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Preparation and structure of mesophase pitch-based thin carbon tape

I. MOCHIDA, SEONG-HO YOON, Y. KORAI
Institute of Advanced Material Study, Department of Molecular Science and Engineering, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan

A mesophase pitch of 100 vol % anisotropy prepared from methylnaphthalene using HF/BF_3 was spun through a slit-shaped nozzle, stabilized in air under strain and carbonized at 1300 °C into a very thin slit-shaped carbon tape 1.6 μm thick and 14 μm wide. Better crystalline orientation of the carbon tape always provided a Bacon anisotropic factor higher by 2% than that of the circular carbon fibre prepared from the same pitch. Excellent mechanical properties of the present carbon tape were obtained. Factors influencing the shape and orientation of the carbon tape were examined in terms of properties of mesophase pitches, spinning temperature, and the extent and strain of stabilization.

1. Introduction

Mesophase pitch-based carbon fibre has been recognized as a strategic material because of its high performance per weight [1, 2]. The well-developed graphitic structure of mesophase pitch-based carbon fibre is known to be the origin of the superior stiffness and conductivity which is attractive for many applications. Fibres achieving graphite-like crystallinity and a high degree of basal plane orientation parallel to the fibre axis have been reported to exhibit high stiffness, as well as excellent thermal and electrical properties. Such ordering can be influenced, or even limited, by certain transverse shapes or texture of the pitch fibre according to a patent [3] and Rodgers *et al.* [4]. A non-circular fibre exhibiting line-origin microtexture has been proved to exhibit better alignment along the fibre axis than a fibre of radial microtexture [4]. The dimension of the pitch fibre is expected to influence greatly the rate of stabilization [5].

In this work, we prepared very thin carbon tape from selected mesophase pitches derived from aromatic hydrocarbons with the aid of HF/BF_3 via melt-spinning through a slit-shaped nozzle, stabilization in the air under some strain, carbonization and graphitization. Carbon material in this shape is expected to show some extraordinary properties.

2. Experimental procedure

2.1. Materials

The mesophase pitches used in the present study are summarized in Table I with some of their analytical properties. They were prepared using HF/BF_3 as the catalyst from naphthalene (NA) and methylnaphthalene (mNA) [6–8]. All mesophase pitches contained 100 vol % anisotropic contents at room temperature.

Melt viscosities calculated from Andrades's equation are shown in Fig. 1. The reflection point of melt viscosity could be inferred to be near 285 °C.

2.2. Spinning of mesophase pitches

Mesophase pitches were spun into slit-transverse shaped tapes of 2–4 μm thick and 12–18 μm wide cross-sectional dimensions under a nitrogen pressure from a steel spinneret. The shape and dimensions of the spinneret are illustrated in Fig. 2.

Detailed spinning conditions of the present study are summarized in Table II.

2.3. Stabilization of mesophase pitch tapes

The prepared slit-transverse shaped pitch tapes were oxidatively stabilized with and without strain at 270 °C for 20 min in air. The heating rate was 5 °C min^{-1}. Table II shows the sample codes which define the conditions of the stabilization process. The strain load is described by gram per denier (g den^{-1}).

2.4. Carbonization and graphitization of stabilized fibres

The stabilized fibres were carbonized and graphitized under an inert atmosphere. Carbonization of stabilized fibres was carried out at 1300 °C for 1 h at a heating rate of 10 °C min^{-1}. Carbonized fibres were further graphitized at 2500 °C for 30 min by heating at 20 °C min^{-1}.

2.5. Characterization of the prepared carbon tapes

The transverse sections of tapes were observed under a scanning electron microscope (Jeol-JSM 25S). The preferred alignment of carbon planes in the tapes was calculated from the orientation intensity of the (0 0 2) diffraction of carbonaceous material according to Bacon and the Japanese Society for the Promotion of Science (JSPS) [9, 10].

