HIGHLY ORIENTED POROUS GRAPHITE FILM PREPARED FROM POROUS AROMATIC POLYIMIDE FILM

Yutaka Kaburagi[a], *Hazumu Aoki*[a], *Akira Yoshida*[b]

Faculty of Engineering[a] and Advanced Research Lab.[b],
Tokyo City University, 1-28-1, Tamazutsumi, Setagaya-ku,
Tokyo, 158-8557, Japan

Introduction

Carbonization and graphitization of aromatic polyimide films have been investigated widely, and graphite films with high crystallinity have been obtained from some type of the polyimide films [1]. Porous aromatic polyimide films have also been prepared [2,3] and the porous graphite film was obtained from the carbonized film [3]. However, no investigation for the texture and properties of the porous graphite films has been reported. In the present study, porous aromatic polyimide films were carbonized and then heat-treated to various temperatures up to 3000^{o}C in Ar gas flow, and their texture and properties were examined.

Experimental

Porous aromatic polyimide films with 28 and 59 μm in thickness and with about 50% porosity provided by Ube Industries Ltd. (PIPF-28 and -59, respectively) were used in this study. The molecular structure of PIPFs is the same as a commercially available polyimide film Upilex-S. PIPFs were carbonized at 900^{o}C in Ar gas and then heated to 2400−3000^{o}C in high purity Ar gas for 1- 30 min. Upilex−RN with 25 μm in thickness was also heat-treated as the same as PIPFs for comparison. The structure and texture of the carbon films derived from PIPFs were examined by the measurements of XRD, Raman spectrum, electrical conductivity and magnetoresistance, and the SEM observations.

Results and Discussion

SEM images of the upper and lower surfaces of PIPF-28 and the carbonized and graphitized films are shown in Fig. 1. These films have porous texture in micrometric scale. The texture of upper surface of each film is different from that of the lower surface, and both textures of the film changed to dense and fine texture by the heat treatment at 3000^{o}C.

Figure 2 shows the X-ray diffraction profile of PIPF-28 and those heat-treated at temperatures between 900 and 2750^{o}C. PIPF-28 was graphitized by 1 min heat-treatment at temperatures around 2700-2800^{o}C. In Fig. 3, values of the interlayer spacing d_{002} evaluated from the 004 diffraction lines are plotted as a function of heat treatment temperature HTT for the heat-treated samples of PIPF-28, PIPF-59 and Upilex-RN. The graphitizability of PIPFs was better than that of Upilex-RN. In addition, it can be assumed from Fig. 2 that the carbon layers orient parallel to the surfaces of the graphitized

