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Modification of pyrolytic graphite surface with plasma irradiation

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The effects of oxygen plasma treatment on the basal and edge surfaces of pyrolytic graphite have been investigated and compared with those of electrochemical treatment on their surfaces. The structural changes caused by the plasma and electrochemical treatments have been characterized by laser Raman and X-ray photoelectron spectroscopies. For the basal surface the plasma treatment causes the slight destruction of the graphitic structure, whereas for the edge surface it causes no marked destruction of the graphitic structure unlike the electrochemical treatment. The amount of surface oxygen both on the basal and edge surfaces increases after the plasma treatment. In particular, for the edge surface, a high surface oxygen concentration can be attained in a short treatment time. In addition, carbonyl-type groups appear to dominate in the plasma-treated basal and edge surfaces over –O– type groups. It can be concluded that oxidation by the plasma treatment is restricted to the vicinities of the surfaces and does not proceed to the internal structure of graphite, unlike the electrochemical treatment.

1. Introduction

The physical and chemical characteristics of the surface of carbon materials such as carbon fibres (CFs) are important factors governing the interfacial adhesion in composite materials. In order to improve the adhesion, a variety of surface treatment methods have been used. In the case of CFs, appropriate electrochemical and plasma treatments oxidize the CF surface moderately, thereby improving the mechanical properties, such as interlaminar shear strength, (ILSS) of CF-reinforced composite materials [1–4].

The effects of anodic treatment on the CF surface and ILSS have been examined by several investigators. Kozlowski and Sherwood [5–7] found that the amount and type of the oxide produced on the CF surface varies depending upon the potential, the reaction time in solution, the pH and the concentration of electrolyte and the type of CFs. Harvey *et al.* [1] proposed that the rise in ILSS with anodic treatment was not dependent upon the O1s/C1s ratios obtained by X-ray photoelectron spectroscopy (XPS) or the amount of carboxyl functionality present on CF surface. Fitzer and Rensch [4] showed that caustic alkaline electrolyte improves ILSS much better than an acid one. Based on anodic treatment data with pyrolytic graphite (PG) as a model CF surface, we have proved that there is a range of treatment in which hydroxyl groups can be added without destroying the surface structure [8]. Moreover, it has been proved that anodic treatment in alkaline electrolyte has a wider permitted range of treatment, in which hydroxyl groups can be added without destroying the edge surface structure, than that in acid electrolyte [9].

On the other hand, the effects of radio-frequency or microwave plasma treatment on the CF surface has been recently investigated. Donnet *et al.* [10] have found that microwave plasma treatment allows an increase in the polar component of the surface energy of CFs. Jang *et al.* [11] have reported that oxygen radio-frequency plasma treatment improves the wettability of the CF surface by epoxy resin.

The structure of the CF surface is generally complex. Because the basal planes and the edges of graphitic crystallites form the CF surface, the interpretation of the experimental results relating to the CF surface is not easy. The use of the basal and edge surfaces of PG as a model carbon surface would be expected to facilitate a better understanding of the plasma treatment effects on carbon materials, especially CFs. In this paper the effects of oxygen radio-frequency plasma treatment on the basal and edge surfaces of PG are discussed with respect to the chemical and physical properties of their surfaces and compared with those of electrochemical treatment.

2. Experimental procedure

The PG sample used in the present study was supplied from Tomoe Engineering Company. Basal surfaces, which are perpendicular to the *c*-axes of graphitic crystallites, were prepared by cleaving PG. Mirror-polished edge surfaces of PG, which are parallel to the *c*-axes of graphitic crystallites, were prepared by the method of Katagiri *et al.* [12]. These surfaces were ultrasonically rinsed in acetone and distilled water successively, and then dried at 100 °C for 20 min in an oven.

Oxygen radio-frequency plasma treatment was carried out with a BP-1 basic plasma kit (SAMCO). A micro-leak attached to the reaction vessel (bell-jar type) was connected to a vacuum pump and the vessel was first evacuated below 0.02 torr (1 torr = 133.322 Pa). A constant pressure of oxygen of 0.75 torr was established during the treatment by combination of the continuous evacuation and oxygen gas inlet through another micro-leak. The flow rate of oxygen was 100 ml min^{-1}. The input power of plasma discharge was maintained constant and equal to 50 W. The treatment time was varied between 5 and 240 min for the basal and edge surfaces of the PG sample.