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TABLE I Some analytical properties of mesophase pitches prepared using HF/BF_3

Code	Raw material	SP(°C)	AC(vol %)	Solubilities(wt %)			H/C	f_a
				BS	BI-PS	PI(QI)		
Na mesophase	Naphthalene	215	100	57	13	30(26)	0.67	0.81
mNA mesophase	Methyl-naphthalene	205	100	52	19	33(29)	0.69	0.86

Notes: SP = softening point; AC = anisotropic contents; f_a = carbon aromaticity.

TABLE II Conditions for spinning and stabilization, and results of characterization of carbon tape from NA and mNA mesophase pitches

Code	Spinning conditions			Stabilization conditions		T/W ratio	DM (%)	L_c (nm)
	Capillary	Temp. (°C)	SR (m min^{-1})	Temp/ST (°C min^{-1})	Strain (g $den.^{-1}$)			
rp[a]-mNA[b]-264	Circular	260	780				80.0	
rc[c]-mNA-264-0		264	780	270/20	0		79.3	
rc-mNA-264-10		264	780	270/20	10		79.4	
c[d]-NA[e]-264-0	Slit	264	400	270/30	0	2.0		
c-NA-264-10		264	400	270/30	10	2.4		
p[f]-mNA-260	Slit	260	300				80.7	
c-mNA-260-0		260	300	270/20	0	6.2	81.3	
c-mNA-260-10		260	300	270/20	10	5.6	82.3	
c-mNA-260-20		260	300	270/20	20	6.9	81.0	
g[g]mNA-260-20		260	400	270/20	20	6.9	93.3	12.1
p-mNA-264		264	400				82.0	
c-mNA-264-0		264	400	270/20	0	4.8	81.3	
c-mNA-264-10		264	400	270/20	10	6.2	81.3	
c-mNA-264-20		264	400	270/20	20	4.1	82.7	
g-mNA-264-10		264	400	270/20	10	6.2	93.1	11.8
p-mNA-270		270	400				80.7	
c-mNA-270-0		270	400	270/20	0	4.2	80.0	
c-mNA-270-10		270	400	270/20	10	4.3	81.0	
c-mNA-270-20		270	400	270/20	20	4.4	82.0	
g-mNA-270-20		270	400	270/20	20	4.5	94.8	13.0

Notes: T/W = thickness/length ratio for the cross-section of carbon tape; DM = degree of crystalline orientation; L_c = crystalline size; SR = spinning rate; ST = soaking time;
[a] Circular transverse shaped pitch fibre.
[b] ■■■
[c] Circular transverse shaped carbonized fibre heat treated at 1300 °C for 1 h.
[d] Slit transverse shaped carbonized tape heat treated at 1300 °C for 1 h.
[e] Mesophase pitch from naphthalene.
[f] Slit transverse shaped pitch fibre.
[g] Slit transverse shaped graphitized tape heat treated at 2500 °C for 30 min.

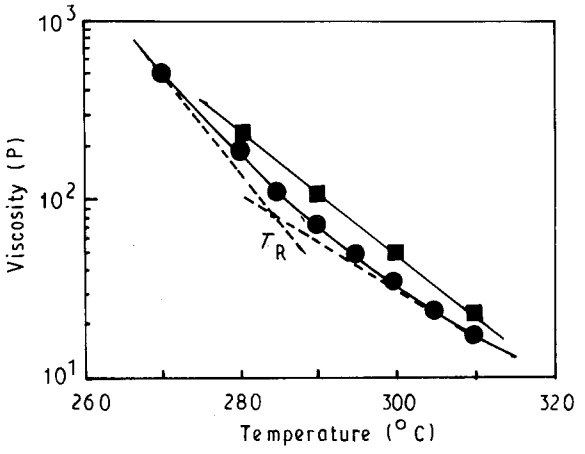

Figure 1 Melt viscosities of mesophase pitches. (■) NA mesophase pitch, (●) mNA mesophase pitch.

