05YFJJJC01900) and Doctor Fund from the Educational Ministry of China (No. 20050056062).

References


Full width at half maximum intensity of the G band in the first order Raman spectrum of carbon material as a parameter for graphitization

Akira Yoshida *, Yutaka Kaburagi, Yoshihiro Hishiyama

Faculty of Engineering, Musashi Institute of Technology, Setagaya-ku, Tokyo 158-8557, Japan

Received 2 March 2006; accepted 17 May 2006

Keywords: Carbon films; Graphitization; X-ray diffraction; Raman spectroscopy

The first order Raman spectrum for carbon materials has been used for structural investigation, because the ratio of the peak intensity of the D band to that of the G band \( \frac{I_D}{I_G} \) can be related linearly to the inverse of the crystallite size along the basal plane \( L_a \) as obtained firstly by Tuinstra and Koenig and then by Knight and White [1,2]. On the other hand, the full width at half maximum intensity of the G band \( G \)-FWHM is known to reflect the surface crystallinity of carbon material [3]. The relationship between \( G \)-FWHM and the interlayer spacing \( d_{002} \), a parameter for graphitization, was investigated in this study for homogeneous carbon materials. For investigation, carbon films derived from Kapton of 25 \( \mu m \) in thickness were selected, because the materials are thin, very graphitizable and typical carbon materials that have a plane orientation texture [4]. The relationship between the intensity ratio \( \frac{I_D}{I_G} \) and \( d_{002} \) for the Kapton-derived carbon films was also studied incidentally.

Rectangular specimens, approximately 20 mm long and 10 mm wide, were cut from a film of Kapton, and were heated to 900 °C for 1 h in a flow of nitrogen by sandwiching them between polished artificial graphite plates [5]. The heat treatments of these carbonized films sandwiched between two polished artificial graphite plates were made of two types in a graphite resistance furnace. The first type of carbonized film was heat-treated at temperatures of 2000, 2050, 2100, 2150 and 2200 °C, respectively, for various heat treatment times ranging between 12 and 300 min and the second type was heated at temperatures between 2300 and 3000 °C with a step of 100 °C for 30 min, at temperatures of 3200 and 3300 °C for 10 min and at a temperature of 3400 °C for 2 min. The homogeneity of each of the heat-treated specimens was confirmed by observation of its cross-section using a field-emission-gun type scanning electron microscope.

The X-ray diffraction measurements with CuKa radiation were conducted for the film specimens, each of which was mounted on a specially designed sample holder, using a rotation-anode type wide angle diffractometer. For the specimens, the 004 diffraction line was measured. After correction for the Lorentz-polarization, atomic scattering and absorption factors, the \( d_{002} \) value was determined by referring to the 004 diffraction line of a thin plate sample of HOPG with the \( d_{002} \) value of 0.3354 nm. Thirty six samples with \( d_{002} \) values ranging between 0.3370 and 0.3421 nm were obtained under the first type of heat treatment, while

* Corresponding author. Tel./fax: +81 3 5707 2175. E-mail address: ayoshida@sc.musashi-tech.ac.jp (A. Yoshida).

0008-6223/$ - see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.carbon.2006.05.020
for the second type 10 samples with $d_{002}$ values between 0.3356 and 0.3370 nm were prepared.

The Raman spectra of the heat-treated specimens (KAP’s) were measured in air at room temperature with a 514.5 nm line of an argon ion laser as the incident radiation perpendicular to the incident plane, using a JOBIN YBON RAMANOR T-64000 instrument. The polarization of the incident radiation was perpendicular to the incident plane. For each sample, measurements were conducted at four different positions on the top and bottom surfaces of the sample with a laser beam of 1 mm diameter focused on each of the following positions; the positions were 5 mm away from both ends and on the central axis on each surface. Measurements were also made at the center of the top and bottom surfaces of a thin square plate of HOPG with 1 cm sides to obtain the reference data.

