PERGAMON

Carbon 39 (2001) 2017–2021

CARBON

Investigation of the pore structure in glass-like carbon prepared from furan resin

Katsuya Fukuyama[a], Takashi Nishizawa[b], Keiko Nishikawa[a,*]

[a]*Division of Diversity Science, Graduate School of Science and Technology, Chiba University, Yayoi, Inage-ku, Chiba 263-8522, Japan*

[b]*Chemical and Environmental Technology Laboratory, Kobe Steel Ltd., Takatsukadai, Nishi-ku, Kobe 651-2271, Japan*

Received 18 October 2000; accepted 19 January 2001

Abstract

Small-angle X-ray scattering (SAXS) measurements were carried out on glass-like carbons (GCs) prepared from furan resin at 950°C and thereafter treated at various temperatures. The scattering intensities grow gradually with increasing heat-treatment temperature (HTT) up to 1600–1800°C, and then the intensities increase abruptly at HTT higher than 1800°C. HTT dependence of the reciprocal width for the 002 peaks shows a similar behavior. Distance distribution functions (DDFs) were obtained by the Fourier transform of the SAXS intensities, from which the changes of the gyration radius and the shape of pores in the GC with increase of HTT are discussed. The HTT dependence of the structural change of the GCs from furan resin is almost the same as that of GCs from phenolic resin. However, it was found that the GC prepared at 1200°C from furan resin shows a peculiar behavior, namely, the largest interlayer spacing in the carbon matrix and the smallest value of the gyration radius for pores.

Keywords: A. Glass-like carbon; B. Heat treatment; C. Small-angle X-ray scattering

1. Introduction

The pores in carbon materials play an important role in their functions and characteristics. When the structural change of carbon materials is considered with relation to the physical properties, the discussion on structural change of pores is important and interesting from scientific and practical viewpoints. Recently, glass-like carbon (GC) has received considerable attention in the fields such as battery and semiconductor industries. GC is prepared by heat-treatment on thermosetting resins in inert atmosphere. They show various unique properties such as great hardness compared with other carbon materials and gas impermeability [1,2]. Hence, the structure of GC has been of interest since its development, and several models for the structure have been proposed [3–9]. According to the models, the pores in GC are closed for air and moisture. When the pores are closed, it is impossible to apply an adsorption method for characterization of the pore structure. Small-angle X-ray scattering (SAXS) occurs in the vicinity of zero degree of the scattering angle, when the local electron density difference ranging from 1 to several 10 nm exists in a sample. It is applied to the structure analysis, irrespective of the pore being open or closed. We have shown the usefulness of SAXS experiments by application to some carbon materials with closed pores [10–13].

In the present SAXS measurement, we studied the structural change of pores in GC prepared from furan resin produced by heat-treatment. The heat-treatment temperature (HTT) dependence of the change is reported and the starting material dependence is discussed by comparison with the GCs prepared from phenolic resin [11].

2. Experimental

GC samples were made from furan resin (Hitafuran VF302; Hitachi Chemical Co., Ltd.). Curing catalyst (*p*-toluenesulfonic acid) was added to the resin in the proportion of 0.3 mass%, and then the mixture was hardened and formed in plate. GC samples were prepared

*Corresponding author. Fax: +81-43-290-3939.

E-mail address: nisikawa@cuphd.nd.chiba-u.ac.jp (K. Nishikawa).

0008-6223/01/$ – see front matter
PII: S0008-6223(01)00014-8

by heat-treatment of the hardened resin at 950°C and thereafter treated at various temperatures under argon gas atmosphere. In the former process, the temperature was increased at the rate of 2°C/h and retained at 950°C for 30 min and then the carbon was cooled down inartificially. In the latter process, the carbon pre-heated as mentioned above was heated at the rate of 100°C/h up to each corresponding temperature, at which the temperature was kept constant for 30 min, and then the heat-treated carbon was cooled down inartificially. The thickness of each sample was about 1 mm. The values of the bulk densities, determined by the flotation measurement using toluene as a solvent, are shown in Fig. 1. For comparison, the bulk densities of GCs prepared from phenolic resin are also shown in the figure. Fig. 1 shows that the values are about 1.4–1.5 g cm^{-3} except for the sample of HTT=950°C. Furthermore, the figure shows that GCs from furan resin and those from phenolic resin [11] have a similar tendency in the change.