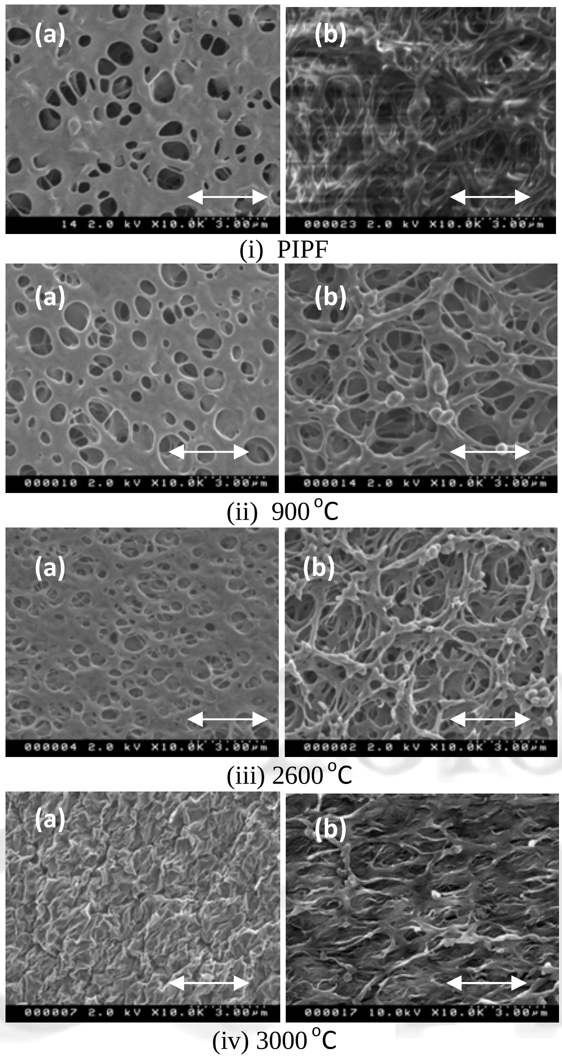

Fig. 1 SEM images of upper (a) and lower (b) surfaces of PIPF-28 (i) and that heat-treated at 900 °C (ii), 2600 °C (iii) and 3000 °C (iv). The length of the bar in the photos are 3 μm.

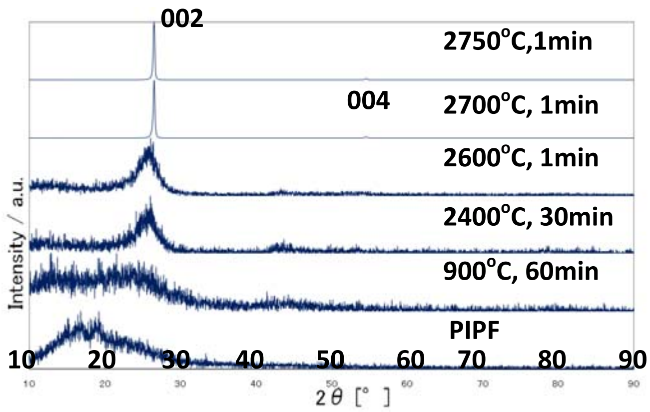

Fig. 2 X-ray diffraction profiles of PIPF-28 and that heat-treated at temperatures between 900 and 2750^{o}C.

films. Values of the mosaic spread MS, which is defined by the full width at the half maximum of the peak intensity recording of 002 diffraction plotted against rotation angle of each film, for PIPFs and Upilex-RN heat treated at high temperatures are shown in Fig. 4 as a function of HTT. Even though PIPFs have porous textures, the graphitized films

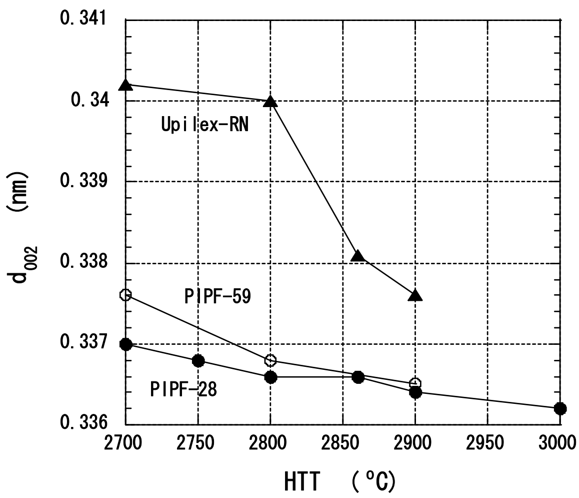

Fig. 3 d_{002} as a function of heat treatment temperature HTT for PIPF-28, PIPF-59 and Upilex-RN heat treated for 1 min at each HTT except 3000°C-treated PIPF-28 (30 min).

