: Fe, Ni, Co, etc., which are very prone to form metallic carbides. The excess carbon is expelled in the form of carbon filament, as shown in Fig. 1. The structure of the grown filament has, as Fig. 2 shows, a hollow channel just in the centre of the fibre.

The enlargement rate of the VGCF due to the catalytic process is controlled by the chemical activity of the gas-phase carbon [7]; when the activity, a_c, is small, as occurs in αFe catalyst, the growth rate is proportional to a_c, but when a_c is high, as in γFe or nickel catalyst, the growth rate is independent of a_c. As the diffusion coefficient and the mass fraction of carbon in the metal chip depend above all on the carbon activity, the growth rate of VGCF cannot be increased to improve the manufacturing process efficiency.

Simultaneously with this catalytic process, the thickening process of the carbon filament takes place through a slow, non-catalytic deposition of pyrolytic carbon; when this coating is sufficiently thick (see Fig. 1), the active seed located at the fibre point has its feed interrupted for the carbon pyrolytic layer, and the lengthening of the fibre ceases. Then, it is said that the growth has been poisoned.
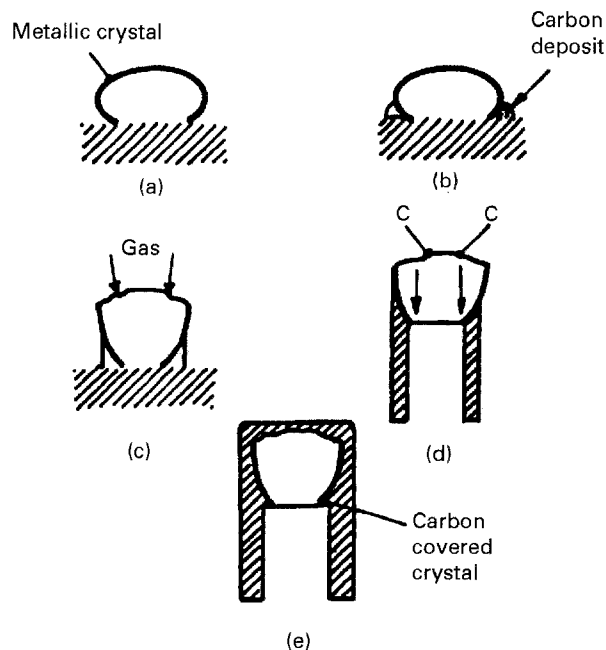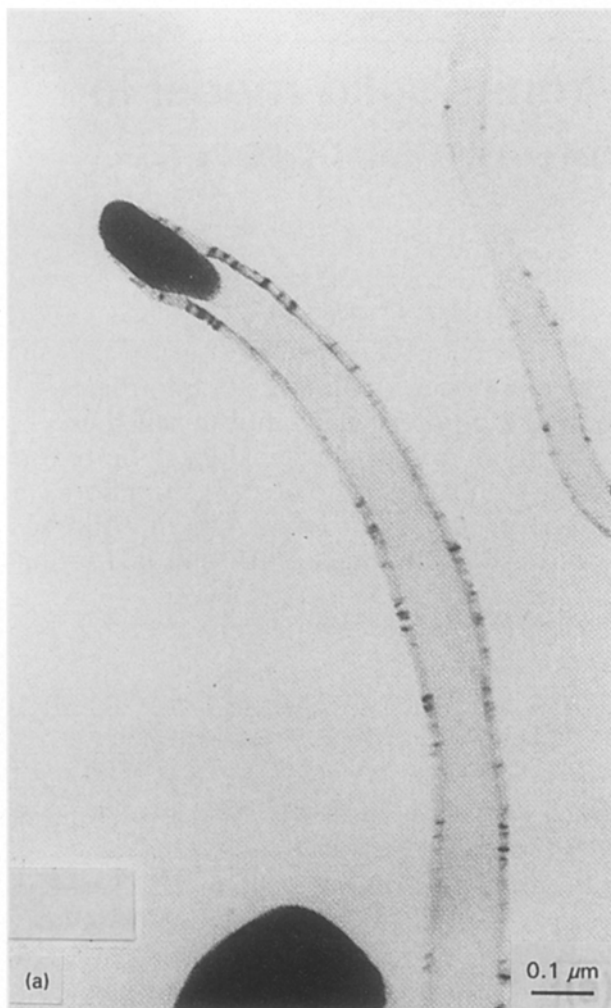
Figure 1 (a) The VS model for the VGCF growth process (from [19]) (b) growing model from [19].