The crystalline size, L_c, of the graphitized fibre was measured according to JSPS [11].

Tensile strength, Young's modulus and strain to break were measured at room temperature using mono-filaments according to the procedure defined by Japanese Industrial Standard (JIS R-7601) using an Instron-type tensile-testing machine (Instron 4200 series) with a crosshead speed of 0.5 mm min^{-1} [12].

3. Results

3.1. Preparation of carbon tapes

Mesophase pitches from NA and mNA using HF/BF_3 as the catalyst were smoothly spun into slit-transverse shaped fibres in the temperature range 260–275 °C. Above 275 °C spinning temperature, the transverse

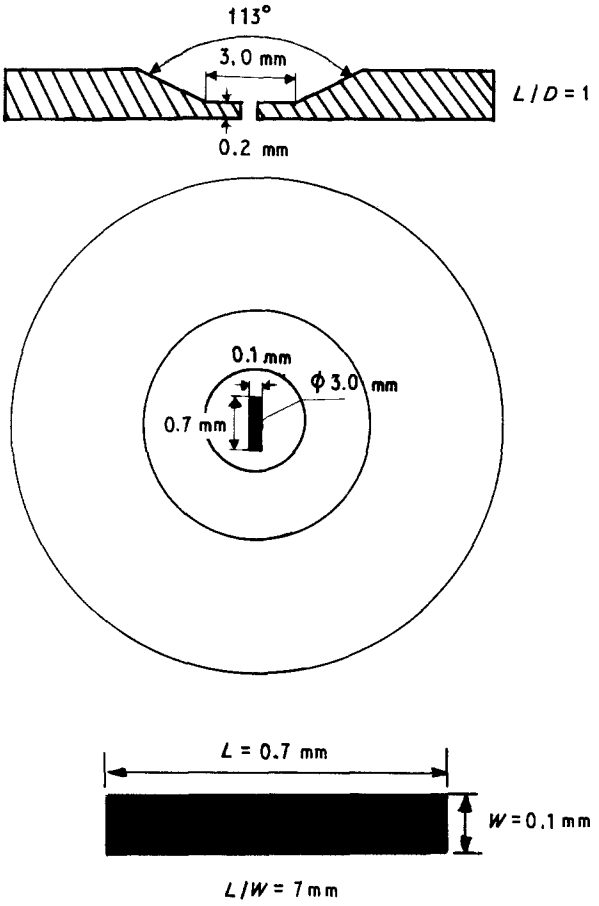

Figure 2 Slit-shaped spinneret capillary used in the present study.

shape of the fibres obtained changed from tape to circular shape, as recognized by Edie *et al.* [5]. Table II summarizes the shapes of tapes obtained in the spinning temperature range 260–285 °C. The ratios of thickness, T, to width, W, of carbon tape cross-sections (T/W) changed from 6.20 (260 °C), which was slightly smaller than that of the spinning slit (7.0), to 1.0 for the perfectly circular shape (285 °C). It is of value to note that 285 °C was near the reflection point in the melt viscosity of mNA mesophase pitch as shown in Fig. 1.

Fig. 3 shows scanning electron micrographs of carbon tapes prepared from NA and mNA mesophase pitches. The T/W ratios of the carbon tapes produced were very much influenced by chemical and physical properties of the mesophase pitch. The tapes prepared from mNA mesophase pitch exhibited larger T/W ratios than those from NA mesophase pitch, even though both tapes were produced under the same spinning and heat-treatment conditions. Table II includes the effects the suspended stabilization on the T/W ratios of the carbon tapes produced from both mesophase pitches. The stabilization under strain increased the T/W ratios of the carbon tapes to 6.90 by 20 g den.$^{-1}$, which is very similar to that of the spinning hole. However, the stabilization under strain failed to increase T/W of NA mesophase pitch-derived tape, as shown in Fig. 3d and Table II.