Electrochemical treatment in 5% ammonium bicarbonate solution was carried out with the edge surface. The specific electric charge (electric charge, C, per unit area m^2) was controlled by changing the current density with a regulated d.c. power supply (METRONIX). Anodic treatment was carried out in three steps : 1000, 5000, and 50000 C m^{-2}, respectively. Cathodic treatment was carried out only at 50000 C m^{-2}. After the surface treatments, the surfaces were rinsed in distilled water and dried at 100 °C for 20 min in the oven.

Laser Raman spectroscopy was used to characterize the structural changes of the treated surfaces. Raman spectra of the surfaces were measured by using the RAMALOG-10 system (SPEX). The 514.5 nm line (200 mW) of an argon-ion laser was used to induce the Raman spectrum.

The functional groups added to the surfaces were examined using XPS. X-ray photoelectron spectra were obtained using an ESCALAB MK II (VG) with MgK_α X-radiation (300 W) with a pressure of about 10^{-9} torr.

3. Results and discussion

3.1 The structural changes of the basal and edge surfaces of PG treated with oxygen plasma

The Raman spectra of the basal surfaces of PG after oxygen plasma treatment, together with the Raman spectrum of the untreated one, are shown in Fig. 1a. The Raman spectra of the untreated and plasma-treated edge surfaces, measured with the incident laser radiation polarized parallel to the stacking graphitic layers, are shown in Fig. 1b. Two Raman bands are observed around 1360 and 1585 cm^{-1}. The Raman band around 1585 cm^{-1} is assigned to the doubly degenerated stretching vibration of the hexagonal ring of graphite [13]. Another band around 1360 cm^{-1}, which is Raman inactive for perfect crystals of graphite is attributed to a defect-induced vibrational mode