The SAXS measurements were performed with the apparatus which had been designed and constructed in our laboratory [14]. The generator was a rotating anticathode type (M06XHF, MAC Science Co., Ltd.) and a point-focused X-ray beam (focus size: 0.3×0.3 mm) was adopted in the diffractometer. A position-sensitive proportional counter (PSPC; PSPC-100, MAC Science Co., Ltd.) was used as the detector. The wavelength of incident X-rays was 0.15406 nm ($CuK\alpha_1$), and the distance from a sample to the detector, namely 'camera length' was 1170.5 mm. All X-ray paths were kept in vacuum of about 10^{-1} Pa, including the room for the sample holder, in order to prevent influence of scattering and absorption of X-rays by air. The accumulation time for the intensity measurement of each sample was 2000 s. The observable scattering parameter s was 0.11–2.85 nm^{-1}, with the definition of $s=4\pi \sin\theta/\lambda$ (2θ: scattering angle; λ: wavelength of X-rays).

To discuss the pore structure and carbon matrix complementarily, we also performed wide-angle X-ray scattering (WAXS) measurements in transmission geometry by use of an apparatus [15] with a two-dimensional detector, so-called 'imaging plate' (DIP-100, MAC Science Co., Ltd.). Radiation used was AgKα ($\lambda=0.05608$ nm) and the camera length was 90 mm. The accumulation time for the intensity measurement of each sample was also 2000 s. The observable scattering parameter s was 9–90 nm^{-1}.

3. Results

3.1. SAXS measurements

The SAXS patterns obtained from each sample are shown in Fig. 2. The intensities are in arbitrary units but are normalized to the scattering intensity from the same number of carbon atoms by correcting differences in thickness and density of samples. To show clearly the change of the scattering intensities upon HTT, scattering intensities at $s=0.11$ nm^{-1} are shown in Fig. 3 as a function of HTT, which is the smallest measurable s-value in the present apparatus. The intensities of carbons from phenolic resin [11] are also shown in the same figure. The scattering intensities of GC prepared from furan resin grow gradually with increasing HTT, the growth stops at HTT=

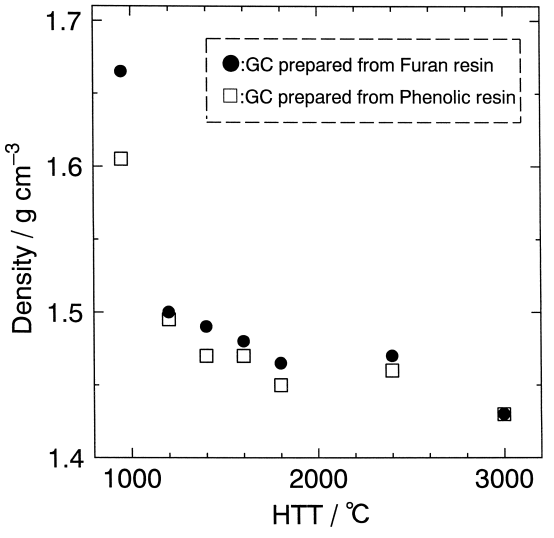

Fig. 1. Bulk densities of GCs prepared from furan resin (●) and from phenolic resin (□), plotted as a function of HTT.

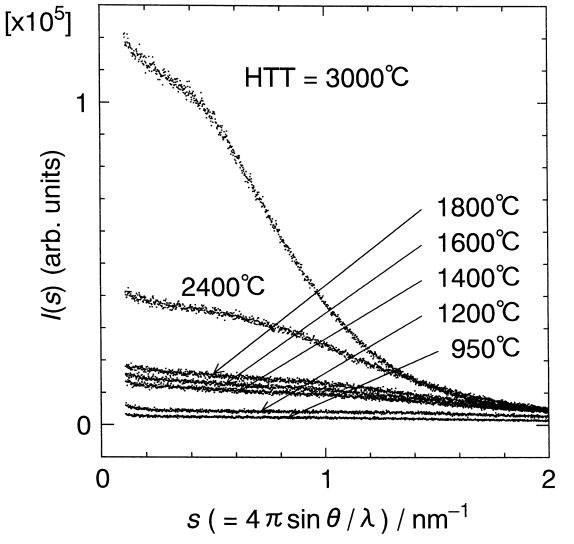

Fig. 2. Small-angle X-ray scattering patterns of GCs prepared from furan resin as a function of scattering parameter s.