The dimensions of the carbon tape produced were also influenced by the stabilization time. Thin slit-

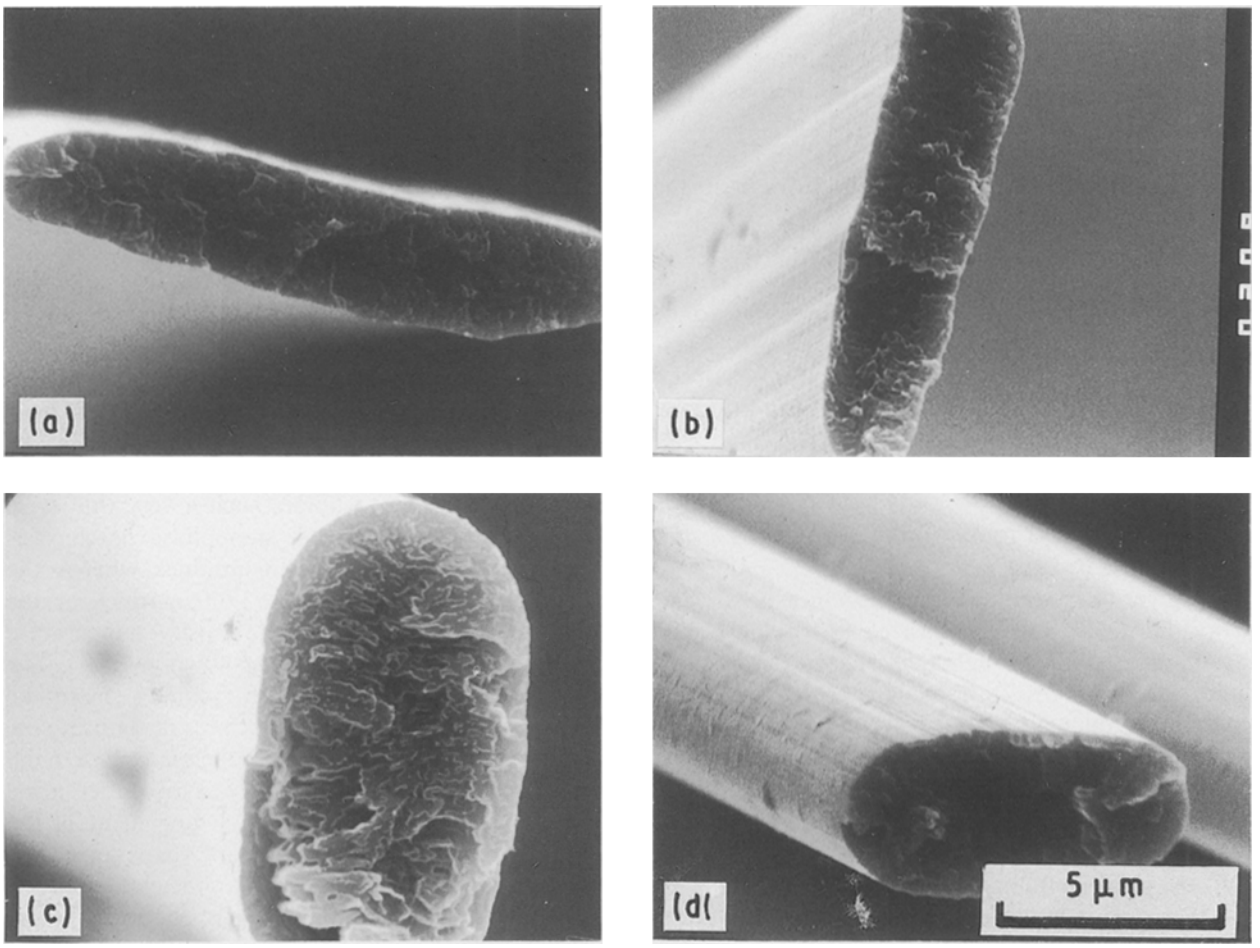

Figure 3 Transverse shapes of carbonized tapes from NA and mNA mesophase pitches (see Table II). (a) c-mNA-264-0, (b) c-mNA-264-10, (c) c-NA-264-0, (d) c-mNA-264-10.