As this poisoning is such a great inconvenience, the habitual reactant atmospheres (i.e. 70% hydrogen plus 30% methane) are rather poor in hydrocarbon content and rich in hydrogen, as required to promote a very weak pyrolytic deposition [8]. The scarcity in hydrocarbon content, also prevents the quick formation of a thick layer of black cake, or lampblack, on the substrate when the metal seeds form, which buries the nascent VGCF filaments and impedes their growth.

Owing to these circumstances, the final length of VGCF is usually too short (about 1 mm) [9] for conventional manufacturing industrial processes of short-fibre composite parts production, such as, for example, resin transfer moulding (RTM), sheet moulding compound (SMC), etc. Because of this excessive shortness, VGCF are not yet in industrial production.

In order to solve the problem of this lack of fibre length we used one facility as described in everywhere [10] to produce VGCF, but with the work routine different from the habitual one, described in [9], for example.

As the nature of the substrate has a remarkable influence on the structure of the grown fibre [11] we used a work routine as shown in Fig. 3. Basically, it consists in a first coating of carbon black on the substrate prior to supplying a spray of an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The small crystal salt was then exposed to an atmosphere 100% H_2, that

converted it into a metal chip. After that, a brief exposure to an atmosphere of 50% methane plus 50% H_2 yields a thin, second, carbonaceous coating on the seeds which rest shallowly buried in a carbonaceous environment with a high content of hydrogen [12, 13]. The effect of the substrate has been nullified.

After this growth process preparation, a standard routine work, as mentioned by Tibbetts [9], for example, having a working temperature of 1060 °C, produced an abundant VGCF formation.

The appearance of VGCFs formed in this way is shown in Fig. 3. Fig. 3b shows how the chip of catalyst remains in the substrate, so that on the tip of a growing fibre there is no active carbide (Fig. 2). In Fig. 3c, a joining of three fibres suggests a welding possibility in the tip of a growing fibre. This allows us to hypothesize that on the tip of each fibre, a non-solid drop of material constituent of the fibre [14] exists during the growth process, instead of the solid oversaturated metal carbide (see Fig. 1), as the VS process imposes. This suggests that a mechanism similar, in some way, to the vapour–liquid–solid (VLS) model, described by Portnoi *et al.* [15] for SiC whiskers, took place in the formation of the fibres in Fig. 3. Several aspects of this as-VLS process will be discussed below.

