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ESR Study of Glass-Like Carbons

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ESR studies were carried out on a variety of glass-like carbons made from different precursors heat-treated in the range 300—2500 °C. It was found that the behaviors of unpaired electrons were nearly identical. The temperature dependence of ESR spectrum showed that the behavior of localized unpaired electrons in the glass-like carbons changed to that of delocalized ones at HTT about 2500 °C. The ESR spectrum of the glass-like carbons heat-treated at 800 °C consisted of a single line under a pressure of above 10^{-4} Torr but split into two components when air was admitted. This strong interaction with unpaired electrons and air (oxygen molecules) is caused by the active structure related to micropores in the glass-like carbons. We suppose that the polyene type radicals are the most suitable as the active structure to interpret the behavior of unpaired electrons in glass-like carbons heat-treated at 800 °C. As another major point in this study, it was found that there is a correlation between unpaired electron concentration and the g value.

In general carbonized organic materials contain high concentrations of unpaired electrons produced by bond breaking during the pyrolysis. The unpaired electrons are usually stable at room temperature or below, and their behavior is easily observed by ESR absorption measurements. There are many reports of ESR studies on carbonized materials and excellent reviews have been made by Singer,[1] Mizushima,[2] and Mrozowski.[3] ESR studies of glass-like carbons made from cure resins have also been reported.[4-6] There have been few studies on ESR absorption measurements for glass-like carbons made from different precursors which have been heat-treated in a temperature range as wide as 300—2500 °C. Heat treatments in this temperature range cover the process of carbon precursor formation and those of carbonization and graphitization, and are required for ESR study of glass-like carbon to get informations on the behavior of the localized and delocalized unpaired electrons through the microstructural change in the course of heat treatment.

In the present paper, ESR absorption measurements are reported for glass-like carbons prepared from three kinds of cure resins heat-treated between 300 and 2500 °C. The effect of adsorbed air on the ESR absorption spectrum is investigated for glass-like carbons obtained at 800 °C in the temperature range −170—200 °C.

Experimental

Three kinds of cure resins, epoxy resin cured with 2,4,6-trinitrophenol (Epikote 828/TNP =90/10), furfuryl alcohol resin and phenol-formaldehyde resin were heat-treated at temperatures between 300 and 2500 °C under the same conditions as those described previously.[7] ESR absorption spectra were measured for the samples by a JEOL X-band spectrometer, model JES-PE-lX, using 100 KHz magnetic field modulation with the microwave power of 8 mW and crystal current of 0.2 mA. No saturation on the spectrum could be seen under this condition. Temperature was measured by a standard copper-constantan thermocouple put close to the sample in the microwave cavity. The temperature in the cavity was controlled within ±1 °C in the temperature range −170—200 °C by flowing cold gas from liquid nitrogen or hot air through the inside of the cavity by a JES-VT-3A variable temperature controller. Samples were powdered and contained in quartz tubes of 6 mm o.d. To study the effect on adsorbed air for the samples, two vacuum conditions were employed: (1) a low vacuum, the sample was sealed in the quartz tube with a pressure of about 10^{-2} Torr (1 Torr=133.322 Pa), (2) a high vacuum, the sample was sealed in the quartz tube after evacuating to a pressure of above 10^{-4} Torr with heating at 150 °C for 1 h.

The g values of the samples were determined by comparison with that of Mn^{2+} in MgO placed in the cavity close to the sample. The g value for Mn^{2+} was predetermined by comparison with that of DPPH (g=2.0036).[8] The g value of the sample was calculated by the equation $g=g_s H/(H-\Delta H_{diff})$, where g_s and H are the g value and the field at resonance of the standard samples, and ΔH_{diff} is the difference between the field at resonance for the test sample and that for the standard sample. The accuracy of the measurement of the g value was ± 0.0002. The line shapes of the ESR spectra for all samples investigated were almost Lorentzian shape. The area S, which is proportional to the absorption intensity was estimated by the equation, $S=(\pi/3)(\Delta H)^2 \cdot h$,[9] where ΔH is the line width of the first derivative spectrum and h is the peak-to-peak height. The unpaired electron concentration was determined by comparing the area on the spectrum of the sample with that of DPPH.

