JOURNAL OF MATERIALS SCIENCE 31 (1996) 6621–6625

Morphological structure study of pitch fibre surfaces by scanning tunnelling microscopy: influence of the mesophase content

JEAN-BAPTISTE DONNET, TONG KUAN WANG
Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue A. Werner, 68093 Mulhouse, France

ZENG-MIN SHEN
Beijing University of Chemical Technology, Heping Street, 100029 Beijing, China

The surface morphology of pitch fibres with different mesophase contents was studied by scanning tunnelling microscopy (STM) and the results were related to their mechanical properties. The tensile strength and modulus increase with the mesophase content and correspondingly the surface structure becomes more anisotropic. Inversely, the STM method can also be used to evaluate the precursor mesophase content of a pitch-based carbon fibre.

1. Introduction

Several methods have been used to study the surface microstructure of carbon fibres, for example, scanning electron microscopy (SEM) [1, 2] which can give information about the pores, fissures and channels of the surface and the cross-sectional morphology, but is not able to see the surface crystal sizes and orientation. Recently, the local probe microscopies (scanning tunnelling microscopy, STM, and atomic force microscopy, AFM) have proved to be very powerful methods to study the surface microstructure. Several authors have studied the surface microstructures of carbon fibres by STM from the surface morphology to atomic resolution [3–6]. Hoffman has reported some STM results of carbon fibre morphology before and after surface treatments [5]. The STM study of thermal-treatment influence on pitch fibre surface organization was also performed by the groups of Effler [6] and Donnet [3]. In this paper, we present an STM morphology investigation of pitch fibres having different mesophase contents, from $< 10\%$ to 100%, treated at carbonization and graphitization temperatures, and we try to correlate it to their mechanical performance.

2. Experimental procedure

Three series of carbon fibre samples were used in this study.

1. 1–01, an isotropic series with two samples, one carbonized at 1000 °C, 1-01CF, and the other graphitized at 2300 °C, 1-01GF.
2. 4-31, mesophase content 80%. This series has also two samples, 4-31CF and 4-31GF, treated, respectively, at 1000 and 2500 °C.
3. 4-57GF, a graphitized sample (2500 °C) with a mesophase content of 100%. The sample 4-57CF, treated at 1000 °C, was only used for mechanical measurement.

These fibres were directly taken from the production line without surface treatment, and were solvent extracted systematically by acetone to eliminate possible contaminants before the sample preparation for STM study.

We used a scanning tunnelling microscope of type Nanoscope II (Digital Co. Santa Barbara, USA). Two types of piezo-head were used: head "A" for measured surfaces smaller than 500×500 nm^2 and head "G" for larger surfaces. The tips (Nanotip^{TM}, Pt–Ir type of size 0.010 in $\times$ 1/4 in; ~ 0.03 cm $\times$ 0.6 cm) were checked with a sample of highly ordered pyrolytic graphite (HOPG) to ensure their quality. The images were mainly obtained by the current constant mode which images better the morphological features of the surface. Using a low-pass filter which decreases the high-frequency noises, the images are presented in the three-dimensional form in two sizes: 500 nm $\times$ 500 nm $\times$ 100 nm and 2000 nm $\times$ 2000 nm $\times$ 300 nm.

Elemental analysis was taken on a Carloerba's EA-1106 element analyser.

Mechanical performances of the fibres were measured by a universal materials machine Instron 1121.