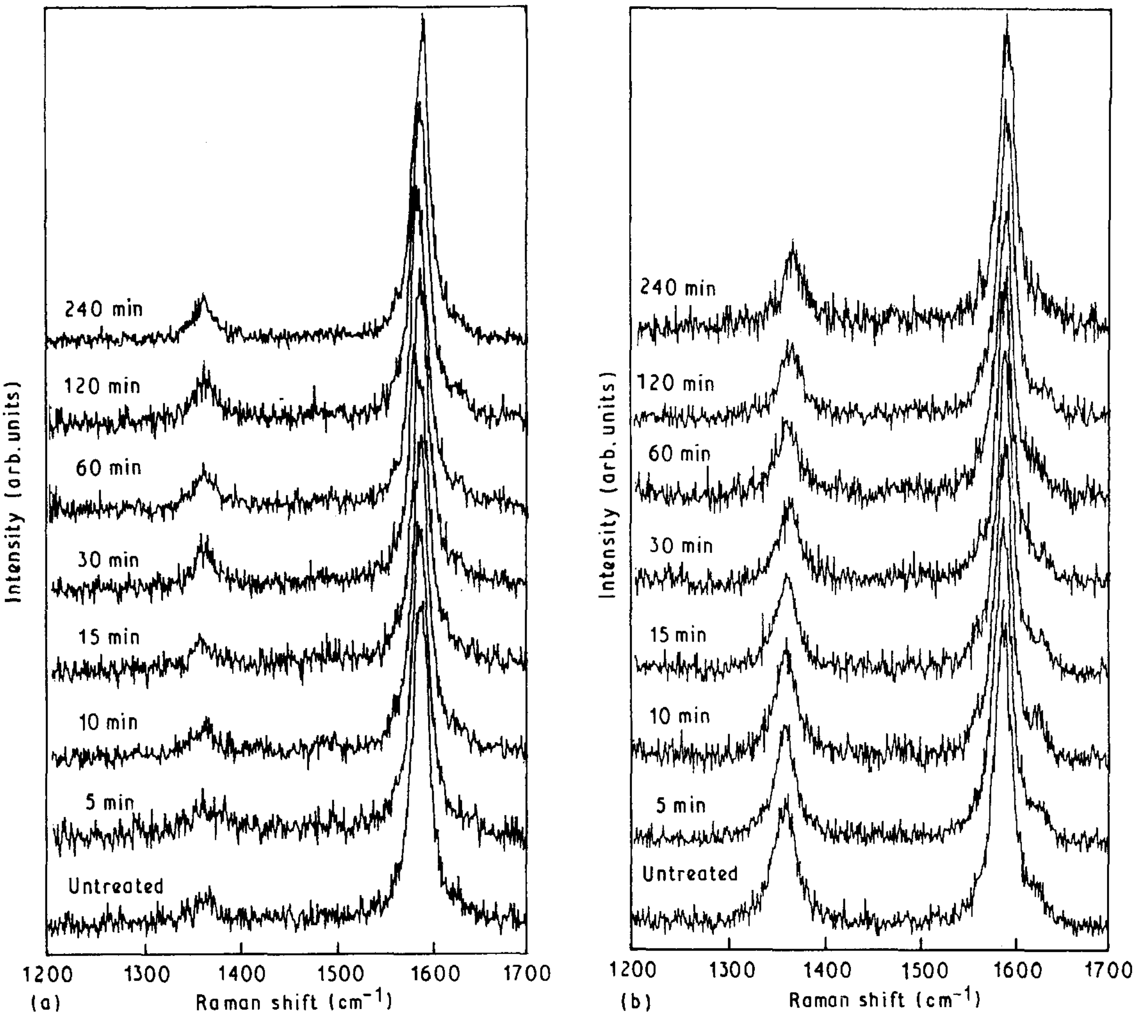

Figure 1 Raman spectra of the untreated and oxygen plasma-treated surfaces of PG. (a) Basal surfaces and (b) edge surfaces of PG.

[13–15]. Therefore, if the orientation of graphitic layers can be assumed to be constant, the intensity ratio, R, of the 1360 cm^{-1} band to the 1585 cm^{-1} band can be related to the number of boundaries and lattice vacancies in the surface graphitic layers [12].

The change in R as a function of oxygen plasma treatment time for the basal and edge surfaces of PG is shown in Fig. 2. Because R is not zero even for the untreated basal surface, very small numbers of edge carbon atoms of surface graphitic basal planes are originally present on the untreated surface. In the case of basal surface, R increases slightly with treatment time up to 30 min and is held constant in the range 30–240 min. This increase indicates that the destruction of the graphitic structure in the basal surface occurs slightly after the plasma treatment. The destruction of the graphitic structure probably results from the removal of the edge carbon atoms from the surface as CO or CO_2. The removal leads to smaller graphitic basal planes or larger lattice vacancies in the surface graphitic layer as shown schematically in Fig. 3. After treatment for 240 min, the decrease of about 0.3% in weight of PG can be detected. This decrease means that many surface graphitic layers are probably removed from the basal surface as CO or CO_2 during the prolonged treatment. Edge carbon atoms in a surface graphitic layer newly exposed to the oxygen plasma would be then removed as CO or CO_2 in the same manner as in the case of 30 min treatment. As a result, the destruction of the surface layer for 240 min treatment may proceed almost in a similar way to that for 30 min treatment (Fig. 3). The value of R of the basal surface treated by the oxygen plasma for 30–240 min is smaller than that of the basal surface oxidized anodically in sulphuric acid solution at 5000 $\mathrm{C\,m}^{-2}$ [8]. It can be assumed that for plasma treatment the destruction of surface graphitic structure proceeds by a mechanism different from that reported previously for the anodic treatment [8].

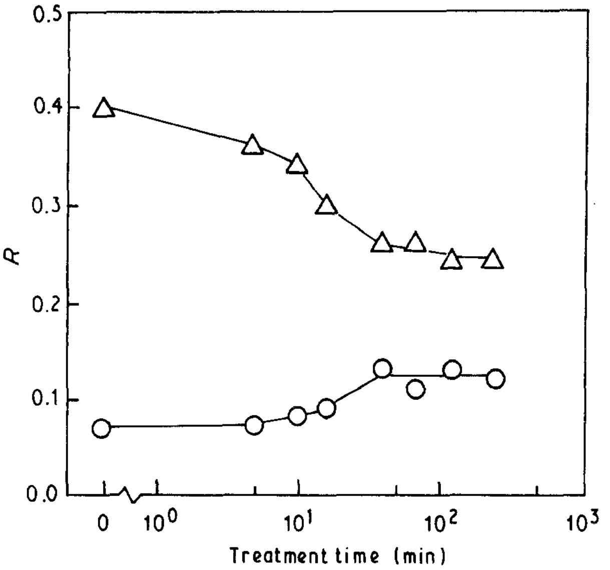

Figure 2 Change in R as a function of the oxygen plasma-treatment time for (○) basal and (△) edge surfaces of PG.