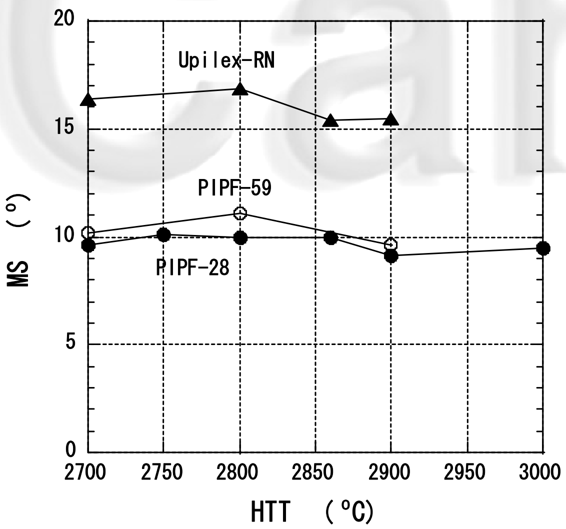

Fig. 4 MS as a function of HTT for PIPF-28, PIPF-59 and Upilex-RN heat-treated for 1 min at each HTT except 3000°C-treated PIPF-28 (30 min).

exhibit approximately a plane orientation of the carbon layers along the film surface.

Because of the porous texture in micrometric scale, the Raman spectra measured at different areas on the surfaces of each graphitized film were not the same as shown in Fig. 5.

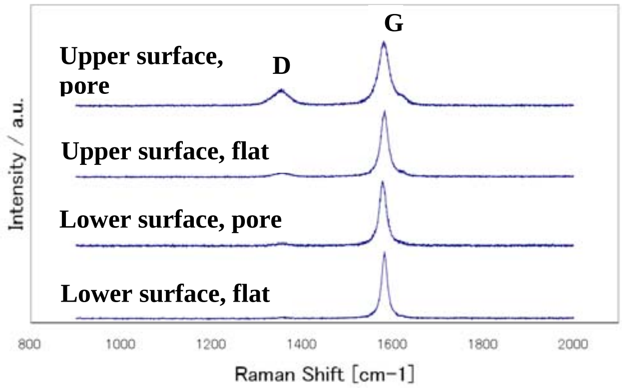

Fig. 5 Raman spectra measured at different areas on upper and lower surfaces of PIPF-28 heat-treated at 2800°C for 1 min.

The results of the maximum transverse magnetoresistance under the magnetic field applying perpendicular to the film surface and electrical conductivity along the film surface for the heat-treated PIPFs and Upilex-RN are summarized in Table 1. These results are consistent with those obtained from the XRD measurements. Consequently, the carbon films derived from PIPFs were found to graphitize well and the graphitized films have porous microtexture with carbon layers oriented parallel along the film surface approximately. It is noted that these carbonized and graphitized films exhibit high permeability to gases and alcoholic liquids.

Table 1. Magnetoresotance and electrical conductivity for heat-treated PIPF-28, PIPF-59 and Upilex-RN.

Sample	HTT (°C)	$(\Delta\rho/\rho)_{max}$ [%] at 77K	σ [S/m] at 290K
PIPF-28	2750	-0.10	2.9×10^4
	2800	1.95	4.4×10^4
	2900	9.94	1.9×10^5
	3000	17.87	------
PIPF-59	2800	-0.04	1.8×10^4
	2900	9.06	9.9×10^4
Upilex-RN	2800	-0.28	1.4×10^4
	2900	- 0.19	2.0×10^4

Acknowledgment

Acknowledgments are made to Ube Industries Ltd. for providing us the porous aromatic polyimide films with 28 and 59 μm in thickness.

References

[1] Inagaki M, Takeichi T, Hishiyama Y, Oberlin A, High Quality Graphite Films Produced from Aromatic Polyimides, Chemistry and Physics of Carbon 1999; 26:245-333, Marcel Dekker, Edits. Thrower PA and Radovic LR.

[2] Hatori H, Yamada Y, Shiraishi M, Preparation of macroporous carbon films from polyimide by phase inversion method, Carbon 1992;30:303-304.

[3]Ohya S, Okamoto K, Newly developed materials for fuel cell, Association of Technology Information,2003; 60-69 in Japanese.