Results

1. Examination in High Vacuum. The ESR absorption spectra of glass-like carbons made from the three kinds of resins heat-treated at the temperatures in the range 300—2500 °C were nearly identical. Figure 1 shows an example of the typical change of the ESR absorption spectrum of glass-like carbons with heat treatment temperature (HTT). The results in Fig. 1 were measured for the glass-like carbon from epoxy resin cured with TNP. The spectra for HTT up to 2000 °C consist of a narrow single line, while the spectrum for HTT of 2500 °C contains two com-

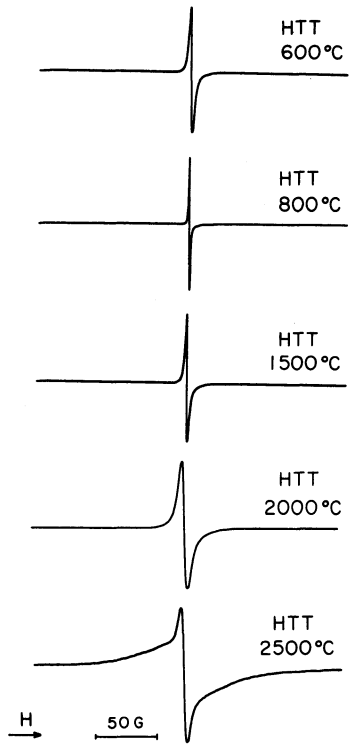


Fig. 1. Change of ESR absorption spectrum of glass-like carbon made from epoxy resin cured with 10 wt% of TNP at different HTT in a high vacuum.

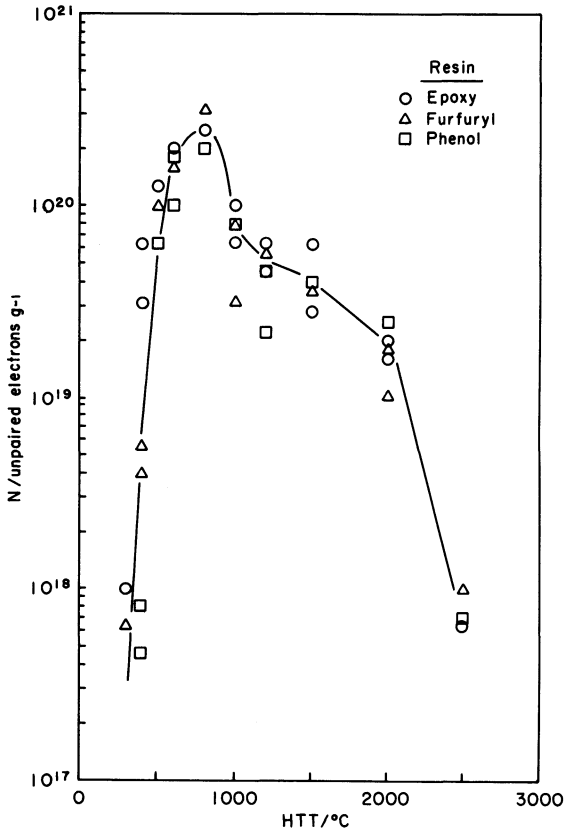


Fig. 2. Changes of unpaired electron concentrations (N) in glass-like carbons with HTT in a high vacuum.

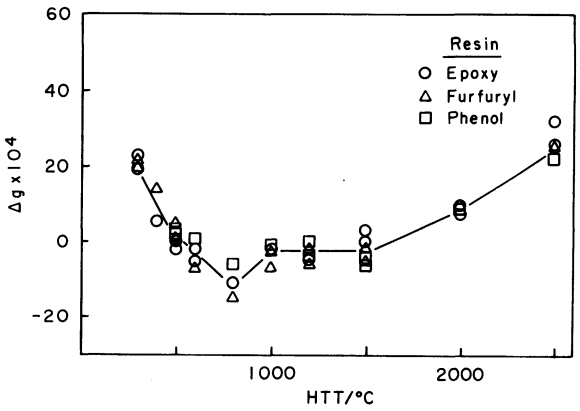


Fig. 3. Changes of Δg on ESR absorption spectra of glass-like carbons with HTT in a high vacuum.

ponents, narrow- and broad-line components. The line widths for narrow-line components are 5—9 G and that for broad one is about 30 G. Broad-line component is not clear to detect quantitatively.