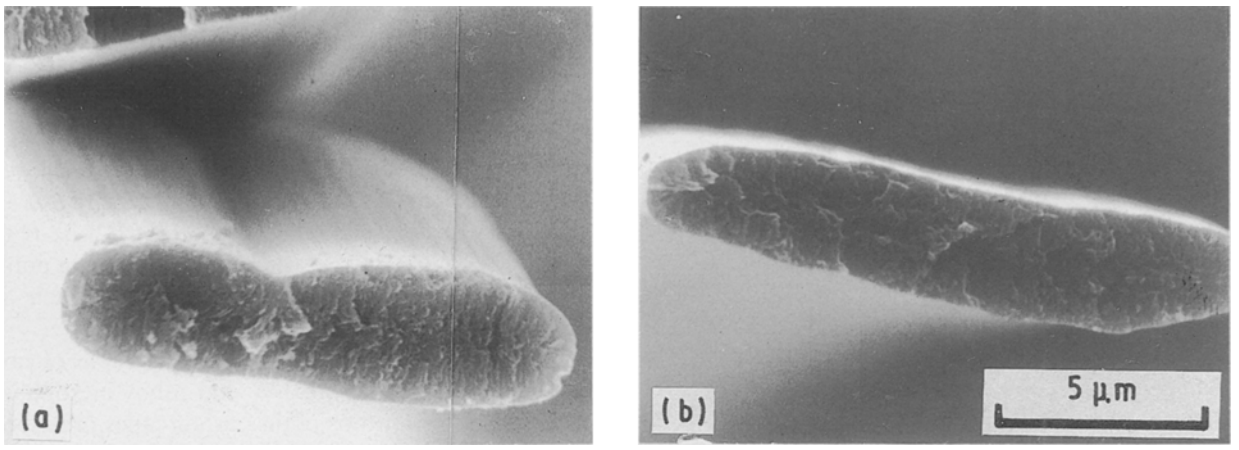

Figure 4 Scanning electron micrographs of carbon tapes stabilized for various times, (a) at 270 °C with no heating time at 5 °C min^{-1}, (b) stabilized at 270 °C for 20 min by 5 °C min^{-1}.

shaped pitch tape was stabilized completely at 270 °C without any holding time when the heating rate was 5 °C min^{-1}, while a circular fibre required 20 min at 270 °C for its complete stabilization.

The T/W ratio of the tape decreased with non-uniform shrinkage at the core of the tape during carbonization and its margin became somewhat irregular, as shown in Fig. 4.

3.2. Dimensions and microtextures of carbonized tapes

Fig. 5 shows scanning electron micrographs of carbonized tapes prepared at various spinning temperatures. The dimensions of the carbonized tapes at 1300 °C were 2–3 μm thick and 12–18 μm wide, varying with spinning temperature. As shown in Fig. 5, the lower spinning temperature tended to increase the width of the carbon tape.

Fig. 6 shows the typical transverse microtexture of graphitized tape. The graphitized tape showed radial-like texture near the surface and random texture in the central region of the transverse section, no leafy texture being observable although this texture has been observed in the thicker eclipse fibre produced by Teijin [3].

3.3. Physical and mechanical properties of carbon tapes

The degrees of crystalline orientation measured by an X-ray diffraction are summarized in Table II. The carbon tapes spun through a slit-shaped nozzle exhibited degrees of orientation higher by 2% in their BAF factor than circular transverse shaped carbon fibres (diameter 7.2 μm) spun through a circular nozzle ($L/D = 1$, $D = 0.3$ mm).