On the other hand, in the case of the edge surface, R decreases with treatment time up to 30 min and is held constant in the range 30–240 min. This decrease suggests that the defects in the edge surface are removed selectively by plasma treatment. This behaviour of the plasma treatment for the edge surface differs from that for the basal surface described above, as well as that of anodic treatment for the basal and edge surfaces reported previously [8, 9]. Fig. 4 shows the change in R as a function of the specific electric charge for the edge surfaces treated in ammonium bicarbonate solution, together with the data reported previously [8, 9]. For not only H_2SO_4 and $(C_2H_5)_4NOH$ solutions but

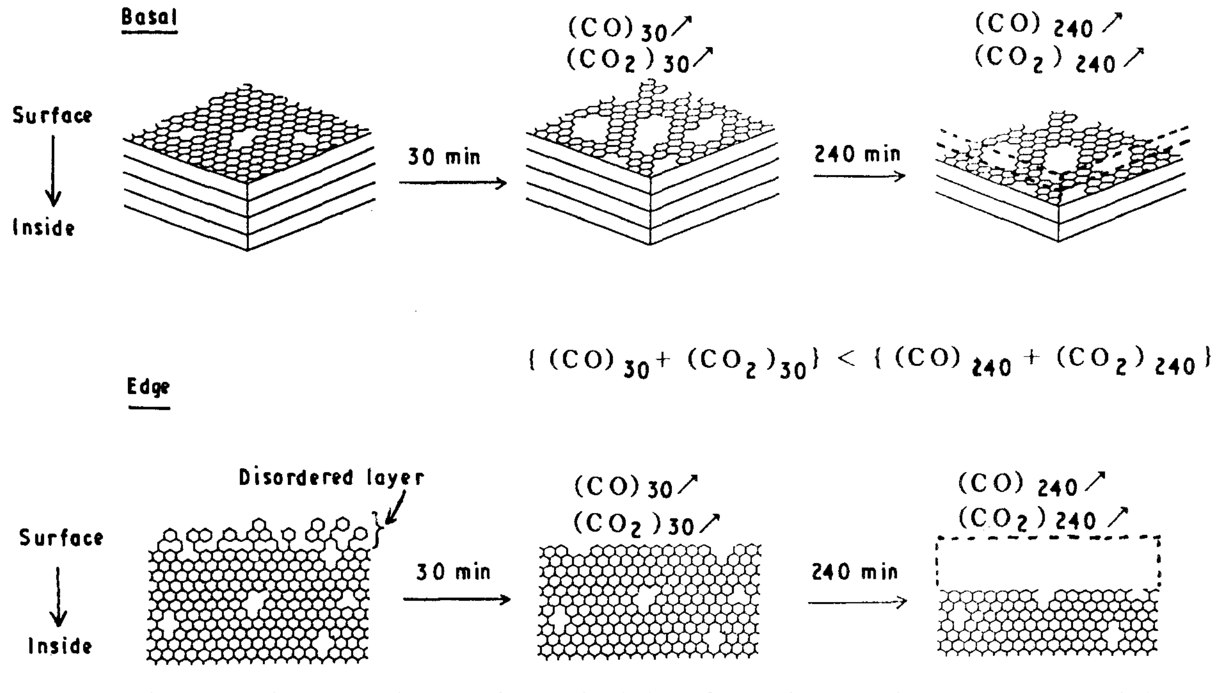

Figure 3 Schematic diagrams of the structural changes of the basal and edge surfaces by the oxygen plasma treatment. $(CO)_{30}$ is the amount of CO evolved after plasma treatment for 30 min and $(CO)_{240}$ for 240 min. $(CO_2)_{30}$ is the amount of CO_2 evolved after plasma treatment for 30 min and $(CO_2)_{240}$ for 240 min.

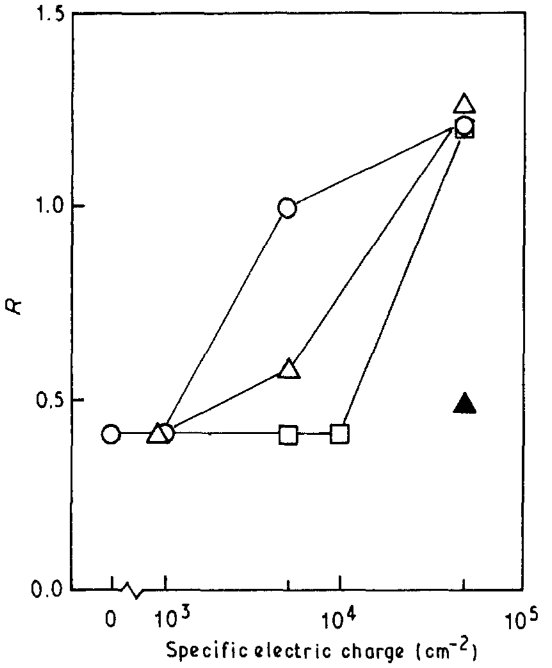

Figure 4 Change in R as a function of the specific electric charge for the electrochemically treated edge surfaces: (○) anodic treatment with H_2SO_4 [8, 9], (△) anodic treatment with NH_4HCO_3, (▲) cathodic treatment with NH_4HCO_3, and (□) anodic treatment with $(C_2H_5)_4NOH$ [9].