The great advantage of this as-VLS process is that the growth rate of the VGCF is now higher than in the VS process, because in such an as-VLS model, the
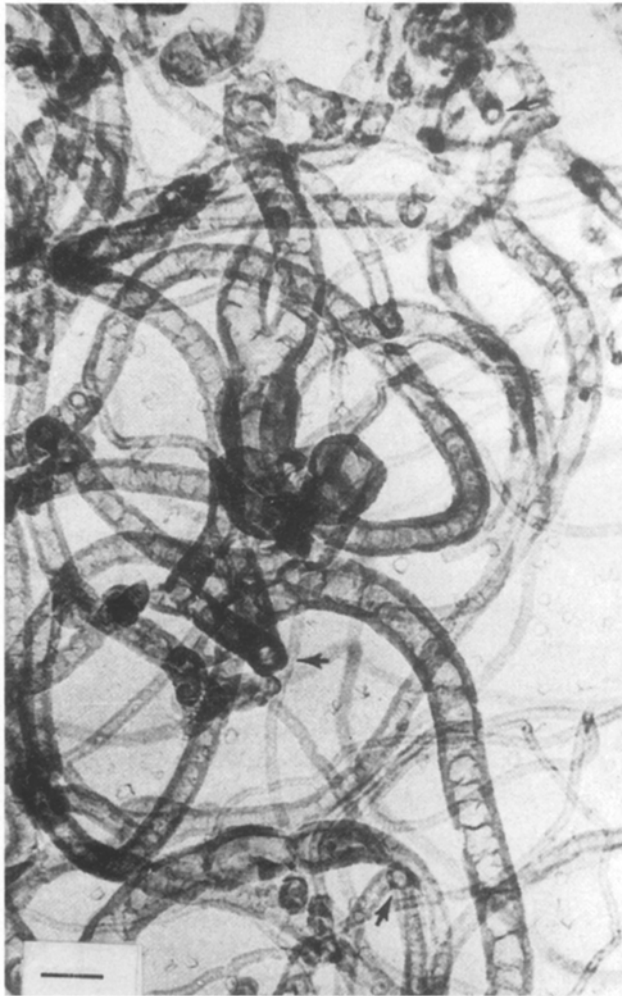
Figure 2 Electron microscopy examination of the filaments, showing the "hollow fibre" structure (from [20]).

growth mechanism is controlled by the diffusion of carbon in a non-solid material drop at the tip of the growing fibre. This explains the length achieved in VGCF produced in our laboratory (see Fig. 3d) under the same experimental conditions (iron chips as seeds, 1060 °C processing temperature, pressure, and atmospheric composition, etc.), as in the literature [9], but using a preparation of the seed as described above.

In the internal grain of VGCF there are also some differences between VS and as-VLS fibres. Fig. 3e shows just the transverse section centre of a fibre grown by the as-VLS technique; instead of a hollow channel, as the VS growth model shows in Fig. 2, in the as-VLS fibre centre there is a spherical segment, like a mushroom cup. The mechanical properties must be almost the same, because in both cases the tree trunk and cortical structures are just the same.

The most difficult aspect to explain in the VLS process for VGCF is the nature of the non-solid drop at the fibre tip; it cannot be molten graphite because the melting point of graphite is about 3727 °C and in our furnace the working temperature is only 1060 °C.

To obtain an explanation for this, we sent a sample of the fibres shown in Fig. 3d to Dr Philip Honeybone at the Physics Laboratory of the University of Kent at

Canterbury (UK) for analysis (Carlo Erba CHN combustion analyser). The results showed that the fibres contained 2% H_2 by weight. Thus in the field of carbon hydride compounds, the VGCF nature must be interpreted.

There are many mineral substances [16–18] with a formula of type C_mH_n having an appearance similar to natural graphite; their structure and hydrogen content are well known and recorded in X-ray diffraction files (evenkite $C_{12}H_{48}$ or 33.3 wt % H_2 (28-2004), idrialite $C_{22}H_{14}$ or 5.3 wt % H_2 (28-2006), kratoch-villite $C_{13}H_{10}$ or 6.4 wt % H_2 (28-2010), pendletonite $C_{24}H_{12}$ or 4.16 wt % H_2 (28-2008), etc.), but neither the whole set of the crystal structures of C_mH_n, substances nor the C–H–T diagram are yet satisfactorily known. The distribution of hydrogen in the graphite network in carbons produced from gaseous hydrocarbons is a topic under study [19]; in this material most of the carbon bonds are single, but there is also a certain proportion of double or aromatic bonds. The greater proportion of total hydrogen content is bonded to the carbon, but molecular hydrogen also exists. The proportion of molecular hydrogen seems to decrease with increasing hydrogen concentration, which suggests that increased hydrogenation leads to a more open network with fewer sites able to trap the molecular hydrogen.

Unfortunately, we had no possibility for analysing the crystal structure at the tip of growing VGCFs, during their formation process; the only route possible is a structural analysis at room temperature of such fibres, when only the final structure exists.