The effects of spinning temperature and stabilization conditions on the degree of crystalline orientation are also summarized in Table II. Spinning at 264 °C provided the largest amount of calcined tape. The graphitized tape at 2500 °C, which was spun at 270 °C, showed the largest degree of orientation in spite of the lowest degree of calcination at 1300 °C. The crystalline sizes, L_c, of the graphitized tapes ranged from 11.8–13.0 nm. Their degree of orientation and L_c tended to increase with higher spinning temperature. Carbon tapes which were stabilized under 10 and 20 g $den.^{-1}$ strain exhibited higher degrees of orientation by 1% and 2%, respectively, regardless of the spinning temperature than that stabilized without strain.

Tensile strength and modulus of the graphitized tape ($T = 2.2$ μm, $W = 12.2$ μm) at 2500 °C were 332 kg mm^{-2} and 93 ton mm^{-2}, respectively, when the spinning temperature was 270 °C. Such performances are noteworthy product in the university laboratory.

4. Discussion

The present study succeeded in preparing very thin carbon or graphite tape of ~2 μm thickness through slit-spinning, stabilization under strain, carbonization and graphitization by selecting mesophase pitch and spinning conditions. Very thin pitch tape was very rapidly stabilized during the temperature rise and the resultant graphite tape exhibited excellent mechanical properties of high tensile and Young's modulus, probably due to the high degree of orientation along the fibre axis.

The selection of mesophase pitch and spinning temperature is the key to obtain such a very thin tape. Methylnaphthalene-derived mesophase pitch was found to give a carbon tape 1.6 μm thick, whereas the naphthalene-derived one gave ~3 μm thick at the thinnest point, although their viscosity–temperature profiles were much the same as shown in Fig. 1. The lowest temperature for smooth spinning should be selected for the thinnest tape. Such results indicate the importance of fluid properties of the mesophase pitch during its spinning. Low viscosity at the outlet of the spinneret relaxes the molecular arrangement of the mesophase pitch to deform the tape shape formed at the slit-shaped nozzle into a circular one of the smallest surface energy. The slow cooling of the pitch at the outlet, as well as a high spinning temperature may keep the viscosity low enough to relax such an arrangement. The melt viscosities of methylnaphthalene and naph-

