Highly oriented porous graphite film prepared from porous aromatic polyimide film

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Porous aromatic polyimide films of 28 and 59 μm thickness and with about 50% porosity (PAPIF-28 and -59) were carbonized and then heat-treated to various temperatures up to 3000 °C, and their texture and graphitizability were investigated. A porous texture on the micrometric scale remained on the surfaces and inside the heat-treated PAPIF-28 and -59 films but the 3000 °C-treated PAPIF-28 film was not porous and showed a dense and fine texture. These heat-treated films, except the 3000 °C-treated PAPIF-28 film, exhibited high permeability to gases and alcohols. The carbonized films of PAPIF-28 and -59 were graphitized by 1 min heat-treatment at 2700 °C and 2800 °C, respectively and exhibited an approximately planar orientation of carbon layers along each film surface, even though the films had porous textures. However, the graphitization degrees of the porous carbon films derived from PAPIF-28 and -59 were much lower than those of carbon films derived from Kapton, Novax and PPT films.

KEYWORDS: Porous graphite film, Porous aromatic polyimide film, SEM, XRD, Magnetoresistance

1. Introduction

Carbonization and graphitization of aromatic polyimide films, such as Kapton (PMDA/ODA), have been investigated by many researchers, and graphite films with high crystallinity have been obtained through simple carbonization and simple heat treatments at high temperatures\cite{1,2}. The graphite films are made of polycrystalline graphite, which is composed of well-developed crystallites and the c-axes of the crystallites align almost perpendicular to each film surface\cite{1,2}. Porous carbon films with micrometric pores have also been prepared by pyrolysis of porous aromatic polyimide films\cite{3,4,5}. Around the years 2002-2006, using the porous carbon films derived from porous BPDA/PDA films an attempt to apply the films to fuel cell membrane was carried out because of their high chemical and thermal resistances, low electrical resistivity and liquid and gas permeability\cite{6,7}. However, the toughness of the films gave a difficulty in the practical use for fuel cell membrane\cite{8,9} and no report on the performance of the porous carbon films for fuel cell membrane has been published. On the other hand, porous graphite films were prepared from the porous carbon films and their textures were observed by a scanning electron microscope (SEM)\cite{8,9}. Sufficient characterization of the porous graphite films, however, has not been reported.

In the present study, porous aromatic polyimide films were carbonized and then heat-treated to various temperatures up to 3000 °C in Ar gas flow, and their texture and properties were investigated in some detail.

2. Experimental

Porous aromatic polyimide films (PAPIFs) of 28 and 59 μm thickness and with about 50% porosity provided by Ube Industries Ltd. (PAPIF-28 and -59, respectively) were used in this study as precursors. The molecular structure of PAPIFs is regarded as the same as a commercially available polyimide film Upilex-S (BPDA/PDA)\cite{5,7}. Each PAPIF was sandwiched between two artificial graphite plates and carbonized by a heat treatment to 900 °C with a heating rate of 2 °C/min in Ar gas flow, and kept for 1 h at the temperature using an infrared furnace. Each carbonized film was sandwiched again between two artificial graphite plates, and the carbonized films were then heated to 2100 °C with a heating rate of 20 °C/min and kept for 30 min and heated further to high temperatures in high purity Ar gas using a graphite resistance furnace. Specifically, the carbonized films of PAPIF-28 were heated to 2400 °C and kept for 30 min, to 2600, 2700, 2750, 2800, 2860, 2900 °C for 1 min and 3000 °C for 30 min,
while the carbonized films of PAPIF-58 were heated to 2700, 2800, 2860, 2900 °C for 1 min. The heat treatments of only 1 min are caused by our furnace condition. The porous carbon films thus obtained were denoted hereafter by the precursor name followed by the heat treatment temperature and time such as PAPIF-28-3000-30. Upilex-RN (BPDA/ODA) of 25 μm thickness, the Upilex film only we have, was also heat-treated as the same as PAPIF-58 for comparison. The molecular structure of Upilex-RN is somewhat different from the expected molecular structure of PAPIFs, but the graphitization behaviour of the Upilex-RN derived carbon films has extensively been investigated\(^1\).

The structure and texture of these porous carbon films heat-treated at high temperatures were examined by the observations using a scanning electron microscope (SEM) and the measurements of X-ray diffraction (XRD) and maximum transverse magnetoresistance at 77 K in a field of 1 T.

The XRD measurements were carried out for the heat-treated films of PAPIFs and Upilex-RN using CuKα radiation. Each film was mounted on a specially designed sample holder for film. The 002 diffraction patterns were corrected for the Lorentz-polarization, absorption and atomic scattering factors. The interlayer spacing \(d_{002}\) was determined using a thin cleaved specimen of HOPG with the \(d_{002}\) value of 0.3354 nm as an external standard. The peak intensity of the 002 diffraction was recorded against rotation angle of each film referred to the maximum intensity, and the full width at the half maximum of the 002 diffraction recording, mosaic spread (MS), was determined\(^1,8\).

The maximum transverse magnetoresistance \(\Delta \rho/\rho_{\text{max}}\) was measured at 77 K under the magnetic field of 1 T applying perpendicular to each film surface and electrical current flowing along the film surface for the heat-treated PAPIFs and Upilex-RN.

3. Results and Discussion

The yield of the porous carbon films derived from PAPIF-28 and -59 was about 58 wt% after pyrolyzed at 900 °C and it was about 65 wt% for Upilex-RN. However, the yield of the porous carbon films after heat treatments at high temperatures was about 15 wt%, while it was about 40 wt% for Upilex-RN. The rapid decrease in the yield of the porous carbon films during heat treatments at high temperatures seems to be due to vigorous sublimation of carbon atoms because of porous texture.