Fig. 4a shows the Debye diffractogram of a sample of the graphitic conductive paint that we normally use in our SEM to bias every sample under electron microscope examination. This paint is simply a suspension of very fine lampblack. According to our information, this sort of laboratory paint is composed of a very fine-grained graphite that must be produced by hydrocarbon reduction in a similar way to our working conditions, an atmosphere with sparse hydrocarbon content. If the carbon black is produced from a mixture rich in hydrocarbon, the resulting lampblack has a coarse grain.

In Fig. 4a two overlapped X-ray diffractograms can be seen: on the one hand are diffraction lines of the hexagonal graphite according to the diffraction file (ASTM 23-0064), and on the other, the diffraction pattern of the pendletonite or karpatite (diffraction file ASTM 28-2008), a natural mineral [20] having a similar structure to the chemical named coronene ($C_{24}H_{12}$) that contains 4% H_2 approximately, is evident. The melting point of coronene is about 434–436 °C. This is a simple explanation of why, when black cake is produced in a reactor by hydrocarbon reduction, the product has the aspect of a cake and not a loose powder; the coronene works as a binder.

Fig. 4b shows the Debye diffractogram (CrK_α radiation) of a thin VGCF, 5–6 μm thickness, germinated from a small seed. Here, only the ring (0 0 2) of the hexagonal structure appears, but with a marked texture (in Fig. 4a such a ring shows no texture at all).
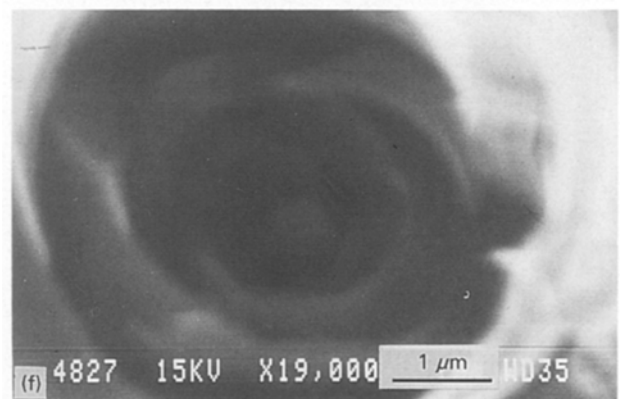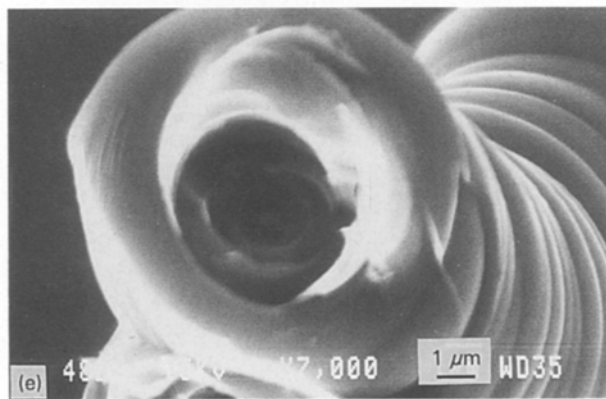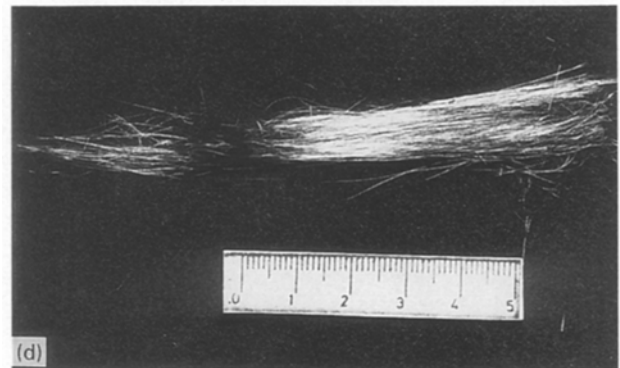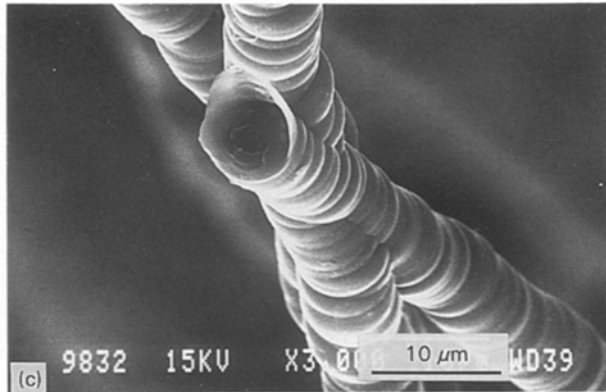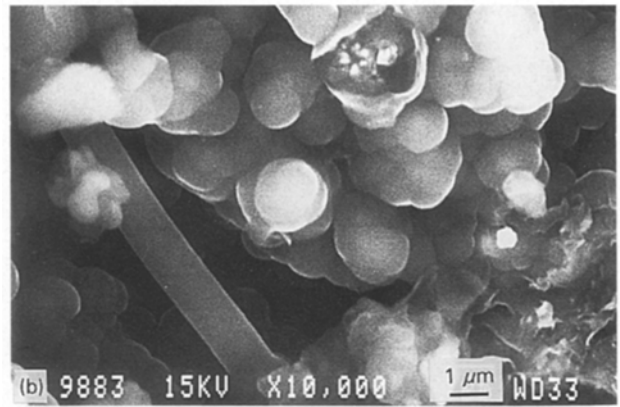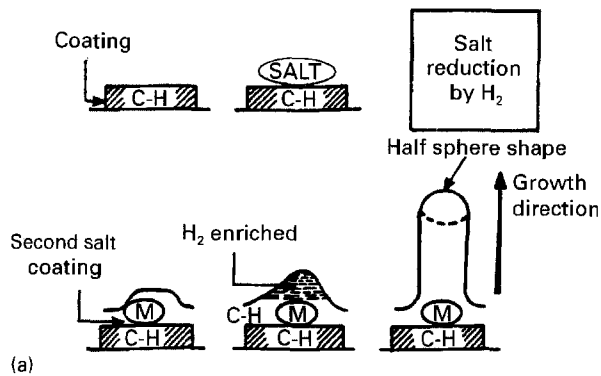
Figure 3 Aspects of VGCF growth. (a) The production process used; (b) the seed remaining in the root; (c) three welded fibres; (d) A sample of VGCF grown by this process; (e) transverse section of a broken fibre; (f) the central area of (e) at higher magnification.