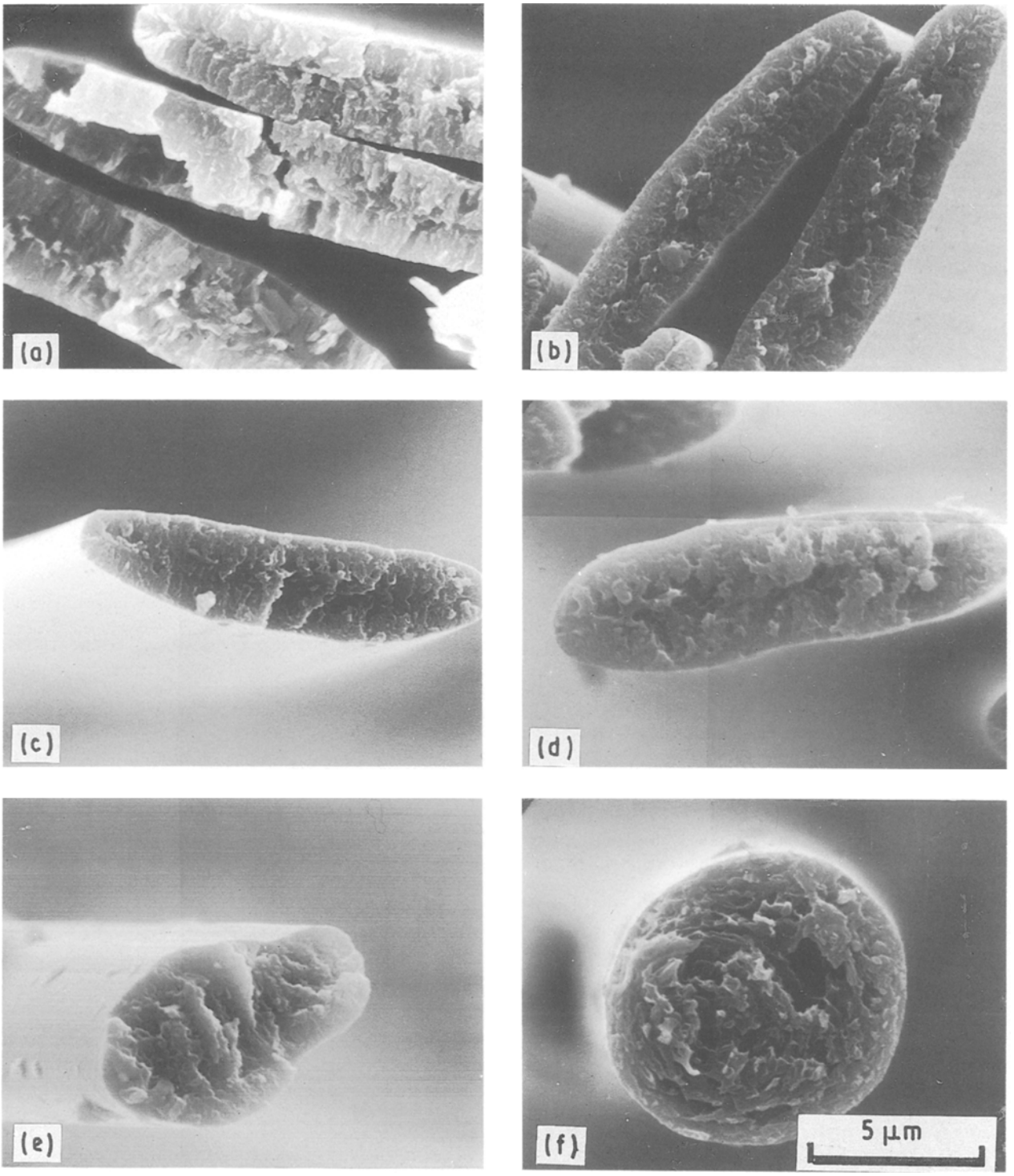

Figure 5 Scanning electron micrographs of carbon tapes prepared at various spinning temperatures (see Table II). (a) c-mNA-260-0, (b) c-mNA-264-0, (c) c-mNA-270-0, (d) carbon tape spun at 275 °C, (e) carbon tape spun at 280 °C, (f) carbon fibre spun at 285 °C with slit-shaped nozzle.

thalene-derived mesophase pitches are much the same around the spinning temperatures. Their differences influencing the relaxation may come from their thermal conductivities for cooling. A higher degree of molecular stacking of the former pitch at its spinning, as observed by melt X-ray diffraction, may be a reason for the better conductivity [13].

The strain at the stabilization is also effective in improving the T/W ratio of the tape and in reducing its thickness through the significant expansion of the tape. Thus, the T/W ratio of the tape can reach the same value as that of the spinneret.

The present carbon tape exhibited a texture of radial skin and random core. The radial skin is natural when the spinning viscosity is high, as is often reported [14]. The random core may originate from the tension during the stabilization by strain, as observed in a previous paper [15]. Rapid stabilization at the skin of the tapes from the present mesophase pitch prevents their adhesion, while the insufficiently stabilized core is extended. Such a skin–core structure may be favourable for the mechanical flexibility of the tape.