3. Results and discussion

Table I reports the main information about the three series of samples studied. With increasing heat-treatment temperature (HTT), the carbon content becomes richer and the oxygen was practically eliminated at the carbonization temperature for the mesophase pitch

0022–2461

TABLE I Influence of different mesophase content on element composition and mechanical performance of CF and GF

	Sample					
	1-01		4-31		4-57	
	CF	GF	CF	GF	CF	GF
Mesophase content of spinnability (%)	< 10	< 10	80	80	100	100
C (%)	94.94	–	98.28	99.67	98.24	>99.0
H (%)	0.33	–	< 0.30	< 0.30	< 0.30	–
O (%)	0.88	–	0.00	0.00	0.00	–
N (%)	3.04	–	< 0.30	< 0.30	< 0.30	–
O/C atom ratio	0.01	–	0.00	0.00	0.00	–
H/C atom ratio	0.04	–	< 0.04	< 0.04	< 0.04	–
Tensile strength (GPa)	0.91	0.59	2.11	2.52	2.60	3.40
Tensile modulus (GPa)	60.8	64.7	–	605.2	–	810.0
Elongation (%)	1.43	0.95	–	0.42	–	0.38

fibres, but hydrogen and nitrogen were always present in weak proportions. For the three GF samples, the tensile strength increased four or five times when the mesophase contents varied from < 10% to > 80%; the tensile modulus followed the same tendency but in a more pronounced way (nearly one order greater),