The enhancer or generator of the textured state of the (0 0 2) hexagonal structure appears to be the (1 0 4) ring of the coronene phase; because the karpatite or pendletonite is formed by directional solidification, its (1 0 4) plane is very textured when formed, acting by epitaxial crystallization on the (0 0 2) plane of the hexagonal graphite, owing to the similarity between the interplanar spaces of both phases.

When the VGCF under the diffraction test has been produced from a very large seed (thick fibre), the monoclinic coronene phase (see Fig. 4c) shows the rings (1 0 2) and (1 0 $\bar{2}$) with texture as well as (1 0 4), as long as all three have the same range of interplanar spacing. It also shows rings (1 0 1), (0 1 5) and (1 1 0), but without texturing provided that they have greater spacings. The hexagonal structure of the external layer, for its part, shows the ring (0 0 2) with a strong texture and the (0 0 4) with a weak crystalline perfection and texture, just as in ex-PAN fibres.

No other diffraction line, under any circumstances, was detected belonging to some diffractogram related to iron carbides (ASTM files 3-400 or 3-411 from FeC, 26-782 or 17-897 from Fe_2C, 36-1249, 34-1 or 35-772 from Fe_3C and 17-333 from Fe_7C).

Fig. 3a shows that the VGCF grows without an iron or carbide tip, because the seed remains shallowly buried under the carbonaceous layer deposited during the second coating. Thus, the role of the transition metal chip as a seed must be interpreted as an initiator of the growth process only. Then it is reasonable to presume that the germination of each metal seed in the as-VLS model (Fig. 3a) is due to a discharge of the hydrogen stored [21] in the metal seed just after its reduction from the salt state. This hydrogenation took place under a pure hydrogen atmosphere, during seed preparation, before the second coating with lamp-black, which was designed to avoid the influence of the substrate as described above.
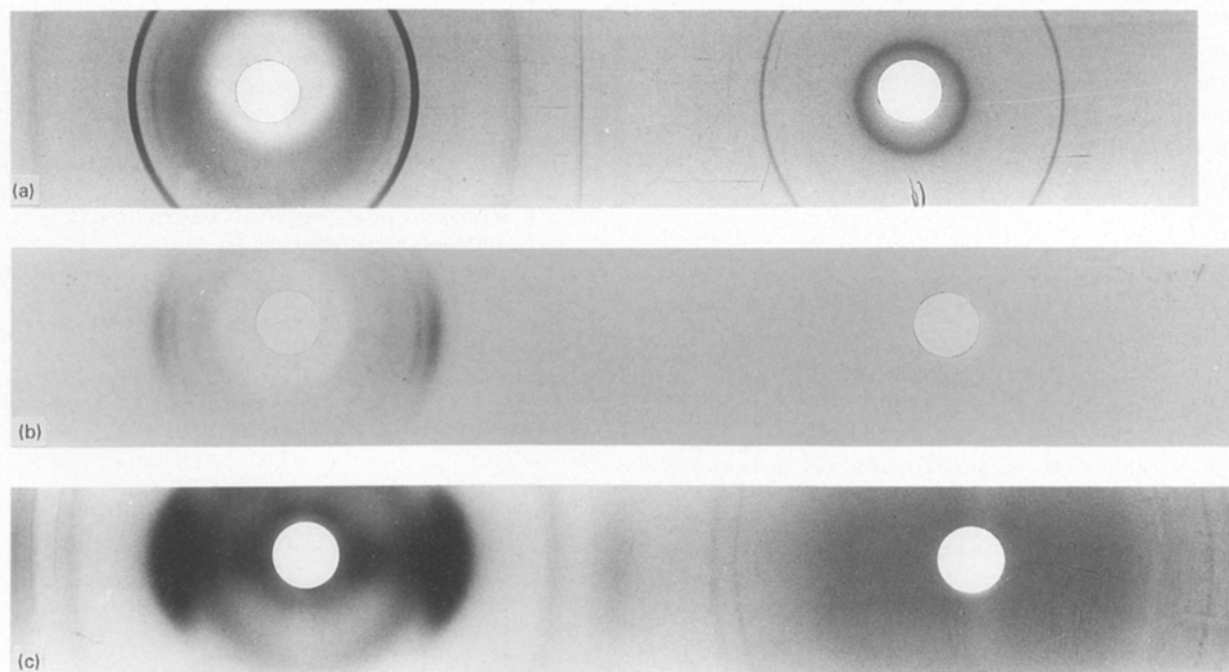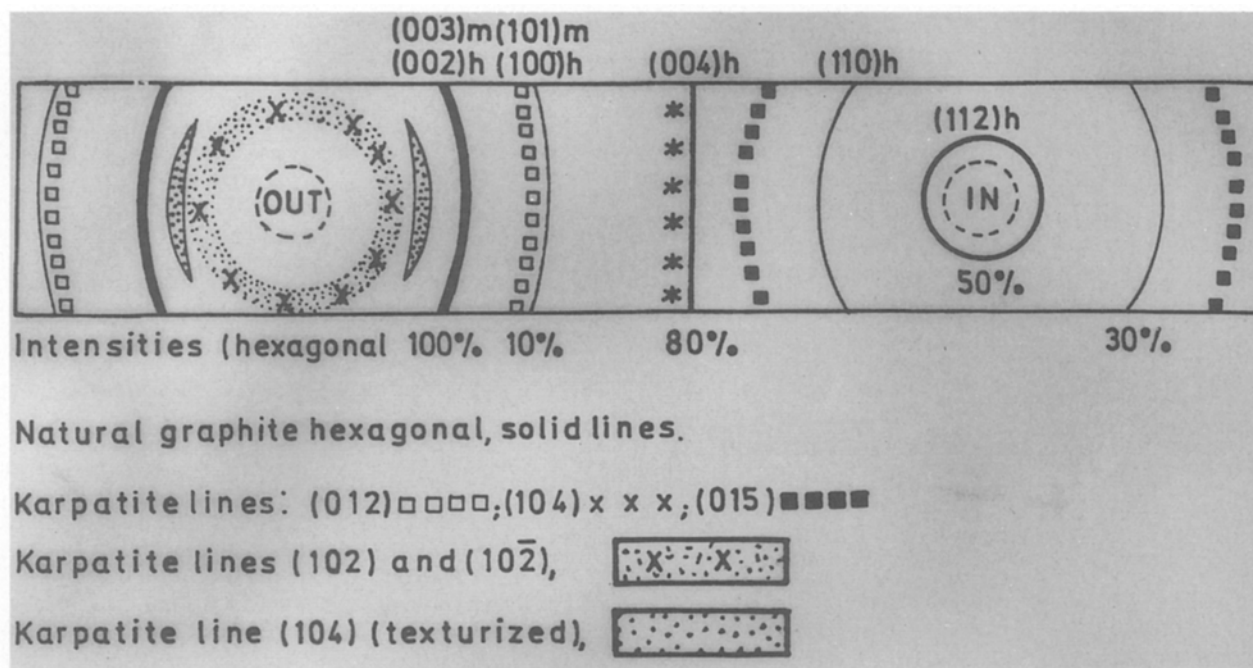
Figure 4 Debye diffractograms of polycrystalline (a) graphite, (b) thin VGCF, and (c) thick VGCF.