also the NH_4HCO_3 solution, the destruction of the surface graphitic structure is caused by the anodic treatment. Moreover, it can be seen that the destruction is also caused slightly by the cathodic treatment in the NH_4HCO_3 solution. Because the graphitic structure of the basal surface is destroyed by the plasma treatment as described above, it is unreasonable to assume that edge surface structure is modified into more graphitized one by the plasma treatment. Thus the decrease in R for the edge surface described above implies that the more disordered structure is removed from the edge surface and the more ordered inherent edge structure is exposed. It is thought that the more disordered structure is produced mechanically during the mirror-polishing process and is already present on the untreated edge surface (Fig. 3.) Katagiri *et al.* [12] have already shown that a disordered layer, to some extent, is present on the mirror polished edge surface of PG and removed after heat treatment in argon and in air. Additionally, they have shown that the removal of the disordered layer leads to the appearance of the ideal edge surface [12]. Similarly, the more disordered structure would be removed as CO or CO_2 after plasma treatment for 30 min (Fig. 3); as a result, more ordered inherent edge structure will appear (Fig. 3) and the appearance of the inherent edge structure will induce a decrease in the value of R.

Fig. 5 shows the Raman spectra of the untreated and plasma-treated edge surfaces, measured with the incident laser radiation perpendicular to the stacking planes of graphite, compared with the Raman spectra with the parallel configuration. In the ideal edge surface having no disordered graphitic planes, the Raman scattering intensity is larger with the parallel configuration than with the perpendicular one, because the Raman active vibrational modes of graphite are attributed to in-plane atomic displacements [12]. In the 240 min plasma-treated sample, the intensity ratio of the 1585 cm^{-1} band with the perpendicular configuration to the 1585 cm^{-1} band with the parallel one, $I_\perp/I_\parallel$, becomes smaller, indicating that the Raman spectra reflect the intrinsic nature of the edge surface. After treatment for 240 min, the decrease of about 0.3% in weight of PG can be detected. This means that many carbon atoms forming surface graphitic layers are removed from the edge surface as CO or CO_2 during the prolonged treatment. These results indicate that neither disorder of the orientation of graphitic planes nor defects are introduced into the graphitic structure forming the edge surface even by very prolonged plasma treatment, unlike in anodic treatment. Consequently, it is proved that the effect of the plasma treatment on the edge surface structure is different from that of electrochemical treatment.

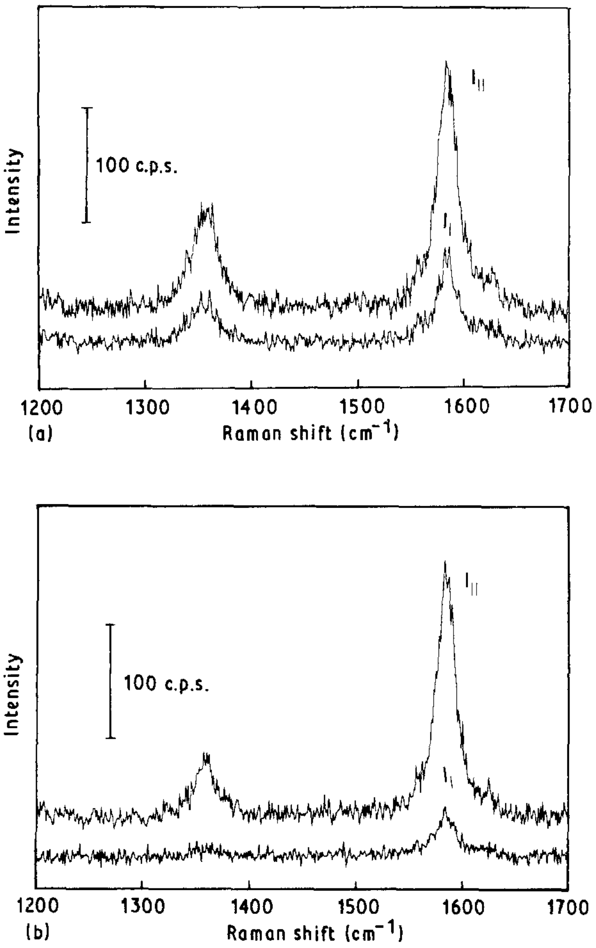

Figure 5 The Raman spectra of the edge surfaces of PG, (a) untreated, $I_\perp/I_\parallel = 0.36$ (b) plasma treated for 240 min, $I_\perp/I_\parallel = 0.16$. The upper spectra were measured with the incident laser radiation polarized parallel to the stacking planes of graphite and the lower spectra with the perpendicular polarization.