Fig. 1 shows plots of G-FWHM as a function of $d_{002}$ for KAP’s with that for HOPG. The values of G-FWHM for the samples with turbostratic structures having $d_{002}$ values of about 0.3420 nm are about 40 cm$^{-1}$. The G-FWHM value decreases with decreasing $d_{002}$ very rapidly at first, then decreases gradually to a value of about 18 cm$^{-1}$ for the $d_{002}$ value of 0.3400 nm, passes through a plateau of $d_{002}$ values ranging between 0.3400 and 0.3390 nm and decreases again rapidly to a value of about 15 cm$^{-1}$ for the $d_{002}$ value of 0.3380 nm. It then levels off to a value of about 14.5 cm$^{-1}$ with the $d_{002}$ value down to about 0.3370 nm and finally decreases to the value 13.1 cm$^{-1}$ for HOPG. The D band disappears for the samples with $d_{002}$ values of 0.3361 nm or below.

The following is our explanation of the curve in Fig. 1.

1. The first rapid decrease and then gradual decrease in the G-FWHM in the $d_{002}$ range between 0.3420 and 0.3400 nm is due to an increase in the average size of the turbostratic crystallites.

2. The plateau for the $d_{002}$ values between 0.3400 and 0.3390 nm could be related to annealing of defects in the turbostratic layer planes before the onset of graphitization at the $d_{002}$ values of 0.3390 nm.

3. The change in G-FWHM for the $d_{002}$ values between 0.3390 and 0.3370 nm is due to the growth of graphite crystallites, leaving some amounts of turbostratic crystallites until completion of the transformation from the turbostratic structure to the graphite structure.

4. For the sample with the $d_{002}$ value of 0.3370 nm, the transformation from the turbostratic structure to the graphite structure seems to complete itself and to appear as a discontinuous point of G-FWHM on the curve [5,6].

5. The final decrease in G-FWHM for the $d_{002}$ values below 0.3370 nm is due to further crystal growth and annealing of crystalline defects.

Fig. 2 exhibits plots of $I_D/I_G$ in a logarithmic scale as a function of $d_{002}$ for KAP’s, showing a variation corresponding to that for G-FWHM in Fig. 1, especially a dis-
continuous change of G-FWHM at the $d_{002}$ value of 0.3370 nm.

The intensity ratio $I_D/I_G$ is known to be sensitive to the laser excitation wavelength [7–9]. The full width at the half maximum intensity of the G band G-FWHM would also be dependent on excitation wavelength. The relationships found in this study could be extended to the further work on the dependence of G-FWHM and $I_D/I_G$ on excitation wavelength.

References


About the endothermic nature of the adsorption of the herbicide diuron from aqueous solutions on activated carbon fiber

M.A. Fontecha-Cámara a, M.V. López-Ramón a, M.A. Álvarez-Merino a, C. Moreno-Castilla b,*

a Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain
b Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Received 4 April 2006; accepted 16 May 2006

Keywords: Carbon fibers; Adsorption; Adsorption properties

Temperature is an important factor that influences adsorption of organic compounds from aqueous solutions onto carbon materials. The expected effect of temperature on adsorption isotherms is a decrease in adsorption with increasing temperature, since adsorption is a spontaneous process. However, different examples have been reported of an increase in the amount adsorbed with a rise in the temperature [1–7]. This is opposite to the effect of temperature on the physical adsorption of a single component (e.g., a gas on a solid), because adsorption from solution involves at least two components, a solute and solvent. Thus, adsorption from solution is not only governed by adsorbent–adsorbate interactions but also by adsorbate–solvent and adsorbent–solvent interactions [1].

The herbicide diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is widely used in agriculture. The diuron molecule is related to that of 3,4-dichloroaniline (3,4-DCA), with the difference that the latter does not possess the urea type chain. The similarity between these molecules is the reason they were selected for this investigation into the effects of temperature on their adsorption from aqueous solutions.

The activated carbon fiber (ACF) used was supplied by Kynol Europe. Its BET surface area was 1709 m$^2$/g and its mean micropore volume and width were 0.734 cm$^3$/g and 1.69 nm, respectively, both calculated from DR equation applied to N$_2$ adsorption isotherm. The mesopore volume obtained from N$_2$ adsorption isotherm was 0.017 cm$^3$/g. The oxygen content of the ACF, obtained by elemental