The unpaired electron concentration (N) and the g value of the three kinds of glass-like carbons are shown in Figs. 2 and 3 plotted as a function of HTT. It should be noted that a maximum occurs in N vs. HTT curve at HTT of about 800 °C and a shoulder in the HTT range 1200—1500 °C as shown in Fig. 2. Similar data have been reported by Mrozowski[10] and Toyoda et al.[5] The g values of the glass-like carbons are very close to that of the free spin, g=2.0023, but small change in g with HTT can be seen. As shown in Fig. 3, as with increasing HTT the g shift Δg($\Delta g = g_s - 2.0023$, g_s: g value of each sample), decreases steeply to a minimum at HTT of 800 °C at first, increases a little bit to a value at 1000 °C, keeps the value up to HTT of 1500 °C, and then increases gradually. If we combine the results in Figs. 2 and 3, it is seen that an inverse relation exists between N and Δg.

Figure 4 shows the typical temperature dependence of the line width, ΔH, and the peak-to-peak height, h of the spectra at HTT's 800 and 2500 °C. At HTT of 800 °C ΔH decreases gradually and h increases monotonically, as the temperature is decreased. This behavior is similar to that of DPPH, which is characteristic of localized unpaired electrons.[11] At HTT of 2500 °C, little change in ΔH or h against temperature is observed.

In Fig. 5 the S_t/S_{20} is plotted as a function of inverse temperature for glass-like carbons heat-treated at various temperatures, where S_t and S_{20} are the areas of ESR absorption spectra of t °C and 20 °C, respectively. A good linear relationship is resulted at each HTT. The slopes of the straight lines are positive for HTT lower than 2000 °C, and that is slightly negative at HTT of 2500 °C.

2. Examination in Low Vacuum. Figure 6 shows the temperature dependence of the ESR absorption spectrum of glass-like carbon made from epoxy resin

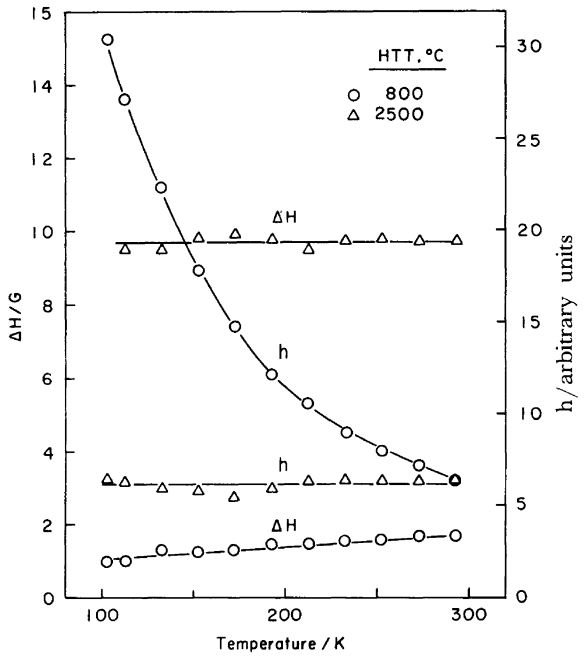


Fig. 4. Temperature dependence of line width (ΔH) and intensity of peak-to-peak height (h) of ESR absorption spectrum of glass-like carbon made from epoxy resin cured with 10 wt% of TNP in a high vacuum.