3.2. Functional groups added to the basal and edge surfaces of PG treated with oxygen plasma

XPS wide-scan spectra are not shown for any of the untreated and treated surfaces, because they are all essentially similar in showing a strong C1s peak and a relatively weak O1s peak (especially very weak for the untreated basal surface). No N1s peak is observed in all cases.

O1s/C1s ratios from XPS narrow-scan spectra for the untreated and plasma-treated surfaces are shown in Fig. 6. For the basal surface, the O1s/C1s ratio gradually increases with increasing treatment time up to 15 min, thereafter remaining almost constant at about 0.34. On the other hand, for the edge surface the ratio initially increases after treatment for only 5 min, thereafter remaining almost constant at about 0.42. These increases in the O1s/C1s ratio after plasma treatment suggest that oxygen-containing functional groups are added to the basal and edge surfaces by the plasma treatment. For the edge surface the O1s/C1s ratio attains to a maximum value more rapidly than for the basal surface. Moreover, for the edge surface the maximum value is higher than for the basal surface. Thus the edge surface structure is more favourable for shortening the optimum treatment time as well as increasing the oxygen concentration on the surface compared to the basal surface structure. This suggests that the orientation of surface graphitic layers of carbon materials such as CF has an important influence on surface oxidation behaviour in the case of the plasma treatment.

Shifted chemical signals at a few electron volts from the main carbon peak due to the formation of oxygen-containing functional groups are expected from the increase in the O1s/C1s ratio after plasma treatment described above. However, none of the shifted chemical signals expected could be recognized in any of the C1s spectra of the plasma-treated surfaces. It seems that oxidation after the plasma treatment occurs only in a limited region near the surface and so the shifted chemical signals cannot be detected. By decreasing the angle, θ, between the surface and the analyser of the XPS equipment as shown in Fig. 7, a higher percentage of atoms from the top few atomic layers of the surfaces can be analysed. In order to obtain the information from the top few atomic layers, the angle was decreased from 75° to 30° which is the limitation of the XPS equipment used in this study.

The C1s spectra of the untreated and 240 min plasma-treated surfaces for the angle 30° are shown in Fig. 7. For the basal surface, the O1s/C1s ratios of the untreated and 240 min plasma-treated surfaces were 0.14 and 0.43, respectively. For the edge surface, they were 0.35 and 0.50, respectively. No shift in the chemical signals which could be expected was recognized in the C1s spectra of the plasma-treated surfaces. These C1s spectra do not prove that oxygen-containing functional groups are added to the surfaces after the plasma treatment. However, taking into account the increase in the O1s/C1s ratio after the plasma treatment, oxidation is expected to occur at the treated surface.

The kinetic energy of O1s electrons is smaller than that of C1s electrons. Surface sensitivity increases with decreasing electron kinetic energy; thus surface sensitivity follows the order O1s > C1s. The O1s spectra of the untreated and 240 min plasma-treated surfaces for the angle of 30° are shown in Fig. 8. In both basal and edge surfaces, the relative area of the signal above 532 eV in the O1s spectra does not change after the plasma treatment, whereas the relative area of the signal below 532 eV increases after the plasma treatment. In addition, the plasma treatment results in a lowering of the binding energy indicating the maximum intensity in the O1s spectrum in both the basal and edge surfaces. The lower energy component below 532 eV arises from =O type groups, and the higher energy component above 532 eV arises from –O– type