Fig. 5 shows how, in the temperature range used for VGCF growth, the desorption of hydrogen took place. Because the hydrogen has a positive heat of fusion (Causey *et al.* report a figure of 139 kJ mol^{-1}), this local hydrogenation produces a punctual heating for hydrogen dissolution in the vicinity of the seed, which produces a molten drop of a carbon–hydrogen material. Then, the VLS mechanism begins.

The main aspect to verify in the future, in this as-VLS model, is the crystalline structure of the growing VGCF, during the process in an environment of 1060 °C and 70% H$_2$ and 30% CH$_4$. The coronene melts at 435 °C (625 °C below 1060 °C), and its natural tendency in an inert atmosphere is to decompose [8] into CH$_3$, CH$_4$, ...; if this does not occur it is due to an atmospheric composition very rich in hydrogen (70%).

This could be a possible explanation for an old misunderstanding. From the point of view of the mass law, in our study of carbon, the decomposition methane → carbon + hydrogen occurs, and the atmosphere to produce VGCF must be poor in hydrogen. In spite of this, in the past [4–6, 9], the high proportion of hydrogen required in VGCF growth was recognized as adequate, because of the need for a very weak pyrolytic deposition, to delay the poisoning as much as possible.

In the scientific literature, there are other alternatives which differ from this hydrogenation of the carbon, to explain this VLS mechanism in VGCF. For example, in recent papers, such as the work of Benissad Aissani *et al.* [24], the VLS process is based upon the possibility that a very small chip of metal carbide,
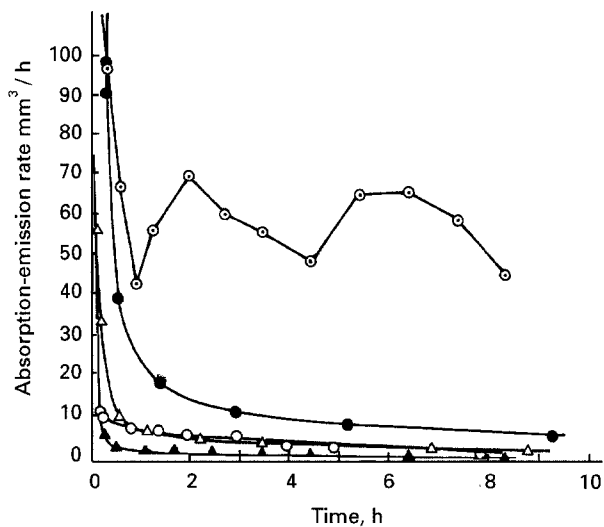
Figure 5 Instability of hydrogen storage in iron (from [22]). (○) 1075 °C, (●) 925 °C, (△) 675 °C, (▲) 440 °C, (○) 25 °C.