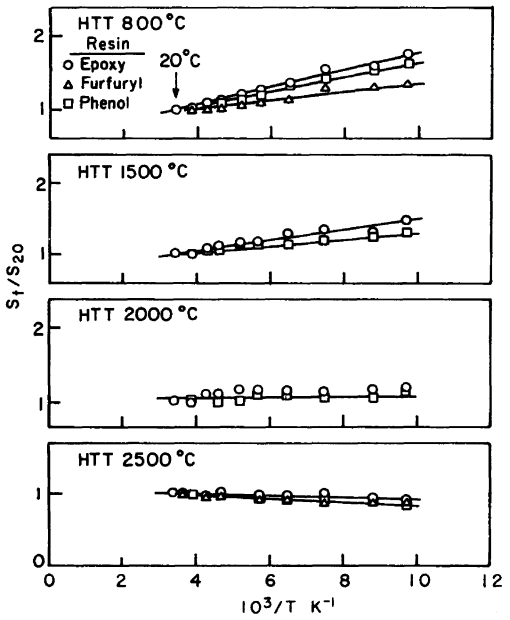


Fig. 5. Relation between relative absorption intensity (S_t/S_{20}) and $1/T$ of glass-like carbons in a high vacuum.

cured with TNP heat-treated at 800°C. In contrast with the spectrum in high vacuum the ESR absorption spectra measured for HTT of 800°C in a low vacuum at room temperature consist of two components, narrow- and broad-line components. The spectrum is common for all three cure resins heat-treated at

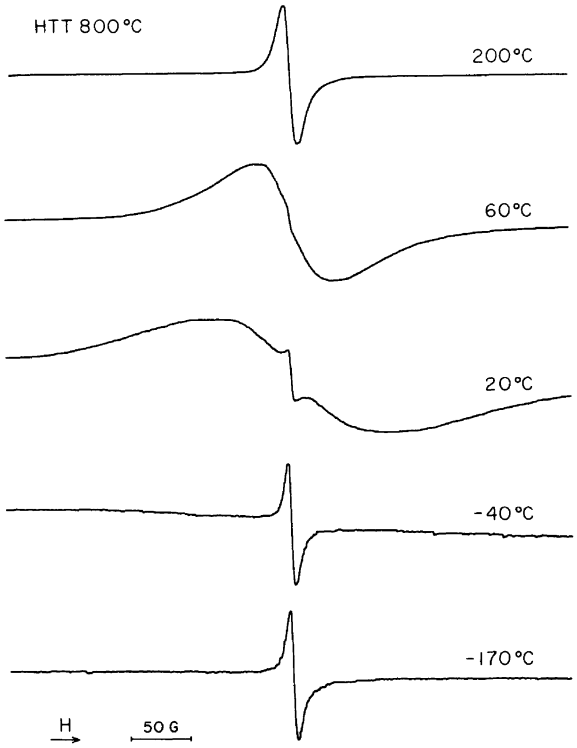


Fig. 6. Change in ESR absorption spectrum of glass-like carbon made from epoxy resin cured with 10 wt% of TNP in a low vacuum.

800°C. The line width of the broad-line component ranges 100 to 500 G and the width of the narrow one 2 to 5G. The vacuum condition and the measurement temperature affect the line width and the intensity of the broad-line component strongly. The broad-line spectrum observed under a low vacuum changed back to the narrow-line spectrum in high vacuum as shown in Fig. 1 (HTT 800°C), and the line broadening appears immediately when air is admitted. The line-broadening seen in the glass-like carbons heat-treated at 800°C was also observed in the glass-like carbon made from furfuryl alcohol resin heat-treated at 1000°C, but not observed in glass-like carbons prepared at other HTT in the range 300—2500°C.

The broad-line component in the spectrum observed at 20°C shown in Fig. 6 becomes broader and weaker as the temperature is decreased, and the line width increases to the width broaden than 1000 G at −60°C. At a temperature below −70°C the broad-line component is too wide to be detected. When the temperature is increased above room temperature, the broad-line component is narrowed, and the narrow-line component can be seen as a slight shoulder on the broad-line component at 60°C as shown in Fig. 6. The narrow-line component is imperceptible on the broad one at 70°C by narrowing of the broad-line component, and the line width of the broad one at 200°C ranges 10—20 G. Therefore, the line width of the broad-line component increases, and the intensity