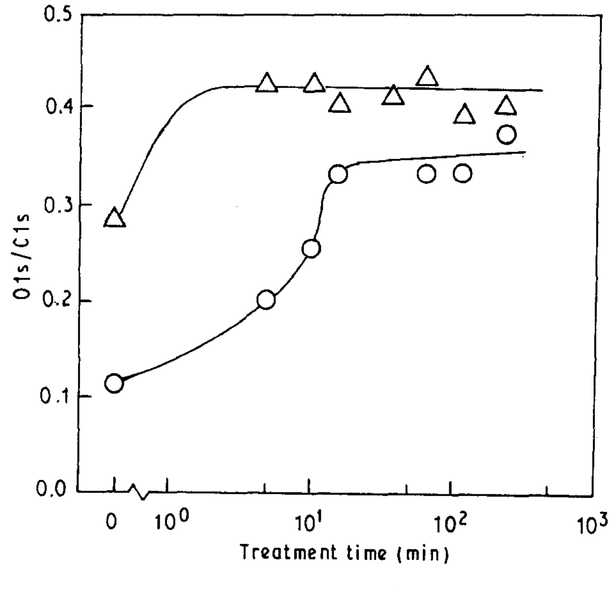

Figure 6 Change in the O1s/C1s ratio from XPS spectra with plasma-treatment time: (○) basal surface, (△) edge surface.

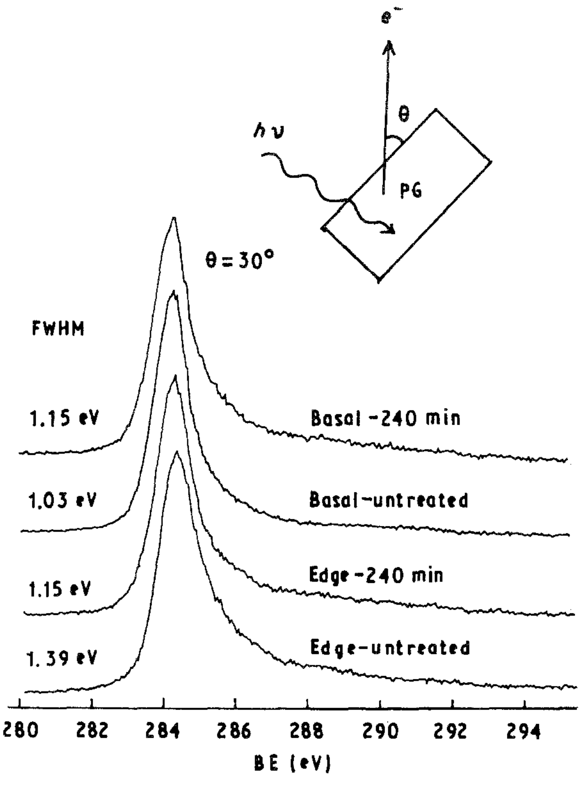

Figure 7 C1s spectra of the untreated and 240 min plasma-treated surfaces for θ = 30°.

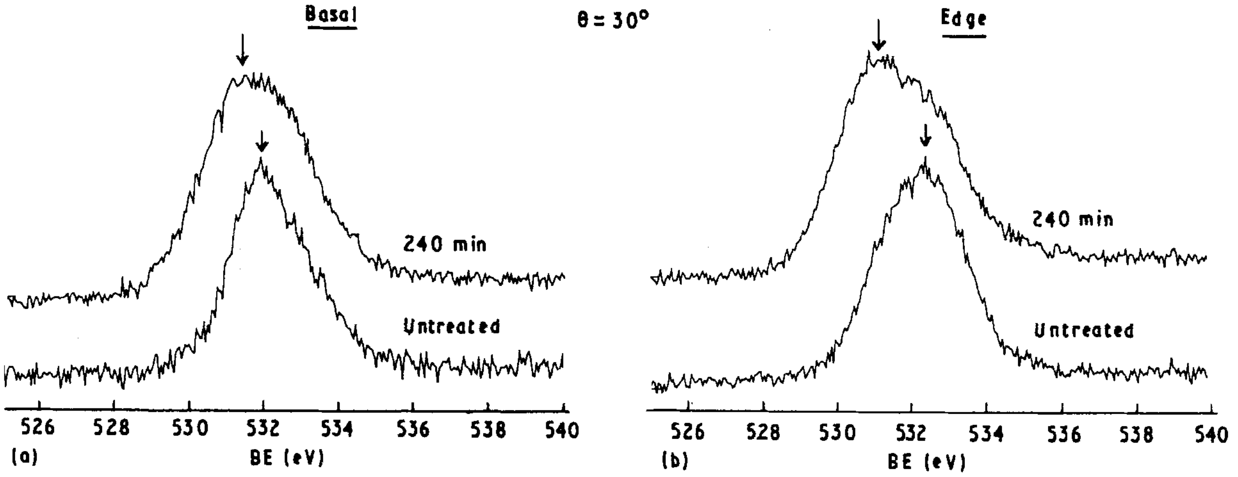

Figure 8 O1s spectra of the untreated and 240 min plasma-treated surfaces for θ = 30°. (a) Basal, (b) edge surfaces.

groups or CO, CO_2, O_2 and H_2O [6, 16]. Thus the above evidence derived from the O1s spectra indicates that $=O$ type groups are mainly added to the basal and edge surfaces after the plasma treatment. Therefore, it can be presumed that the plasma treatment produces mainly carbonyl groups including only $=O$ type groups on both the basal and edge surfaces.