The texture of the one side (hereafter denoted as upper surface) of the surfaces of each precursor film (PAPIF-28 and -59) was different from that of the other side (hereafter denoted as lower surface). The texture of the upper surface of each porous carbon film prepared from PAPIF-28 and -59 was also different from that of the lower surface. As examples, the SEM images of the upper and lower surfaces of PAPIF-28 and those of the carbonized and further heat-treated films are shown in Fig. 1. A porous texture on the micrometric scale was clearly observed for these films. Almost the same surface texture as each side of PAPIF-28, upper or lower surface, was observed for that of PAPIF-59. The difference in texture between the upper and lower surfaces should be due to the preparation procedure of PAPIF-28 and -59\(^6,8\). The upper surface may be the side of the film contacting with substrate during polymerization. For the heat-treated PAPIF-59 films, almost the same surface texture as each side of the heat-treated PAPIF-28 films was also observed. It was found that both textures of the upper and lower surfaces of PAPIF-28 changed to dense and fine by the heat treatment at 3000 °C for 30 min. Fig. 2 shows the SEM images of the cross sections for PAPIF-28-2800-1 and -3000-30. Porous texture was also observed the inside of PAPIF-28-2800-1, while PAPIF-28-3000-30 exhibited dense and contiguous texture. It can be assumed that the carbon films became somewhat ductile at 3000 °C and were a little pressed by the artificial graphite plates which sandwiched the sample. It should be noted that these carbonized and graphitized films except PAPIF-28-3000-30 exhibited high permeability to gases and alcohols.

Fig. 3 shows the XRD profile of PAPIF-28 and those heat-treated at temperatures between 900 and 2750 °C. The XRD profile for PAPIF-28 changed suddenly from that for the 2600 °C-treated sample.
to that for 2700 °C-treated one. The carbonized film of PAPIF-28 was graphitized by 1 min heat-treatment at 2700 °C. In the case of PAPIF-59, the carbonized film was graphitized by 1 min heat-treatment at 2800 °C. Fig. 4 shows the XRD profiles of the film specimens of PAPIF-28-2700-1, -2800-1, -2900-1 and -3000-30. The carbon layers seem to orient parallel to the surfaces of the graphitized films because 00l diffractions can only be observed in Fig. 4(a). There is a possibility that the difference in texture between the upper and lower surfaces of the porous carbon films heat-treated at high temperatures observed by SEM (Fig. 2) is reflected in the structural difference. The 004 diffraction patterns of the porous carbon films, however, show nearly symmetrical profiles except for PAPIF28-3000-30 as shown in Fig. 4(b). The unsymmetrical profile for PAPIF28-3000-30 is due to the separation of $K_a1$ and $K_a2$ peaks observed for well graphitized carbons. Therefore, the graphitization behavior of the present porous carbon films is not the case of inhomogeneous graphitization observed for nongraphitizing carbons$^9$.

Values of the mosaic spread MS for PAPIFs and Upilex-RN heat-treated at high temperatures are shown in Fig. 5 as a function of heat treatment temperature (HTT). The MS values for the heat-treated PAPIF-28 were almost independent of HTT. Similar trend was observed for the heat-treated PAPIF-59 and Upilex-RN. The preferred orientation of carbon layers is supposed to be scarcely changed after graphitized. The values of MS for the heat-treated PAPIF-28 and -59 were about 8-10° and 9-12°, respectively, and much smaller than those for the heat-treated Upilex-RN (MS = 15-17°). The MS values for graphite films prepared from aromatic polyimide films Kapton and Novax by heat treatment at 3100 °C are 6.7 and 6.9°, respectively and that for 3600 °C-treated pyrolytic graphite is 8.6°$^{10}$. The graphitized films of PAPIF-28 and -59 exhibits approximately a planar orientation of the carbon layers along the film surface, even though PAPIFs have porous textures.

In Fig. 6, values of $d_{002}$ evaluated from the 002 diffraction lines are plotted as a function of HTT for the heat-treated samples of PAPIF-
The graphitizability of PAPIFs was much better than that of Upilex-RN and the $d_{002}$ value reached 0.3362 nm for PAPIF-28-3000-30. However, the graphitization degrees of the PAPIF-28 and -59 derived porous carbon films were much lower than those of carbon films derived from Kapton, Novax and PPT. For example, the $d_{002}$ value for PAPIF-28-3000-30 corresponds to those for a Kapton derived film heat-treated at 2400 °C for 30 min, PPT derived film heat-treated at 2500 °C for 30 min and a Novax derived film heat-treated at 2500 °C for 30 min. The carbonization and graphitization behaviors of Upilex-RN of 25 μm thickness have been studied systematically and different degrees of graphitizability were found. It was concluded that the graphitization of the Upilex-RN film is erratic from one film to the other, and the behavior is attributed to the random mobility of the imide part of the molecule when carbonization starts. The graphitizability of the Upilex-RN film used in the present study was not so well ($d_{002} = 0.3376$ nm for the film heat-treated at 2900 °C).

4. Conclusions

The carbon films derived from PAPIFs were found to graphitize and the graphitized films have porous microtexture with carbon layers oriented parallel along each film surface approximately. The graphitizability of the heat-treated PAPIF-28 is better slightly than that of the heat-treated PAPIF-59. However, the graphitization degrees of the porous carbon films derived from PAPIF-28 and -59 were not good enough and much lower than those of carbon films derived from Kapton, Novax and PPT. It is noted that these carbonized and graphitized films except PAPIF-28-3000-30 exhibit high permeability to gases and alcohols.

Acknowledgment

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