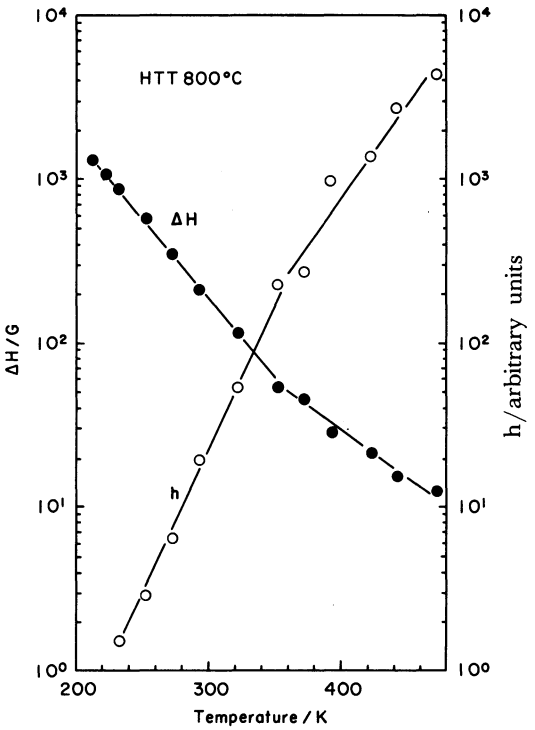


Fig. 7. Temperature dependence of line width (ΔH) and intensity of peak-to-peak height (h) of broad-line component of ESR spectrum of glass-like carbon made from epoxy resin cured with 10 wt% of TNP in a low vacuum.

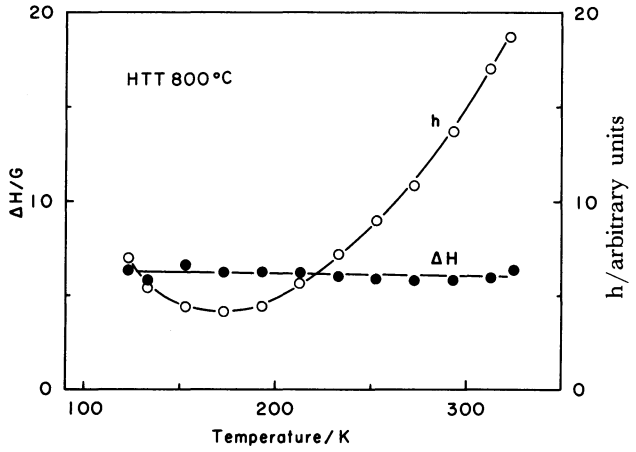


Fig. 8. Temperature dependence of line width (ΔH) and intensity of peak-to-peak height (h) of narrow-line component of ESR spectrum of glass-like carbon made from epoxy resin cured with 10 wt% of TNP in a low vacuum.

decreases markedly, as the temperature is decreased. The trend is shown in Fig. 7. On the other hand, as shown in Fig. 8, the line width of the narrow-line component is almost constant, and with decreasing temperature the peak-to-peak height decreases to a minimum at around 173 K (−100°C) and then increases. The ratio S_t/S_{20} is plotted as a function of inverse temperature for narrow- and broad-line components for HTT of 800°C in Fig. 9. A minimum

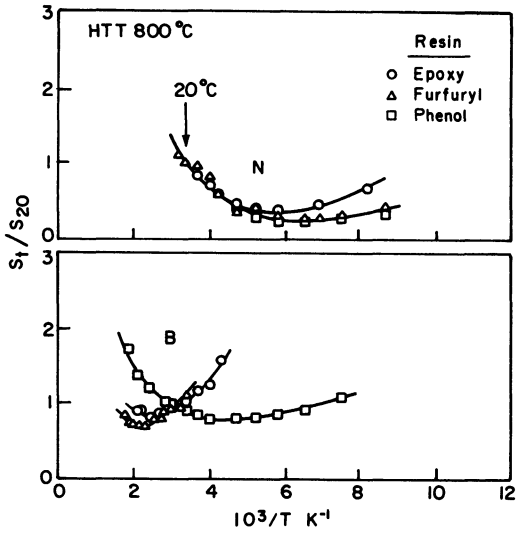


Fig. 9. Relation between relative absorption intensity (S_t/S_{20}) and $1/T$ of glass-like carbons in a low vacuum, N for narrow-line component and B for broad-line component.

of the narrow-line component appeares in the range 153—183 K. On the other hand, a minimum is also observed for broad-line component, but the minimum appears at higher temperature than that for the narrow-line component.