owing to its size, could melt in a temperature range around 1100 °C. In a similar way, Tibbetts *et al.* [25], after demonstrating that small additions of sulphur increase the production of VGCF, believe that it is due to the sulphur liquifying the iron particles, thus enhancing filament nucleation. We hope that in the future such theoretical possibilities could be widely proved.

Acknowledgement

References

1. C. P. BEETZ, D. W. SCHMUESER and W. HANSEN, *Carbon* **27** (1989) 767.
2. S. BECK, in "How to apply advanced composites technology", ASM International Congress, Dearborn, MI (1988) p. 467.
3. G. P. DAUMIT, *Carbon* **27** (1989) 759.
4. P. CHITRAPU, C. R. F. LUND and J. A. TSAMOPOULOS, *ibid.* **30** (1992) 285.
5. A. SACCO, in "Carbon fibers, filaments and composites", edited by Figuereido *et al.* NATO AISI. Series E. Applied Science Vol. 177 (Kluwer Academic, Dordrecht, The Netherlands, 1990) 459.
6. G. G. TIBBETTS, *ibid.* 525.
7. S. A. SAFVI, E. C. BIANCHINI and C. R. F. LUND, *Carbon* **29** (1991) 1245.
8. C. DAVID, P. SUBERT, A. AURIOL and P. RAPPENAU, *ibid.* **1** (1989) 139.
9. G. G. TIBBETTS, *J. Crystal Growth* **73** (1985) 431.
10. *Idem, Carbon* **27** (1989) 745.
11. X. Y. ZHAO, C. W. BOWERS and I. L. SPAIN, *ibid.* **26** (1988) 291.
12. P. LUCAS and A. MARCHAND, *ibid.* **28** (1990) 207.
13. A. R. NYAIESH and W. B. NOWAK, *J. Vac. Sci. Technol.* **A1** (1983) 308.
14. A. MADROÑERO, in "ISATA Proceedings on New and Alternative Materials for the Automotive Industries" Florence, Italy, 1–5 June 1992. S. Tosto (Ed.), Croydon, UK.
15. K. I. PORTNOI, A. A. MUKASEEV, V. N. GRIBKOV, A. S. ISAIKIN and E. L. UMANTEV, *Sov. Phys. Crystal.* **19** (1974) 198.
16. J. MURDOCH and T. A. GEISSMAN, *Am. Mineral.* **52** (1967) 611.
17. F. KAMENETSKY, *Mineral. Sbornik.* **21** (1967) 275.
18. K. SUNDARAJAN, *Z. Kristallogr.* **93** (1936) 238.
19. R. J. NEWPORT, P. J. R. HONEYBONE, S. P. COTTRELL, J. FRANKS, W. S. HOWELLS and R. J. CERNIK, *Surf. Coat. Technol.* **47** (1991) 668.
20. J. MURDOCH and T. A. GEISSMAN, *Am. Mineral* **53** (1968) 1061.
21. A. R. MIEDEMA, K. H. J. BUSCHOW and H. H. VAN MAL, *J. Less-Common Metals* **49** (1976) 463.
22. D. P. SMITH, "Hydrogen in metals" (The University of Chicago Press, Chicago, IL, 1948).
23. R. A. CAUSEY, T. S. ELLEMAN and K. VERGHESE, *Carbon* **17** (1979) 323.
24. F. BENISSAD AISSANI and P. GADELLE, *ibid* **31** (1993) 21.
25. G. G. TIBBETTS, C. A. BERNARDO, D. W. GORKIEWICZ and R. L. ALIG, *ibid.* **32** (1994) 569.