Very thin carbon tape of excellent mechanical properties is now available for various applications. It can

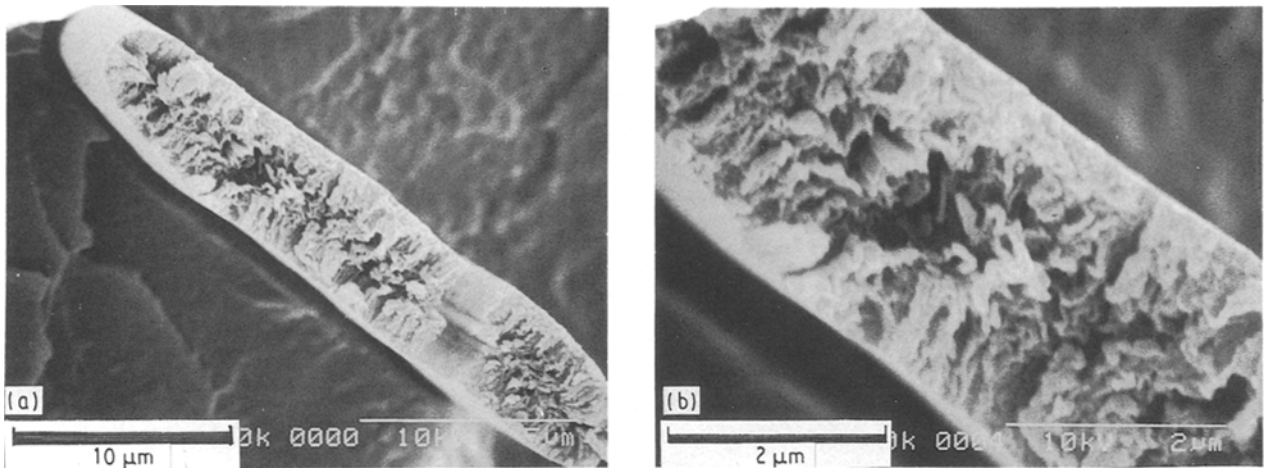

Figure 6 (a, b) Scanning electron micrographs of graphitized tape (g-mNA-264-10)

serve as an excellent high density filler for advanced composite, a bundle electrode and host for intercalation compounds.

References

1. S. OTANI, K. OKUDA and H. S. MATSUDA, "Carbon Fibre", (Kindai, Tokyo, 1983) p. 231.
2. K. KAWATA, S. UEKAWA, and K. KOBAYASHI, in "Composites '86: Recent Advances in Japan and United States" (Japan Society for Composite Materials, Tokyo, 1986) p. 1.
3. H. SASAKI, T. SAWAKI and Y. YOSHIOKA, US PAT., 4628 001 (1988).
4. D. K. RODGERS, K. E. ROBINSON, C. C. FAIN, and D. D. EDIE, "Extended Abstracts of 20th Biennial Conference on Carbon" (American Carbon Society, Santa Barbara, 1991) p. 248.
5. D. D. EDIE, N. K. FOX and B. C. BARNETT, *Carbon* **24** (1986) 481.
6. I. MOCHIDA, K. SHIMIZU, Y. KORAI, Y. SAKAI and S. FUJIYAMA, *Chem. Lett.* **11** (1989) 1893.
7. I. MOCHIDA, K. SHIMIZU, Y. KORAI, H. OTSUKA, Y. SAKAI and S. FUJIYAMA, *Carbon* **26** (1988) 843.
8. Y. KORAI, M. NAKAMURA and I. MOCHIDA, *ibid.* **29** (1991) 561.
9. G. E. BACON, *J. Appl. Chem.* **6** (1965) 477.
10. Carbon Society of Japan, "Tanso Zairyo Jitugen Gijuitsu" (Kagaku Gijuitsu, Tokyo 1978) p. 46.
11. Japan Society for the Promotion of Science (JSPS), *TANSO(Carbon)* **36** (1963) 25.
12. Japanese Industrial Standard, JIS R-7601, 1980.
13. Y. KORAI and I. MOCHIDA, in "Extended Abstracts of 20th Biennial Conference on Carbon" (American Carbon Society, Santa Barbara, 1991) p. 148.
14. T. MATSUMOTO, *Pure Appl. Chem.* **57** (1985) 1553.
15. I. MOCHIDA, H. TOSHIMA, Y. KORAI, and T. MATSUMOTO, *J. Mater. Sci.* **24** (1989) 57.

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