Discussion

1. Examination in High Vacuum. The unpaired electrons at HTT 800°C are mainly localized because of the positive slope of the S_t/S_{20} vs. $1/T$ plots (Fig. 5). The decrease of the slope with increasing HTT indicates that there is a gradual decrease in the localized spin centers and increase in the delocalized spin centers, and the decrease is probably due to the growth of the carbon layer planes. The behavior of the localized unpaired electrons observed in these carbonized resins changes to delocalized one at HTT around 2500°C, because of the slight negative slope as shown in Fig. 5.[12]

The change of g value with HTT is very small in each sample in the HTT range 300—2500°C, but this change is strongly correlated to the unpaired electron concentration as mentioned in Results (Figs. 2 and 3). Logarithm of the value of the unpaired electron concentration shows a good linear relationship against Δg as shown in Fig. 10. The relationship can be fitted to $\log N = A + B \cdot \Delta g \times 10^4$, by a linear least-squares analysis, where $A = 19.7 \pm 0.4$, $B = -0.068 \pm 0.025$. The interaction of unpaired electrons becomes stronger as the unpaired electron concentration is increased, and the strong interaction makes the g value to decrease.

2. Examination in Low Vacuum. Singer et al. studied the effect of paramagnetic gases on the ESR absorption of carbon material[13] and found that O_2 and NO affects strongly on broadening the ESR ab-

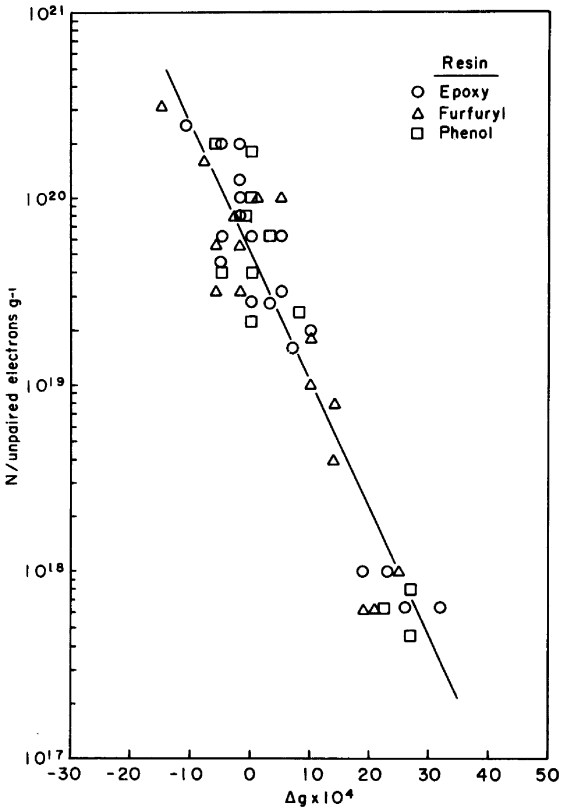
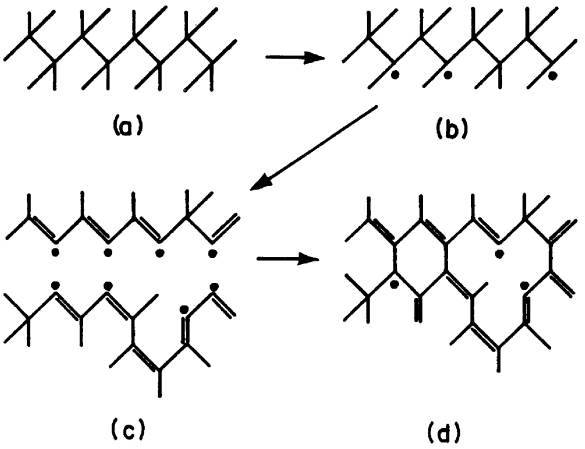


Fig. 10. Unpaired electron concentration as a function of Δg for glass-like carbons made from cure resins.