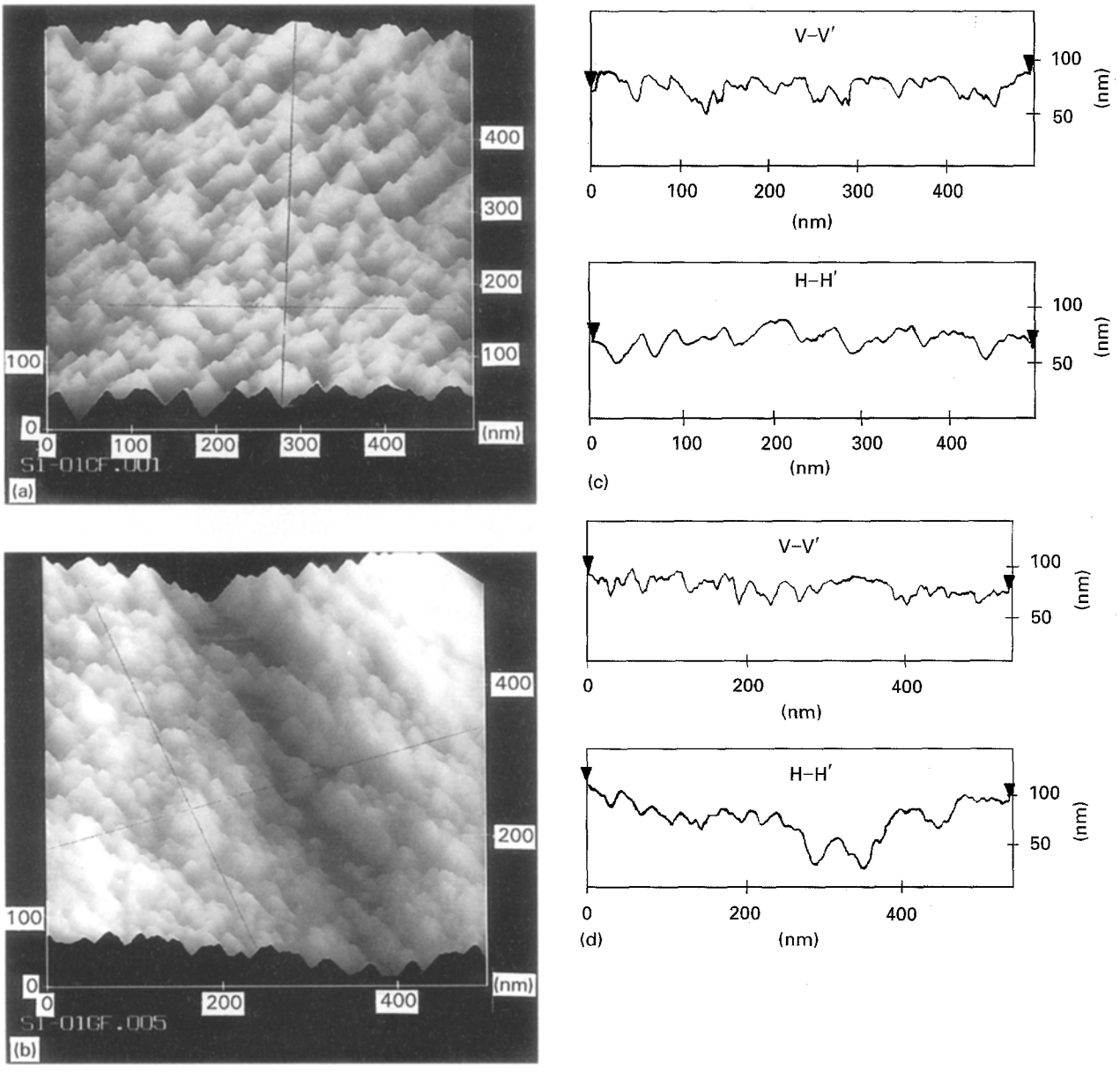

Figure 1 (a, b) Morphological structure of isotropic pitch fibres: (a) 1-01CF, (b) 1-01GF, observed by STM (500×500 nm^2) and (c, d) their respective height profiles in the fibre axis direction (V–V′) and cross-sectional direction (H–H′).

consequently the elongation decreased. We can also see in Table I that for isotropic pitch fibres, 1-01 series, the tensile strength decreased with increasing the HTT, while the tensile modulus increased. However, the tensile strength for two other mesophase fibres increased with HTT.

Fig. 1 shows the morphology of isotropic pitch fibres as seen by STM at a medium enlargement; both the carbonized and graphitized samples have no preferential orientation (compare the height profiles in the two directions). The carbonized fibre exhibits some rugosities with "peaks" and "valleys" up to about 40 nm deep (Fig. 1a), the "peak" density being relatively high. This confirms the similar observation of an isotropic pitch fibre (Kureha) treated at 900 °C [7] but the egg-like microstructure we described earlier [7] was not observed here at the 100 nm scale. For the graphitized sample, the image seems to be a little different but its height profiles have essentially the same feature as for the 1-01CF (Fig. 1b).

The surface morphology of the 4-31 series shown in Fig. 2 is very different from the morphology observed with isotropic fibres. The "peak" and "valley" character disappears, as seen in the profiles, and the surfaces look much more smoother. There are ribbons parallel to the fibre direction, the width of the bands is about 150–200 nm. This surface feature was observed early for similar carbon fibres [3, 6]. The graphitized sample (Fig. 2b) has a more pronounced orientation than the carbonized one (Fig. 2a). The ribbons are believed to be formed during the spinning process followed by stretching [3] and seem to be reinforced by heat treatment. We can also compare the substructure change with the HTT. The carbonized sample has a surface composed of "grains" with different sizes from 30–100 nm with their borders a little diffuse, and apparently with little deformation, but these "grains" become greatly dilated in the graphitized sample surface. This type of structure development with HTT was also observed earlier [8]. We