For the basal surface, the full width at half maximum (FWHM) of the C1s spectrum of the 240 min plasma-treated surface is broader than that of the untreated one (Fig. 7). On the other hand, for the edge surface, the FWHM of the C1s spectrum of the untreated surface is broader than that of the 240 min plasma-treated one (Fig. 7). When the *R* of the Raman spectra increases, the FWHM broadens. The FWHM appears to correspond to the *R* rather than the O1s/C1s ratios. Morita *et al.* [17] found that FWHM values decrease systematically with increased graphitization degree. Xie and Sherwood [18] suggested that disordering of the surface graphitic lattice leads to broadening of the C1s graphitic peak. The C1s spectra shown in Fig. 7 would provide mainly information concerning the structural changes of the basal and edge surfaces of PG. In addition, as can be seen from Fig. 7, the FWHM values of the basal surfaces are relatively smaller than those of the edge surfaces. Consequently, the FWHM values are presumed to be dependent upon the orientation of graphitic layers, as well as defect concentration in graphitic layers.

The C1s spectra of the edge surfaces anodically treated at 5000 C m^{-2} in the 5% ammonium bicarbonate solution for both the angles of 75° and 30° are shown in Fig. 9. For the angle of 75°, a shift in the chemical signal at around 2.0 eV from the main carbon peak is observed. This chemical shift suggests that hydroxyl/ether and carbonyl groups are produced after anodic treatment [6]. For the angle of 30° two chemically shifted signals at around 2.0 and 4.5 eV from the main carbon peak are observed. These chemical shifts suggest that carboxyl/ester groups as well as hydroxyl/ether and carbonyl groups are produced after anodic oxidation [6]. It is found that the types of functional groups produced near the surface are different from those produced in the internal region. Clearly, the surface oxidation mechanism of the plasma treatment is different from that of the electrochemical one. Consequently, it is proved that for the electrochemical treatment, oxidation proceeds more deeply into the internal graphitic structure than for the plasma treatment.

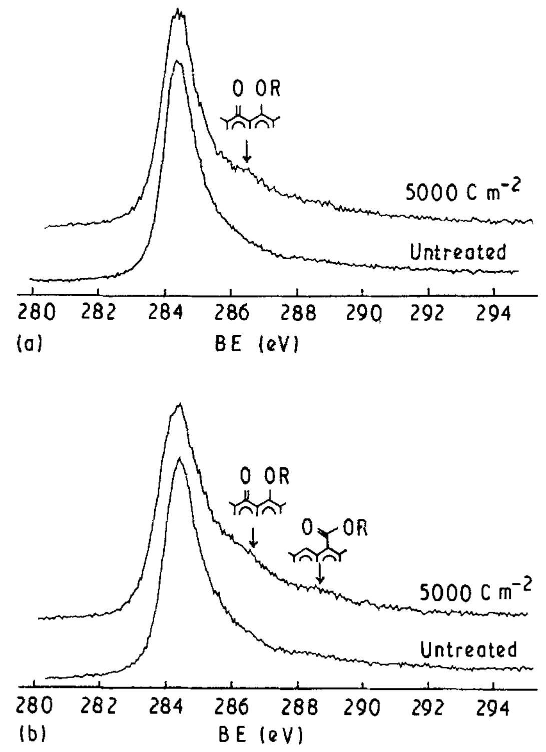

Figure 9 C1s spectra of the untreated and anodically 5000 cm^{-2} treated edge surfaces. (a) θ = 75°, (b) θ = 30°.

4. Conclusions

The oxygen radio-frequency plasma treatment can change the graphitic structure of the basal and edge surfaces of PG as well as their surface chemistry. The plasma treatment introduces small numbers of defects to the graphitic structure forming the basal surface, whereas it introduces no defects to the graphitic structure forming the edge surface, unlike the electrochemical treatment. The plasma treatment increases the O1s/C1s ratios of the basal and edge surfaces. For the edge surface more oxygen atoms are added to the surface in a shorter treatment time than for the basal surface. In both the basal and edge surfaces, oxidation by plasma treatment is limited to the vicinities of their surfaces and does not proceed into their internal graphitic structures.

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