sorption spectrum, while N_2 no influence. Therefore, line broadening seen in the spectrum for HTT of 800°C is caused by the strong interaction between unpaired electrons in glass-like carbons and adsorbed oxygen molecules. The broadening phenomenon was also observed by Fielder et al. in the ESR study of pyrolysis of acrylonitrile homopolymer fibers (PAN).[14] They found that the ESR spectrum of char made from PAN pyrolysis at 700—850°C showed a single narrow line in vacuum. When the sample was exposed to air, the spectrum separated into two components with a narrow line of about 2 G width and a broad line of about 40 G width, and only a broad line was observed after a long exposure to air. Analysis of the volatile products produced from PAN during pyrolysis at 800°C showed that the major constituent was HCN, and most likely nitrogen came from heteroaromatics, thus leaving highly reactive fragments. They assumed that this effect of air on the spectrum is the formation of the highly reactive fragments produced by the rupture of heteroaromatics. Our finding of the broadening of the ESR absorption spectrum of glass-like carbons in low vacuum at HTT 800°C is basically the same phenomenon. In addition, we believe that the strong physical adsorption of air on the surface of glass-like carbons at HTT 800°C is caused by micro-pores developed during pyrolysis. Noda et al.[15] and Fitzer et al.[16] reported that the surface area attained in the glass-like carbons showed a maximum at HTT near 800°C, indicating development of an open micropores. As shown in Fig. 9, changes in narrow-line components of three glass-like carbons are almost the same as those in broad-line components except a little difference in temperature for the minimum point. These trends indicate that the narrow-line component is also influenced by the adsorption of air indirectly. Since for localized unpaired electrons S_t/S_{20} increases with increasing inverse temperature and for delocalized unpaired electrons S_t/S_{20} decreases, the variations in Fig. 9 are due to a mixed behavior for the localized and the delocalized unpaired electrons. Unpaired electrons in glass-like carbon heat-treated at 800°C are very much influenced by oxygen molecules adsorbed on the surface.

The formation of unpaired electrons through the pyrolysis of cure resins can be explained as follows;



Here, the Structure (a) indicates the hydrocarbon chain in the original cure resin. The unpaired electrons appear by the dehydrogenation reaction and chain breaking during pyrolysis as shown in Structure (b). The unpaired electrons in radical structures increase at near HTT of 800°C as shown in Structure (c) and decrease gradually by the recombination of unpaired electrons as shown in Structure (d) as HTT is increased. A strong interaction of unpaired electrons caused by the exchange of the position is expected in the polyene type radicals (Structure (c)). And also the behavior of this type of radicals can be easily affected by oxygen molecules adsorbed on the active surface on which micropores are developed well. A strong exchange interaction between unpaired electrons of glass-like carbons and oxygen molecules makes the spin-spin relaxation time T_2 shorter, T_2 is given by $T_2=\hbar/\sqrt{3}g\beta\Delta H$, where $\hbar$ is the Plank constant devided by 2π and β is the Bohr magneton,[17] and as the result broadening of the ESR absorption spectrum is observed.

Summary

ESR studies were carried out for glass-like carbons

prepared from the cure resins (epoxy resin, phenol-formaldehyde resin and furfuryl alcohol resin) in the HTT range 300—2500°C. The measurements were made at temperatures in the range −170—200°C under conditions of a high and a low vacuum. The ESR absorption spectra of the glass-like carbons obtained from these resins were almost identical. The unpaired electron concentration shows a maximum at HTT near 800°C. When air is admitted to the glass-like carbons obtained at HTT 800°C, the ESR absorption spectra split into two components. This splitting is caused by the exchange interaction of unpaired electrons in the glass-like carbons and oxygen molecules absorbed on the surface. From the ESR data in a high vacuum, for the glass-like carbons made from the cure resins heat-treated at the temperature around 2500°C unpaired electrons are delocalized ones. The value of the unpaired electron concentration (N) and the g-shift, $\Delta g(\Delta g=g_s-2.0023)$ can be fitted to $\log N = A+B\cdot\Delta g$, independent of the particular carbon.

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