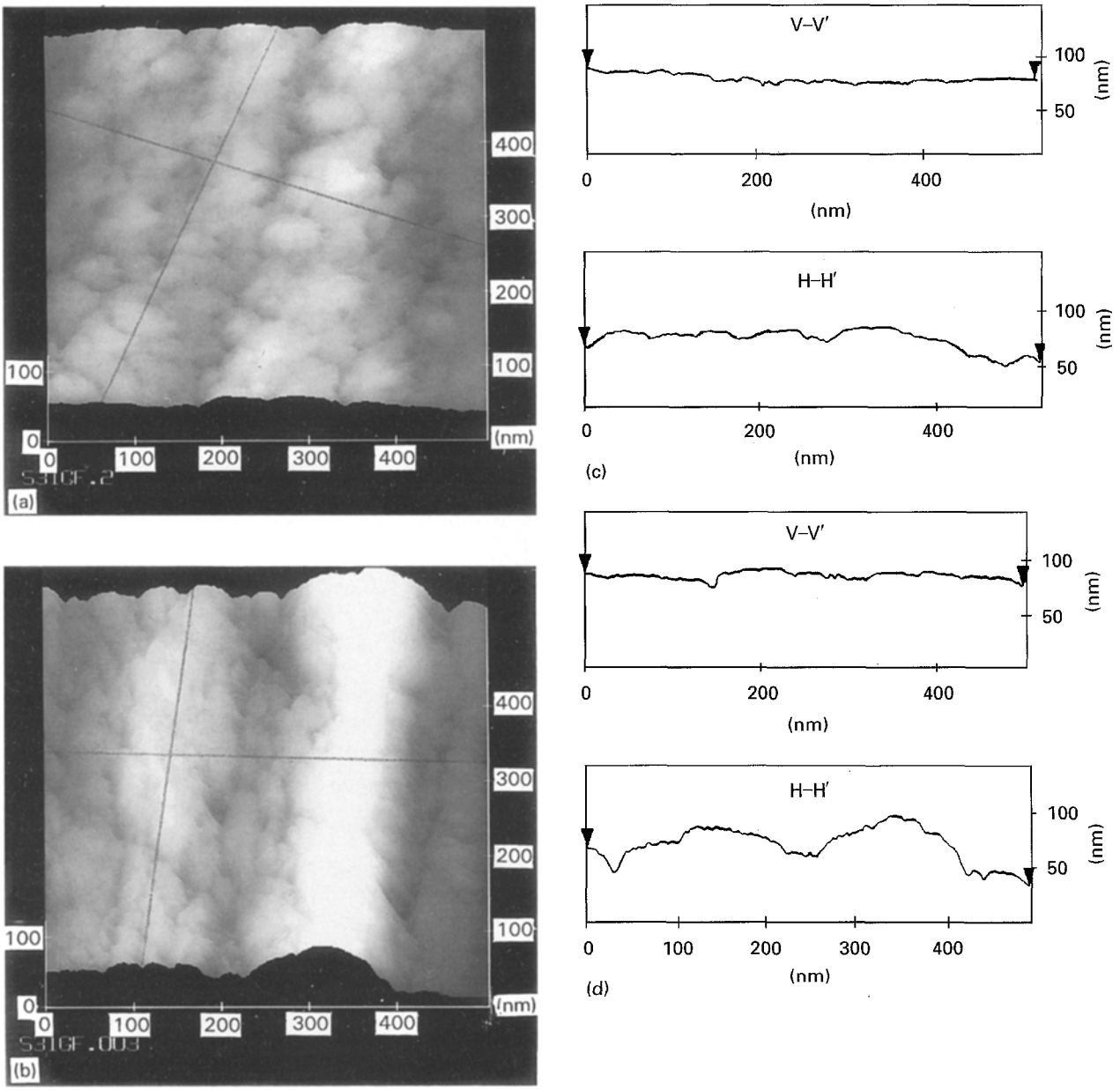

Figure 2 (a, b) Morphological structure of mesophase pitch fibres, (a) 4-31CF, (b) 4-31GF, observed by STM (500 × 500 nm^2) and (c, d) their respective height profiles in the fibre axis direction (V–V′) and cross-sectional direction (H–H′).

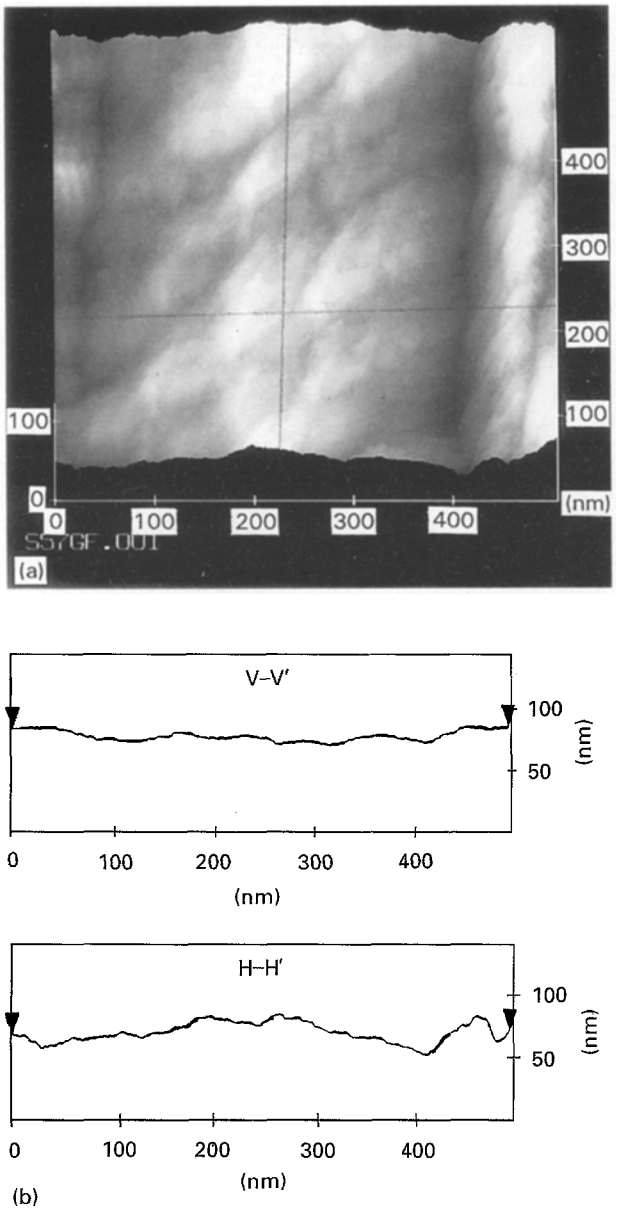

Figure 3 (a) Morphological structure of mesophase pitch fibre (4-57GF) observed by STM ($500 \times 500\ nm^2$) and (b) its height profiles in the fibre axis direction (V–V′) and cross-sectional direction (H–H′).

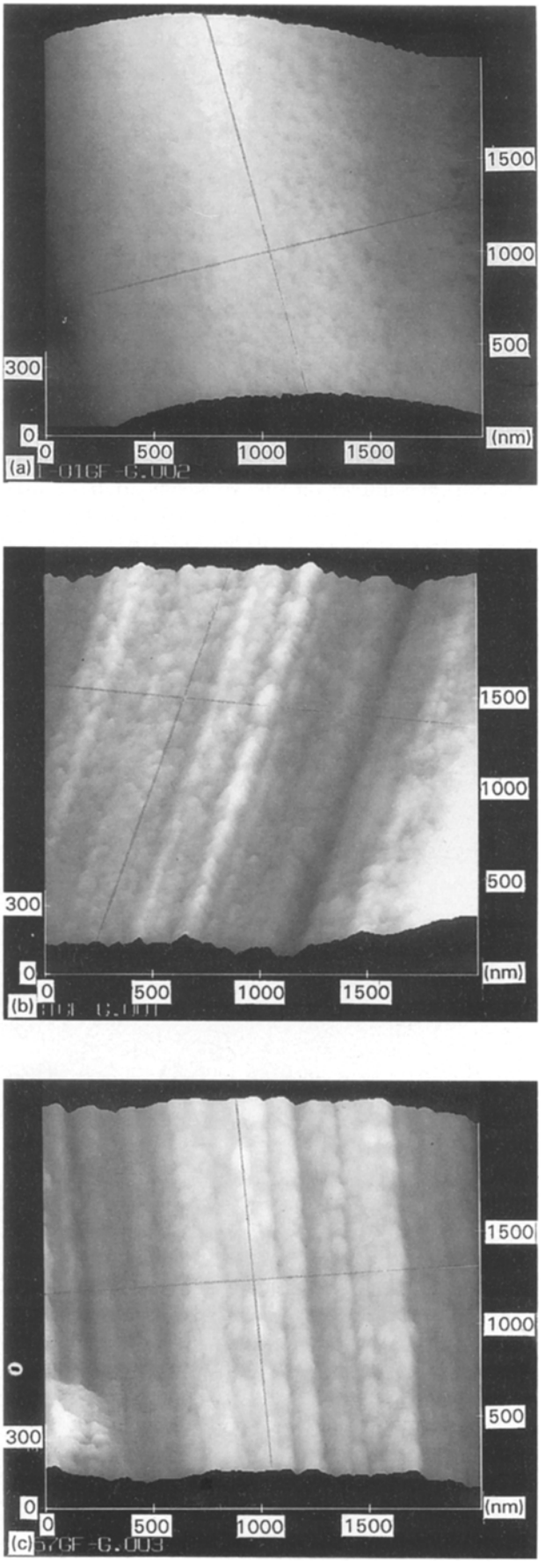

Figure 4 (a–c) Morphological structure of three graphitized fibres with different mesophase contents, (a) 1-01GF, (b) 4-31GF, (c) 4-57GF, observed by STM ($2000 \times 2000\ nm^2$) and (d–f) their respective height profiles in the fibre axis direction (V–V′) and cross-sectional direction (H–H′).

think that the change of mechanical performance is related, at least partly, to this surface structure evolution at different HTT.

In Fig. 3, we present an image of the 4-57GF sample which is constituted of 100% mesophase pitch. Apart from the main orientation parallel to the fibre direction, we have observed also a cord-like sub-structure with a twist angle of about 45° to the fibre direction, a similar feature observed for other carbon fibres [3, 4]. This structure is probably responsible for the high tensile strength and modulus exhibited by this fibre.

The three graphitized samples are compared in Fig. 4 on a larger scale (lower enlargement, $2000 \times 2000\ nm^2$). These images confirm the observations illustrated by Figs. 1–3. We can see more clearly that the isotropic sample has a surface without preferential orientation (Fig. 4a) but the sample with 100% mesophase content shows very clear parallel ribbons

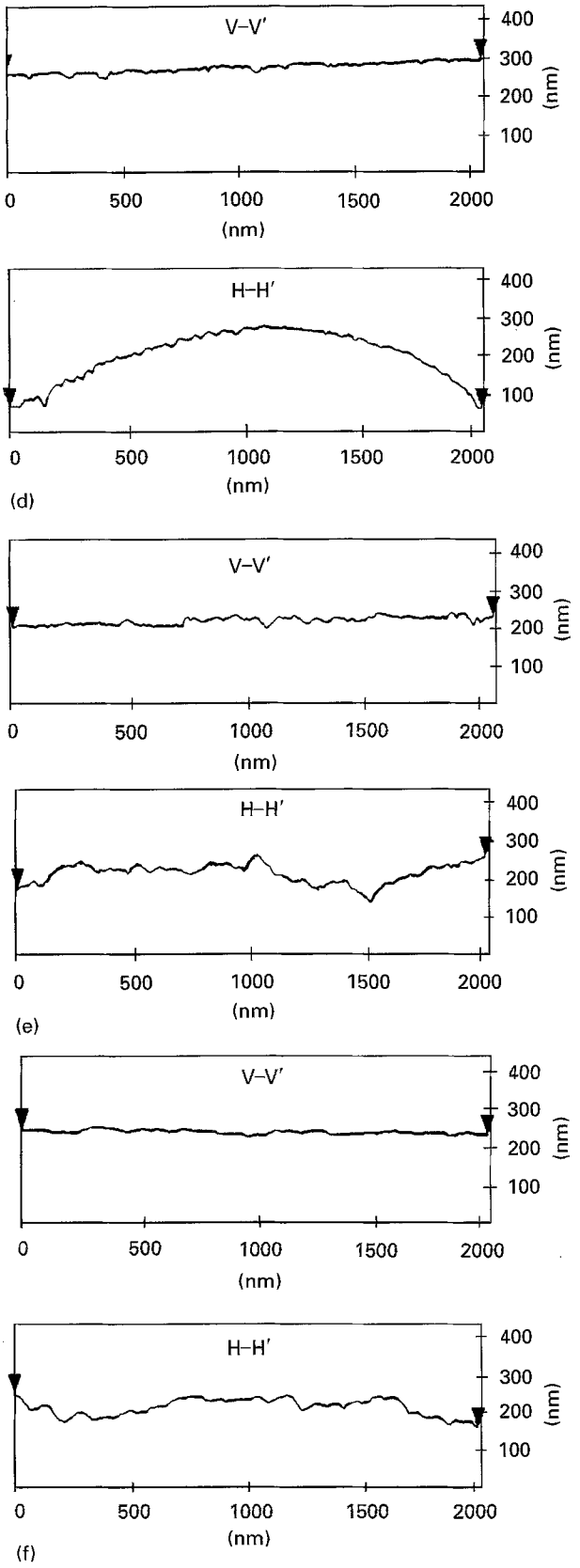

Figure 4 (Continued)

which seem to be composed of aligned "grains" (Fig. 4c). The 4-31GF has a similar ribbon pattern (Fig. 4b) with the "grain" structure being not as clear as in Fig. 4c but which also has some features of Fig. 4a. Therefore, the STM image at this scale can give a qualitative estimation of the mesophase contents of a graphitized pitch fibre.

From the above discussion, we can see that there is a good correlation between the surface morphology and the mechanical performance of the fibres. The surface structure orientation order observed by STM increases with the mesophase content, and the mechanical properties change in the same direction, as indicated in Table I. The heat treatment has the effect of increasing crystallization and orientation (compare Figs 1 and 2a and b), thus improves the mechanical performance of the mesophase pitch fibres. For the isotropic fibres, the STM images also show the same tendency of structural change with heat-treatment temperature. On the other hand, the decrease of the tensile strength with the graphitization treatment seems related adversely to factors other than the surface morphology.

4. Conclusion

A correlation between the surface morphology of the carbon fibres observed by STM and their mechanical properties is shown. For three series of samples with mesophase contents from $< 10\%$ to 100%, the mechanical performance increases and the surface structure has more and more anisotropic features. For the 100% mesophase content sample, 4-57GF, both parallel band and twist substructures, were observed which correspond to the best fibre performance.

Acknowledgements

This research was supported by NAMCC (China) and the "Foundation pour l'Ecole Nationale Supérieure de Chimie de Mulhouse", associated with CRPCSS/CNRS, Mulhouse, France.

References

1. Z. M. SHEN, R. Y. QIN, M. Y. LIU, Y. B. WANG and W. LIN, in "36th International SAMPE Symposium and Exhibition", Vol. **36** edited by Sandia Lab (USA, 1991) pp. 1109–17.
2. Z. M. SHEN, H. L. GUO, Y. X. SHI, W. P. CHANG, Y. B. WANG and Y. J. SHANG, in "21st Biennial Conference on Carbon" 13-18 June 1993, edited by American Carbon Society (University of Buffalo), pp. 352–353.
3. J.-B. DONNET and R.-Y. QIN, *Carbon* **30** (1992) 787.
4. *Idem, ibid.* **31** (1993) 7.
5. W. P. HOFFMAN, *ibid.* **30** (1992) 315.
6. L. J. EFFLER, J. F. FELLERS and B. K. ANNIS, *ibid.* **30** (1992) 631.
7. R.-Y. QIN, PhD Thesis, University of Haute Alsace (1992).
8. S. N. MAGANOV, H. J. CANTOW and J. B. DONNET, *Polym. Bull.* **23** (1990) 555.

Received 1 December 1994
and accepted 1 December 1995